Volume 111, Numbers 1–4 (1996)
PREEDF 111(1–4) 1–216 (1996)
ISSN: 1042-6507

PHOSPHORUS, SULFUR, and SILICON
AND THE RELATED ELEMENTS

**Proceedings of the
Thirteenth International Conference
on Phosphorus Chemistry (XIIIth ICPC)
Jerusalem, Israel
July 16–21, 1995**

Part 2 of 2

Conference Editor: Eli Breuer

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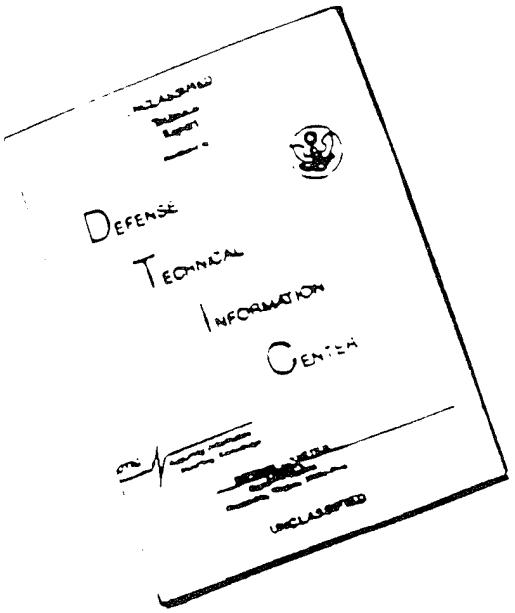

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 1996	Final Proceedings - Part II 21 DEC 94 - 20 DEC 95

4. TITLE AND SUBTITLE
The XIIIth International Conference on Phosphorus Chemistry

5. FUNDING NUMBERS
DAMD17-95-1-5011

6. AUTHOR(S)
Eli Breuer, Ph.D.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Symposium Chairman, International Conference on Phosphorus Chemistry
Tel Aviv 61500 Israel

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Commander
U.S. Army Medical Research and Materiel Command
Fort Detrick, Frederick, MD 21702-5012

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200*

14. SUBJECT TERMS Conference, Phosphorus, Chemistry, CD

15. NUMBER OF PAGES
905

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

AD_____

GRANT NUMBER DAMD17-95-1-5011

TITLE: The XIIIth International Conference on Phosphorus Chemistry

PRINCIPAL INVESTIGATOR: Eli Breur, Ph.D.

CONTRACTING ORGANIZATION: Symposium Chairman, International Conference on Phosphorus Chemistry
Tel Aviv 61500 Israel

REPORT DATE: June 1996

TYPE OF REPORT: Final Proceedings

PREPARED FOR: Commander
U.S. Army Medical Research and Materiel Command
Fort Detrick, Frederick, Maryland 21702-5012

DISTRIBUTION STATEMENT: Approved for public release; distribution unlimited

Phosphorus, Sulfur, and Silicon
and the Related Elements

Aims and Scope

Phosphorus, Sulfur, and Silicon and the Related Elements welcomes submissions involving the organic, inorganic, and biochemistry of phosphorus (including arsenic, antimony, and bismuth), sulfur (including selenium and tellurium), and silicon (including germanium and tin). In addition to research describing new chemistry of a particular element, especially welcome are presentations emphasizing relationships between elements and families of elements: for example, research comparing synthetic, mechanistic, or structural features providing new insight leading to a more rapid advance of science in these areas.

Original articles, communications, and selected reviews of broad interest will be considered for publication. Manuscripts may include illustrative material in color if this will enhance the presentation. There are no page charges and 25 free reprints will be supplied to the principal author. Regular papers may be sent to R. R. Holmes in Amherst or to L. Maier in Basel. Communications and reviews should be sent to W. Walter in Hamburg or J. G. Verkade in Ames.

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Distributed by International Publishers Distributor.
Published in The Netherlands.
Printed in Malaysia.
APRIL 1996

Continued on inside back cover

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THIRTEENTH INTERNATIONAL CONFERENCE ON PHOSPHORUS CHEMISTRY (XIIITH ICPC)

held in Jerusalem, Israel

July 16 – 21, 1995

Part 2 of 2

Conference Editor

Eli Breuer

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School of Pharmacy
The Hebrew University of Jerusalem
Israel

PHOSPHORUS, SULFUR, AND SILICON
Volume 111(1–4) (1996)

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ACKNOWLEDGEMENTS

The Conference is organized under the auspices of:

The Israel Academy of Sciences

The Hebrew University of Jerusalem

Israel Chemical Society

The Organizing Committee wishes to express its gratitude to the following public and private institutes and companies for their support of the XIIIth International Symposium on Phosphorus Chemistry:

David R. Bloom Center for Pharmacy, The Hebrew University of Jerusalem, Israel

Ciba-Geigy AG, Switzerland

Gordon and Breach Publishers, USA

ICL – Israel Chemicals Ltd.

Lancaster Synthesis Ltd., UK

Makhteshim Chemical Works, Israel

Parke-Davis, USA

Procter & Gamble, USA

Teva Pharmaceutical Industries Ltd., Israel

US Army Medical Research Acquisition Activity

Yissum Research Development Company of The Hebrew University of Jerusalem

Thanks are also due to the following for their contributions:

Akzo Nobel, USA

Avanti Polar Lipids, Inc., USA

Bayer, AG, Germany

Boehringer Mannheim Ltd., Germany

Buchi Labortechnik AG, Switzerland

El Al Israel Airlines

The Alex Grass Center for Drug Design and Synthesis of Novel Therapeutics, Israel

The Hebrew University of Jerusalem, Israel

Hoechst Aktiengesellschaft, Germany

Israel Chemical Society

Lilly Research Laboratories

Lucas Meyer, USA

Ministry of Tourism, Israel

Monsanto, USA

Municipality of Jerusalem

Wilhelm Rosenstein Ltd., Israel

Upjohn Laboratories, USA

3M Research and Development Center, USA

Wellcome Foundation Ltd., USA

PREFACE

It is a pleasure to introduce this special issue of *Phosphorus, Sulfur, and Silicon* which consists of the Proceedings of the XIIIth International Conference on Phosphorus Chemistry, held on July 16–21 in Jerusalem, Israel. The Conference attracted 366 participants and 54 accompanying persons from 32 countries, among these 86 from Eastern European, formerly communist, countries. The largest delegations were: France (25), Germany (74) Israel (77), Poland (22), Russia (38) UK (40) and the USA (56).

The Conference was held in the Holiday Inn Crowne Plaza Hotel, where about a third of the participants stayed. Most of the other participants stayed in hotels within walking distance from the Conference venue. The Holiday Inn Crowne Plaza has pleasant ambiance, excellent facilities and a great deal of experience in hosting successful scientific meetings. It proved to be an excellent choice.

The structure of the scientific program was similar to previous ICPC's in the series, insofar as not having plenary sessions except for the opening one. The scientific program started with a lecture given by Professor Robert R. Holmes entitled "HORIZONS IN PHOSPHORUS CHEMISTRY" which was the only plenary in the Conference. Following this, the 175 oral presentations were split to five parallel sessions to accommodate the many faces and multidisciplinary implications of phosphorus chemistry. In addition, there were 274 posters presented in two sessions.

In order to reflect recent advances in life sciences, our goal was to have in this meeting a strong representation of the bioorganic and biomedical aspects of phosphorus chemistry, in addition to all the traditional aspects which were represented in the previous ICPC's. We considered that exposing the phosphorus chemists' community to these new frontiers and opportunities for development, will widen horizons and stimulate the conception of new ideas. To achieve this, there was a need to attract scientists who normally do not participate in such a Conference. Thus, we contacted several pharmaceutical companies, medicinal chemists, biochemists and biologists. We succeeded at least partially in this goal, as it is apparent from the various special minisymposia:

* Biologically active bisphosphonates (7 lectures)
* Phosphorus related abzymes (8 lectures)
* Nucleotides (8 lectures)
* Phospholipids (7 lectures)
* Biological applications of P-31 NMR spectroscopy (4 lectures)
* Phosphorus containing NMDA antagonists (6 lectures)
* Inositol phosphates (7 lectures)
* Phosphorus containing agrochemicals (6 lectures)

In addition to these, there was a general bioorganic-medicinal session (9 lectures) as well as sessions devoted to computational phosphorus chemistry (4 lectures), inorganic phosphorus chemistry (9 lectures), coordination chemistry (26 lectures) and to flame retardants (4 lectures). Still, as in previous ICPC's the major portion of the Conference consisted of contributed presentations in various aspects (synthetic, structural and mechanistic) of organophosphorus chemistry (70 lectures).

One of the risks one takes when organizing a Conference in a place like Jerusalem (*there is no place like Jerusalem – so central in the history of three major religions: Judaism, Christianity and Islam*), is that many of the participants may find touring the city more attractive than attending the Conference. I think we overcame this difficulty successfully, as both the lectures and the poster sessions were all very well attended. The Conference participants were rewarded with a social program which included a sound and light show at the Tower of David Citadel along the wall of the Old City, a reception and a visit in the

Israel Museum (containing among other unique exhibits, the famous "Dead-Sea Scrolls") hosted by the Municipality of Jerusalem, as well as a half day tour of selected sites and sights of the city. The conference ended with a farewell dinner.

We wish to acknowledge the donations received from the numerous institutions and companies (their list appears at the page preceding this preface) which enabled us to extend financial support to needy participants especially from the Former Soviet Union and other Eastern European Countries.

Finally the Chairman wishes to thank all the members of the National and International Committees, and last but not least, all the participants, without whom this Conference could not have succeeded. We look forward to meeting again in Cincinnati in 1998.

Eli Breuer
(Chairman, XIIIth ICPC)

POSTERS

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LUMINESCENT PROPERTIES OF SOME RARE EARTH PHOSPHATES

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Abstract Luminescent properties of scandium and yttrium phosphates are discussed and mechanisms involving their emissions proposed.

Key Words: Scandium, Yttrium, Lanthanides, Luminescence, Inorganic Materials.

The tetrahedral PO_4 group is considered "transparent"in the visible and ultraviolet spectrum, up to about 1750 Å, so the possibility that $LnPO_4$ may display their own optical properties was scarcely admitted [1]. The aim of the present work is to study the luminescent activity of the dynamic matrix $Sc_xY_{1-x}PO_4$ and related $ScVO_4$. Pure $ScPO_4$ exhibited a red luminescence (excit. 314, 445 *nm*; emis. 680 *nm*), while pure YPO_4 showed only a weak blue emission. Intermediate solid solutions with $x = 0.25$; 0.5 and 0.75 reproduce $ScPO_4$ emissions while relative intensities increase with x. The phosphates were regarded as systems in which optical activity is due to an interaction between the cationic and anionic orbitals. The xenotime structure implies a D_{2d} site symmetry for Sc in a distorted octahedral environment. So, the non-occupied ***d*** orbitals are split into four levels belonging to the irreducible representations A_1, B_1, B_2 and E, while the non-occupied ***s*** orbital transforms as A_1. The highest occupied molecular orbitals of the complex have essentially characteristics of the ligands. Thus, the absorption of radiation by the system corresponds to a charge transfer process. After fast internal relaxations to the state $|1>$ emission may then occur through a transition to the state $|0>$, corresponding to the annihilation of an electron-hole pair. An alternative way to deal with this process is to consider the transition $|1> \Rightarrow |0>$ as an interband transition in which the state $|1>$ would be associated with a ***spd*** type band and the state $|0>$ would correspond to a band of the ***sp*** type. The YPO_4 emission can be rationalized by the fact that, since the ***d*** and ***s*** orbitals of Y^{3+} are higher in energy, the gap between the states $|1>$ and $|0>$ is larger than in the case of Sc^{3+}. In the case of $ScVO_4$ an additional low lying energy level belonging to the VO_4^{3-} group must be considered within the scheme: if it is close to the cationic ***d*** and ***s*** orbitals a quenching effect on the $|1> \Rightarrow |0>$ emission might take place. This explains the fact that no red emission is observed and the band agrees in position with the optical activity of the VO_4^{3-} ion.

REFERENCE

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 2
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PRECIPITATION OF RARE EARTH PHOSPHATES FROM H_3PO_4 SOLUTIONS

B. Zakharova, L. Komissarova, V. Traskin, S. Naumov, P. Melnikov

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Abstract A study of several factors has been carried out in order to determine their influence on rare earth phosphates precipitation from H_3PO_4 solutions obtained after the treatment of the Kola phosphate rock.

Key Words: *Lanthanides, Rare Earth Phosphates, Precipitation.*

Neutralization of H_3PO_4 solutions obtained after phosphate rock treatment leads to the formation of colloidal systems which give rise to the poorly soluble rare earth (RE) phosphates. They represent predominantly the Ce group, Y and Sc[1]. A study of several factors (temperature, pH, presence of Ca^{2+}, Al^{3+}, Fe^{3+}, F^-, SiF_6^{2-}),has been carried out in order to determine their influence on the properties of the phosphates precipitated as well as on the recovery of RE. Turbidimetric and electron microscopy techniques allowed the measurements of the particles sizes. The processes may be described by the equation:

$$dc/d\tau = -kc^2 ,$$

where c represents particle concentration at the moment τ. It explains the prolonged time needed for decantation and the difficulties in the filtration processes. High temperatures stimulate faster aggregation of the particles. Several cations stabilize colloidal dispersions. In spite of the relatively large size of the particles the precipitation rate is low owing to the tendency of such systems for gel formation. The anions reduce the size of the particles considerably reducing RE extraction from the acid. In contrast, at lower pH the average particle size grows and pH = 2 allows the precipitation of the RE up to 90%. Sc and Y recoveries are much inferior, 45 and 29% respectively.

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Acknowledgments: CNPq, FAPESP

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 3
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KINETICS OF THE KOLA APATITE ROCK INTERACTION WITH H_3PO_4

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Besides the production of fertilizers, Kola phosphate rock may be used as a source of lanthanides, strontium and fluorine. It implies the necessity to carry out a study of kinetics and mechanisms of the process in order to choose optimal conditions for the realization of the technological scheme [1]. The fluorapatite concentrate used had the following composition: $\sum Ln_2O_3$ - 0.89; Y_2O_3 - 0.04; SrO - 2.80; CaO - 45.40; Fe_2O_3 - 0.42; Al_2O_3 - 0.86; MgO - 0.10; F - 2.80; SiO_2 - 1.80; P_2O_5 - 39.40 weight %; molar ratio CaO : P_2O_5 = 1.5; the content of the apatite - 98.5%. The reaction of H_3PO_4 with fluorapatite was studied using a laboratory reactor with a stationary layer. The following parameters were varied: H_3PO_4 concentration (20, 30 and 50 weight % P_2O_5), temperature (20, 75, 150, 200 and 250°C) and time of contact (1 - 180 min.). A multimethod approach was used. X-ray diffraction, electron probe microanalysis and paper chromatography were applied to follow the bulk structural aspects of the apatite powders. It was shown that at the first stage of reaction a thin film of calcium monophosphate $Ca(H_2PO_4)_2 \cdot H_2O$ is deposited on the apatite particles (avg. diameter 150 nm). The reaction is thought to proceed at the interphase solid/liquid and its kinetics may be described by the equation

$$H(\alpha) = (1 - \alpha)^{-2/3} - 1 = k_R \tau,$$

where α is the fraction reacted. At higher temperature (175 - 200°C) calcium monophosphate $Ca(H_2PO_4)_2 \cdot H_2O$ is transformed into calcium diphosphate $CaH_2P_2O_7$ forming a blocking layer on the apatite surface and thus making access to the surface difficult. Consequently, the diffusion at the next stage is described by the equation:

$$I(\alpha) = 1 - 2\alpha/3 - (1 - \alpha)^{2/3} = k_D \tau$$

The relationship between the two rates may change with time. Graphic representations of both functions H (α) and I (α) vs time show the corresponding kinetic and diffusion areas. The best conditions of Kola apatite treatment with phosphoric acid are: T = 200°C and H_3PO_4 concentration 30%.

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Acknowledgments: CNPq, FAPESP

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 4
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CHEMICAL MECHANISM FOR FLUORAPATITE DISSOLUTION IN ACIDS

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Abstract New chemical mechanism for acidic dissolution of fluorapatite is discussed.

Modern level of knowledge about the dissolution chemistry of fluorapatite in acids is limited by chemical reaction:

$$Ca_5(PO_4)_3F + 7H_3PO_4 = 5Ca(H_2PO_4)_2 + HF \quad (1)$$

But reactions having such high molecularity values are impossible. By using of various methods of solid surface state analysis (Scanning electron microscopy, Auger-electron and IR-spectroscopy, measurements of surface electrokinetical potential) and chemical analysis of acid solutions, I supposed a new five-steps dissolution mechanism for the chemical process (1), where the each step (reaction) has the molecularity value equal 2 or 3:

$$Ca_5(PO_4)_3F + H_3O^+ = Ca_5(PO_4)_3OH + H_2F^+ \quad (2)$$

$$Ca_5(PO_4)_3OH + H_3O^+ = Ca_5(PO_4)_3^+ + 2H_2O \quad (3)$$

$$2Ca_5(PO_4)_3^+ \triangleq Ca^{2+} + 3Ca_3(PO_4)_2 \quad (4)$$

$$Ca_3(PO_4)_2 + 2H_3O^+ = Ca^{2+} + 2CaHPO_4 + 2H_2O \quad (5)$$

$$CaHPO_4 + 2H_3O^+ = Ca^{2+} + H_3PO_4 + 2H_2O \quad (6)$$

The obtained mechanism is useful for better understanding of chemical processes occurring in dental caries and artificial bones *in vivo*. More detailed description see[1,2].

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 5
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SYNTHESIS AND CHARACTERIZATION OF Na AND Mg CONTAINING CARBONATEFLUORAPATITES

MERIKE PELD, KAIA TÕNSUAADU, MIHKEL VEIDERMA
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The apatites were precipitated in an aqueous NH_4OH-NH_4NO_3 solution with pH 9-10 at temperatures 20°C and 80°C. The synthesized materials were studied by chemical and thermal analyses (TG/DTG/DTA, TG/FTIR-EGA), IR-spectroscopy, XRD-powder analysis and specific area measurements.

The precipitated materials are poorly crystallized carbonatefluorapatites (CFAp) with a large specific area. Their chemical composition can be expressed with the general formula $Ca_aMg_bX_c(HPO_4)_x(PO_4)_{6-x-d}(CO_3)_dF_{2-y}(OH)_y \cdot nH_2O$, where X is Na^+ or NH_4^+ and a=4-10, b=0-5, c(Na^+)=0,2-0,4, c(NH_4^+)=0-0,9 and d=0,05-0,75. A higher temperature of precipitation diminishes the content of CO_3^{2-} and NH_4^+ ions in the product. Sodium stabilizes the structure of CFAp and avoids the introduction of NH_4^+ ions into the apatite structure.

On heating water evolves stepwise at the temperatures up to 500°C and ammonia in the temperature range 100-400°C, followed by the appearance of P-O-P bonds. Carbon dioxide evolves in a wide temperature range from 100°C up to 800-1000°C. The heating products consist of well-crystallized CO_3^{2-} free apatite.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 6
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DETERMINATION OF INCORPORATION FORMS OF IMPURITIES IN APATITE BY TIME-RESOLVED LUMINESCENCE

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Abstract Apatite of various genesis accommodates trace elements by diverse ways: the structural substitution is preferencial in magmatic type, while the adsorption of independent phases is the main form in sedimentary one.

The chemical analysis of magmatic and sedimentary apatite provides evidence of the existence of many traces which may act as luminescence centers. It is the purpose of our work to utilize the technique of laser-induced time-resolved spectroscopy in order to distinct between the various forms of their accommodation in magmatic and sedimentary apatite. The main results are represented in the following Table.

IMPURITY	APATITE	
	MAGMATIC	SEDIMENTARY
U^{4+}	Structural substitution on the place of Ca (ESR).	
UO_2^{2+}	Not discovered.	Adsorption on the surface as uranyl aquacomplexes and secondary minerals.
U^{6+}	Not discovered.	After heating at 800 ^{o}C U^{6+} diffuses in fluorite which forms as result of heating.
REE^{2+}	Eu and Sm: structural substitution instead of Ca.	Adsorption on the surface.
REE^{3+}	Ce, Tb, Tm, Ho, Dy, Pr, Sm, Eu, Nd: structural substitution instead of Ca.	At 800 ^{o}C REE diffuse in apatite (fluorite) lattice.
Mn^{2+}	Structural substitution on the place of Ca.	Adsorption on the surface and structural substitution instead of Ca (ESR).
Mn^{5+}	Structural substitution on the place of P.	After heating at 800 ^{o}C Mn^{5+} diffuses on the place of P.
Cr^{5+}	Structural substitution on the place of P (ESR data).	Not discovered.
Cr^{3+}	Structural substitution or in the	independent mineral phase.
H_2O	Not discovered	Structural and adsorbed.
O_2^-	Not discovered	Structural.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 7
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THE SYNTHESIS AND CRYSTAL STRUCTURES OF NEW CONDENSED PHOSPHATES OF MANGANESE

ELENA V. MURASHOVA, NATALIA N. CHUDINOVA
Institute of General & Inorganic Chemistry of RAS, Moscow, Russia

This work deals with the synthesis of condensed phosphates of Mn(II), Mn(III), and also their combinations with Na, Cs. The reaction of MnO_2 with molten polyphosphoric acids, partially neutralized with carbonates of Na and Cs is used. In the course of reaction of MnO_2 with molten polyphosphoric acids, Mn(IV) is reduced to Mn(III) or/and Mn(II). The ratio Mn(III)/Mn(II) depends on the conditions of synthesis (temperature, time, presence of oxidants or reductants etc.). By varying these parameters we obtained 7 new manganese phosphates and determined their structures.

Mn(II) Products: MnP_4O_{11} (a=9.306, b=9.271, c=10.758 A, α=71.43, β=71.07, γ=90.34°, $P\bar{1}$) - an ultraphosphate with a new type of anion. $NaMn(PO_3)_3$ (a=14.429, b=14.429, c=14.431 A, Pbca) - polyphosphate.

Mn(III) Products: $Na_3MnP_8O_{23}$ (a=11.914 A, $P4_132$) - an ultraphosphate, which contains an isolated "cage" anion, isostructural to $Na_3FeP_8O_{23}$. $CsMnHP_3O_{10}$ (a=8.994, b=8.629, c=6.511 A, β=113.39°, C2) - a new type of triphosphate with a framework structure.

Mn(II)+Mn(III) Products: $CsMn(II)Mn(III)P_6O_{18}$-I (a=10.329, b=13.356, c=6.277 A, β= 113.05°, C2/m), $CsMn(II)Mn(III)P_6O_{18}$-II (a=12.942, b=12.505, c=5.061 A, β=110.59°, C2/m) -cyclohexaphosphates with a statistical distribution of Mn(II) and Mn(III) atoms. First of two cyclohexaphosphates has 10 isostructural analogs: $CsM^1M^2P_6O_{18}$ (M^1=Zn, Mg, Mn, Co, M^2=V, Fe, Al, Ga). $Cs_3Mn(II)_3Mn(III)(P_6O_{18})_2$ (a=16.166, b=9.953, c=12.435 A, β=127.23° C2/m) - a cyclohexaphosphate, where Mn(II) completely occupies one crystallographic position, while the other position is shared with Mn(III). We synthesized one more isostructural analog of similar composition - $Cs_3Mg_3In(P_6O_{18})_2$.

Present work was made in part of ISF (grant N M4R300) and Russian Fund of Basic Research (grant N 95-03-09693a).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 8
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MICROWAVE-ASSISTED RAPID SOLID-STATE CHEMISTRY OF PHOSPHATE MATERIALS

NATALIA ANISIMOVA
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Abstract The present work reports some applications of microwave processing in the synthesis of inorganic condensed phosphates.

Key words: microwave technique, phosphates

The efficient and specific coupling of microwave radiation to chemicals in solution and in the solid state was recently reported [1]. No data concerned phosphate materials have been known.

To simplest order, one would expect advantages for microwave synthesis over conventional synthesis similar to the advantages of microwave food processing over conventional oven cooking: the rapidity and the economy. Table 1 summarizes some first results concerned with microwave-induced synthesis of condensed phosphates starting from hydrogen phosphates.

TABLE 1 Microwave-induced transformations of solid hydrogen phosphates.

Compound	Time, min.	Product
$Al(H_2PO_4)_3$-C	5	$Al(PO_3)_3$
$Al(H_2PO_4)_3$-C + KH_2PO_4	5	$KAlP_2O_7$
$Al(H_2PO_4)_3$-C + $2KH_2PO_4$	5	$KAlHP_3O_{10}$
α-$Zr(HPO_4)_2 \cdot H_2O$	15	ZrP_2O_7

Present work was possible in part due to financial support of the Russian Foundation for Base Research (Grant 95-03-09693a).

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 9
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VIBRATIONAL SPECTRA OF MAGNESIUM HYDROGENPHOSPHATE TRIHYDRATE AND OF ITS MANGANESE ANALOGUE

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Abstract The infrared (IR) and Raman spectra of $MgHPO_4 \cdot 3H_2O$ and of a series of partially deuterated analogues as well as the IR spectra of $MnHPO_4 \cdot 3H_2O$ have been recorded and interpreted. The analysis of the IR spectra in the HOD bending region rules out the possibility of existence of H_3O^+ ions in the structure.

Key Words: Infrared spectra, Raman spectra, magnesium hydrogenphosphate trihydrate, manganese hydrogenphosphate trihydrate, newberyite, deuterated analogues.

Recorded and interpreted were the infrared (IR) spectra of $MgHPO_4 \cdot 3H_2O$ (newberyite) and $MnHPO_4 \cdot 3H_2O$. Also recorded were the IR spectra of a series of deuterated analogues of newberyite and the Raman spectra of $MgHPO_4 \cdot 3H_2O$ and its fully deuterated analogue. The close resemblance of the IR spectra of $MgHPO_4 \cdot 3H_2O$ and $MnHPO_4 \cdot 3H_2O$ is not surprising since the two title compounds are isomorphous [1,2].

Of the Raman bands present in the ν(PO) region, three are due to modes localized in the PO_3 fragment (they are found above 950 cm^{-1}), whereas the P–O(H) stretch gives rise to the band around 892 cm^{-1} which on deuteration shifts to 877 cm^{-1}. In the IR spectrum the assignment is more difficult since the corresponding band is overlapped with the γ(P–O–H) one. The analogue of the latter band in the spectrum of the deuterated newberyite is found around 650 cm^{-1}.

The appearance of the IR bands at approximately 2200 and 2400 cm^{-1} is in line with the appreciable strength of the hydrogen bonds formed by the HPO_4^{2-} ions [1]. The presence of chains of such bonds shows that the two studied compounds are potential proton conductors. In the IR spectra of the partially deuterated analogues, bands due to δ(HOD) modes are present with shapes practically identical to those of the corresponding HOH ones. The presence of these bands definitely rules out the suspected [3] possibility of existence of H_3O^+ ions in the structure of the studied compounds since in the latter case bands due to the H_2DO^+ and HD_2O^+ species would be present.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 10
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EXPLANATION OF ANOMALOUS GAS-CHROMATOGRAPHIC (GC) BEHAVIOUR IN A HOMOLOGOUS SERIES OF 2-CHLOROETHYL PHOSPHONIC ACID DIALKYL ESTERS

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The study of GC separation of 2-chloroethylphosphonic acid di-*n*-alkyl (1-5 C atoms) esters (synthesised by us) on silicone stationary phases (OV-1, OV-17, OV-225) revealed a deviation from the expected linear dependence of retention indexes (RI) versus the number of C atoms of the alkyl chain: the first member of the series presents stronger retention than one can expect. This anomalous behaviour was observed especially on polar stationary phase (OV-225, see Figure 1), and was emphasised with the increase of the column temperature. In an attempt to rationalise the above mentioned facts, we tried to relate the RI values to a global polarity parameter: the dipole moment, μ. The μ values for $ClC_2H_4P(O)(OR)_2$ were calculated by a method described in [1] (tested by comparing the calculated μ values with experimental ones for alkyl phosphonic acid dialkylesters), using molecular mechanics (COSMIC package) in the search of the conformational space, AM1 method (MOPAC 6.0) for the μ values of the conformers, and Boltzmann distribution for the global value (see Table I). At low temperature, the μ values are not related to the Kovats indexes. Those calculated at 200°C (column temperature range) demonstrate that, indeed, only in the case of the methyl derivative, the temperature rising led to a higher μ (enhanced population of the more polar conformers: *ac* position for the C-Ethyl group - *ac* for the Cl, $\mu \approx 2.7$ D, or *±ap* for one R, $\mu \approx 3.8 \div 4.3$ D). It can be concluded that dipole-dipole forces contribute to the separation process of the first members of the series.

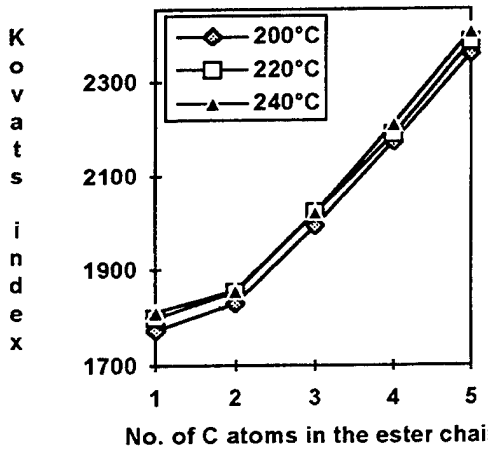

FIGURE 1 Kovats indexes versus no. of C atoms in the ester chain for OV-225 column

TABLE I Conformations and μ values

R	Most stable conformations				μ(D)	
	R	R	C-Ethyl	Cl	25°C	200°C
CH_3	*sc*(±*sp*)	±*sp*	±*sp*(±*ap*)	*ac*(±*ap*)	**2.01**	**2.20**
C_2H_5	±*sp*(*sc*)	±*sp*	±*sp*(±*ap*)	*ac*(±*ap*)	2.06	2.08
C_3H_7	±*sp*(*sc*)	±*sp*	±*sp*(±*ap*)	*ac*(±*ap*)	2.08	2.09

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 11
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OPTIMIZATION OF PLANT SAMPLE PREPARATION AND ICP PARAMETERS FOR ANALYSIS OF PHOSPHORUS

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Abstract Parameters of HNO_3-H_2O_2 wet digestion sample preparation method and inductively coupled plasma atomic emission spectrometer (ICP) are discussed for phosphorus analysis.

A LABTAM 8440M type inductively coupled plasma atomic emission spectrometer (ICP) and one of the wet digestion methods for plant sample preparation was tested. As phosphorus is one of the most important element of the periodic table and an ICP instrument is able to measure in UV range where the wavelength of phosphorus is, we can measure its content in plant samples with this instrument by emission spectroscopy. If we want to get acceptable results then the parameters of ICP and sample preparation are very important. The effect of ICP adjustable parameters has been investigated on the signal to background ratios of elements. The ICP parameters investigated in details included the next ones: viewing height, forward power, sample gas, coolant gas, auxiliary gas and flushing gas flow rate and sample uptake flow rate.

A simple, fast and relatively inexpensive sample preparation method with satisfactory accuracy and precision has been developed for a LABOR MIM OE-718/A electronic block digest apparatus with 15000 samples/year effectiveness. Therefore the effects of wet digestion parameters on the effectiveness of sample preparation have been investigated. These parameters were the next ones: quantity of dry weight, quality of digestion acid (HNO_3, HCl, H_2SO_4, $HClO_4$), quantity of cc. HNO_3, quantity of H_2O_2, duration of predigestion and digestion, the temperature of predigestion and digestion and the final filtration. The optimal parameters have been determined for HNO_3-H_2O_2 wet digestion method and ICP instrument:

Optimal parameters of HNO_3-H_2O_2 wet digestion sample preparation method:
Dry weight, generally 2 g; digestion acid, 10 cm^3 HNO_3; 3 cm^3 30% H_2O_2; duration and temperature of predigestion: 30 min. and 60 °C, for final digestion: 45 min. and 120 °C.

Optimal parameters of the ICP instrument:

Parameters:	Optimal value:
Viewing height	6 mm
Forward power	1000 W
Sample gas flow rate	1.14 dm^3/min.
Coolant gas flow rate	10 dm^3/min.
Auxiliary gas flow rate	0.1 dm^3/min.
Flushing gas flow rate	0.13 dm^3/min.
Sample uptake rate	4 cm^3/min.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 12
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PURITY DETERMINATION OF PHOSPHORUS COMPOUNDS BY INTERNAL STANDARD ^{31}P NMR SPECTROSCOPY. AN EXPERIMENTAL STUDY AND VALIDATION.

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Due to the proportionality between the area of the NMR signal and the number of nuclei, internal standard ^{31}P NMR spectroscopy is in principle a rapid and simple method for determination of the purity of phosphorus compounds.
In principle the ratio of the integrals of the two resonances in a ^{31}P-NMR spectrum of a solution containing known amounts of a standard and a sample of known purity corresponds to the molecular ratio. Therefore, knowing the purity of the standard the purity of the sample can easily be determined.
In order to make a critical evaluation of the FT NMR measurements used in this method a number of new organic compounds containing two non-equivivalent phosphorus atoms have been synthesised. Since these compounds must yield ^{31}P-NMR spectra with two resonances with a 1:1 integral ratio, they provide an efficient tool in an analysis of how (mis-)adjustment of different aquisition and processing parameters will affect the purity analysis. Using these compounds for the evaluation of the method we found that during the aquisition and processing of the spectrum the following points must be followed strictly:

- The relaxation delay must be at least 5 times the longest T_1
- The carrier frequency must be positioned exactly between the two resonances
- Use Invers Gated decoupling to suppres nOe.
- Manual phasing of the spectrum
- Baseline correction before integration

A validation of the method has been carried out on samples of the insecticide Malathion in a xylene matrix with tributyl phosphate as internal standard. Five samples were prepared by mixing a Malathion standard of known purity with xylene. For each sample the recovery and the precision were determined. The results are summarized in the table below.

Conc.(calc)	20.5%	49.8%	74.4%	89.6%	99.5%
Conc.(meas)	20.2 ± 0.1%	49.4 ± 0.2%	74.1 ± 0.4%	89.0 ± 0.2%	99.3 ±0.5%
Recovery	98.5%	99.2%	99.6%	99.3%	99.8%
Precision	1.2%	1.0%	0.5%	0.3%	0.7%

As can be seen excellent recoveries are generally obtained. Furthermore, the precision of the method is excellent and significantly better than what is normally required of analytical methods for registration purposes.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 13
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CHARACTERISATION OF PHOSPHORUS COMPOUNDS BY $^{31}P,^{n}X$-SHIFT CORRELATED NMR TECHNIQUES IN ONE AND TWO DIMENSIONS

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Examples for 2-D shift correlations between ^{31}P and another heteronucleus via ^{n}X-detected 2D-INEPT or ^{31}P-detected HMQC experiments are presented. The former technique is best suited for $^{31}P,^{15}N$ correlations and permits the determination of intramolecular connectivities as well as of relative signs of couplings.[1] The "inverse" HMQC experiment allows easy recording of the ^{77}Se NMR spectrum of an equilibrium mixture of **2** and **3**[3], disregarding the severe exchange broadening of the ^{77}Se-resonances (Figure 1).

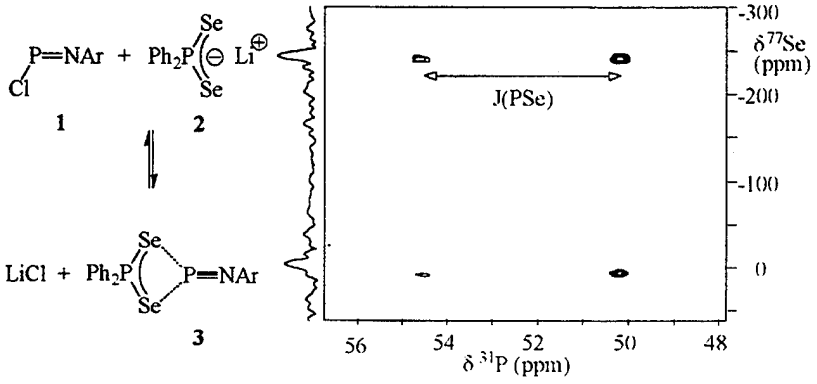

Figure 1: 121.5 MHz $^{31}P,^{77}Se$ HMQC spectrum (-30°C) of a 1:2 mixture of **1** and **2**.

In addition, schemes for $^{31}P,^{n}X$ correlations with selective 1D-experiments are suggested. These are based on a combination of tailored excitation of selected ^{31}P nuclei and non selective $^{31}P,^{n}X$ magnetisation transfer. The tailored excitation is achieved by application of shaped pulses on the ^{31}P channel, or alternatively by selective $^{1}H,^{31}P$ cross polarisation.[2] With the latter method, the sensitivity gain is in favourable cases similar to $^{1}H,X$ INEPT experiments. The new techniques are employed for determination of the stereochemistry in phosphorus-nitrogen ring systems[1], and signal assignment in product mixtures[2].

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 14
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P-31 SOLID STATE NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS ON CYCLOPHOSPHAZENES

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The present study deals with solid state NMR investigations on cyclophosphazenes with the following substituents: $-NH_2$, -OMe, -F, -Cl, -Br, at which the substituent atoms are elements of the 2nd period (N, O, and F) or elements of the 7th main group (F, Cl, and Br). The NMR spectra were obtained by a BRUKER MSL 300 spectrometer using a resonance frequency of 121.496 MHz. With each compound a static powder spectrum, a high speed MAS spectrum, and several side band spectra were recorded.

RESULTS

The pattern of a P-31 solid state spectrum is mainly caused by the anisotropy of the P-31 chemical shift.
By means of the analysis of spinning side band intensities the principal values of the chemical shift tensor (δ_{11}, δ_{22}, δ_{33}) could be obtained. From that it is possible to get the parameters Isotropic chemical shift, Span (Anisotropy), and Skew (Axiality)[1]. In table I the results of the solid state NMR measurements are shown.

TABLE I Solid state NMR parameter for some cyclophosphazenes

Compound	Isotropic chem. shift [ppm]	δ_{11}	δ_{22}	δ_{33}	Span [ppm]	Skew
$N_3P_3(NH_2)_6$	18.8 / 12.7	61.3 / 82.4	35.8 / 7.8	-40.8/ -52.0	102.1/134.4	0.5 / -0.1
$N_3P_3(OMe)_6$	21.8	57.9	21.8	-14.3	72.2	0
$N_3P_3F_6$	3.8	83.0	0.1	-72.0	155.0	-0.1
$N_3P_3Cl_6$	19.6	75.0	43.0	-59.2	134.2	0.5
$N_3P_3Br_6$	-44.3	29.0	10.0	-173.0	202.0	0.8

Additionally, quantum chemical calculations by the IGLO method to determine the principal values and the orientation of the shielding tensor were carried out. The orientation of the axes in the case of the $N_3P_3Cl_6$ molecule[2] shows that δ_{33} is perpendicular to the Cl-P-Cl plane and decisively influenced by the conditions (electron density and distribution) in this plane. Thus, the influence of substituents is reflected especially in δ_{33}.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 15
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MULTINUCLEAR NMR STUDY OF CATIONIC BINUCLEAR MONO- AND TRIHYDRIDO PLATINUM (II) BISPHOSPHINE COMPLEXES

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Abstract · Magnitude and signs of J(Pt,Pt), J(Pt,P), J(Pt,H) and J(P,P) scalar couplings and hydride T_1 relaxation values characteristic for chelating systems are discussed.

Earlier reports on dinuclear platinum complexes involving **dppm** as bridging bidentate phosphine ligand suggested correlations that may exists between the magnitude and sign of the ^2J(Pt-P) and/or ^3J(Pt-P) coupling constant and the strength of the Pt-Pt bond [1]. In the case of cationic electron-deficient complexes where a hydrogen atom bridges the two metals the direct Pt-Pt bonding is expected to be rather weak, if any.

Bisphosphines with biting angle larger than that of **dppm** form chelates rings of different sizes rather then bridge between the Pt atoms. By systematic changing the biting distance of the chelating bisphosphines used (**dppe, chiraphos, dppp** and **bdpp**) we were looking for such correlations between the strength of the Pt-Pt interaction and the Pt-Pt coupling constants. The interesting Pt-Pt constants were obtained from the spin-simulation of the ^{31}P NMR spectrum of the relevant isotopomer. Magnitude and sign of the relevant Pt-P and P-P coupling values were determined from 1D ^{31}P and 2D P,P-COSY spectra.

The data obtained cast doubt on the existence of direct Pt-Pt bonding, but no unambiguous correlation could be obtained. Regardless of the chelate ring size the trihydrides studied all exhibit similar spectral features and show fluxional behaviour in agreement with earlier reports [2]. The temperature dependence of the hydride T_1 relaxation times of the different isotopomers confirms the low barrier of the exchange.

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Acknowledgement: the authors thank the OTKA (numb. T016260) for finantial support.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 16
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CHALCOGENO METHYLENE PHOSPHORANES 2,4,6-tBu$_3$C$_6$H$_2$–P(=X)=C(SiMe$_3$)$_2$, X = O, S, Se CRYSTAL STRUCTURE, ^{31}P CP MAS NMR AND IGLO CALCULATIONS

V. VON DER GÖNNA‡, M. NIEGER‡; E. NIECKE‡
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Chalcogeno methylene phosphoranes 2,4,6-tBu$_3$C$_6$H$_2$P(=X)=C(SiMe$_3$)$_2$ with X = O, S or Se were synthesized and their crystal structures characterized by means of X-ray structure analysis. ^{31}P CP MAS NMR measurements and IGLO calculations of model compounds C$_6$H$_5$P(=X)(=CH$_2$) allow to study the influence of the chalcogeno substituent X on the principal values of the nuclear magnetic shielding tensor σ_{ii}.

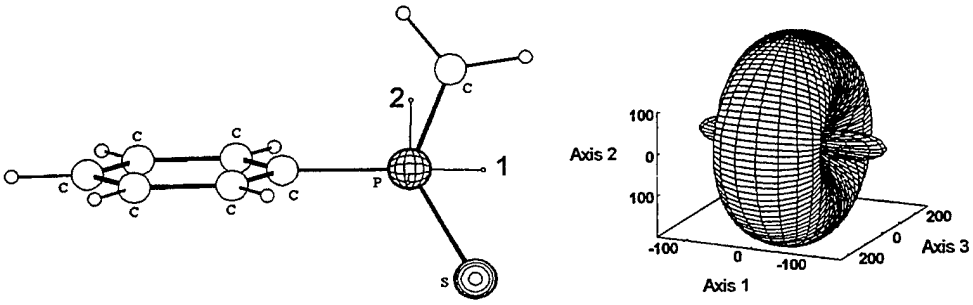

FIGURE 1 Orientation of the principal axes 1, 2 and 3 in the molecular framework of C$_6$H$_5$P(=S)(=CH$_2$) with the corresponding ^{31}P tensor ovaloid

IGLO calculations for the model compounds C$_6$H$_5$P(=X)(=CH$_2$) reflect the experimentally observed trends in σ_{ii} for X = O to Se in a satisfactory manner. The IGLO calculations allow also the assignment of the principal axes in the molecular framework and a discussion what reasons account for the changed assignment of axes 2 and 3.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 17
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^{31}P SOLID-STATE NMR INVESTIGATIONS ON PHOSPHONIC ACIDS AND PHOSPHONATES

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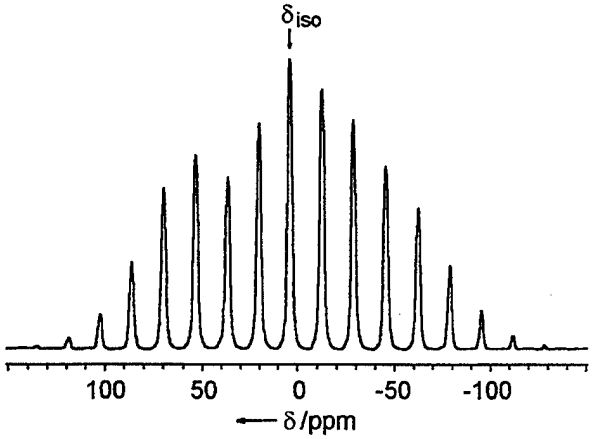
As known from ^{31}P solid-state NMR investigations of inorganic phosphates there is a correlation between chemical shift anisotropy parameters and crystal lattice parameters. For phosphonic acids and phosphonates similar correlations are not known.

The solid-state NMR spectra of various C_6 phosphonic acids $RP(O)(OH)_2$ (R = hexyl, cyclohexyl, 1-hydroxy-cyclohexyl, cyclohex-1-enyl and phenyl) reflect the different geometric and electronic situation at the α-C atom. The principal component at lowest frequency δ_{33} shows the largest changes.



For the two series of acylphosphonates R–C(O)–P(O)(OR')(OX) and hydroxyiminophosphonates R–C(=N–OH)–P(O)(OR')(OX) no correlation between anisotropy parameters and substituent R has been observed. Only variations of the phosphonate group (acid, salt, ester) lead to significant changes.

FIGURE 1 ^{31}P CP/MAS spectrum of Ph-C(O)-P(O)(OH)(ONa)

Acknowledgement

This work was supported by the German Israeli Foundation for Scientific Research and Development.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 18
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STRUCTURE OF LOW-COORDINATED PHOSPHORUS (III) COMPOUNDS INCLUDING PHOSPHORUS-NITROGEN MULTIPLE BOND: ^{13}C, ^{15}N AND ^{31}P NMR INVESTIGATION

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VITALII V. POLOVINKO.
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A wide series of low-coordinated phosphorus (III) compounds including iminophosphines **1**, two- **2** or mono-coordinated **3** phosphorus-containing cations, and anion **4**, where Mes* = 2,4,6-tris-(*tert*-butyl)phenyl, has been investigated by ^{13}C, ^{15}N and ^{31}P NMR spectroscopy. The spectral parameters obtained are considered in connection with the *ab initio* (6-31G*) calculation data of the model compounds.

Mes*-N=P-X **Mes*-NX-P^+-NR_2** **Mes*-N=P^+** **Mes*-N=P^-=NR Me_4N^+**

1 **2** **3** **4**

1 X= Alk, Ar, NR_2, OR, SR, PR_2, Hal; **2** X= H, $AlCl_3^-$, $GaCl_3^-$

In spite of the absence of the conjugation between the P=N and Mes* π-systems, essential ^{13}C shielding variation is found for all carbon-13 nuclei in Mes* moiety within the series **1-4**. The π-inductive nature of the ^{13}C shielding variation in the aromatic moiety is suggested. The found peculiarity of the Mes* substituent to be polarized by electronegative substituents seems to be an additional factor promoting the total stability of low-coordinated phosphorus (III) compounds involving the Mes* moiety. The ^{13}C NMR data analysis makes it possible to determine the isomers configuration for compounds **1,2**.

The ^{15}N and ^{31}P NMR chemical shifts of corresponding nuclei in Mes*-N=P-X moiety, as well as phosphorus-nitrogen coupling constants, are shown to be sensitive both to the hybridization type of the P and N atoms and to inductive and resonance properties of the X substituent. The largest deshielding of ^{15}N nuclei (δN=+163.6 ppm) is found for anion **4**. The P=N bonds have the double character in this compound but they are highly polarized to N atoms.

The authors thank Prof. Dr. Leonid N. Markovsky and Mr. Bogdan Zdirko for the synthesis of the compound **4**.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 19
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^{31}P AND ^{13}C NMR INVESTIGATIONS OF A TERT.BUTYLCALIX[4]ARENE-DIPHOSPHATE

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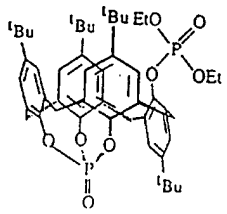
Abstract The lanthanide induced ^{31}P and ^{13}C shifts for calix[4]arenediphosphate **1** are studied. From these investigations an exact assignment of all the 48 C atoms was possible.

The aim of our investigations was to perform an exact assignment of all the 48 C atoms in the tert.butylcalix[4]arenediphosphate **1** [1]. In the ^{31}P NMR spectrum of **1** we found two signals in the typical region. It is remarkable that the shift behaviour of the cyclic and the acyclic phosphate group is very different. By addition of $Eu(FOD)_3$ the acyclic P atom shifts very strongly towards high-field but the chemical shift of the cyclic P atom is constant [2]. This behaviour is due to a steric effect of the aromatic ring with the tert.butyl substituent in the near of the cyclic P=O group. In the ^{13}C spectrum of **1** we found 34 signals, and after addition of $Eu(FOD)_3$, 36 signals. By adding the shift reagent the chemical shifts of **all** C atoms change but not the coupling constants . The shift effect is stronger in the near of the acyclic phosphorus and far from the acyclic phosphorus this effect is weaker.



partial cone form

1

An exact assignment of all the 48 C atoms can be deduced from a combination of the chemical shift values of the C atoms before and after adding $Eu(FOD)_3$, the magnitude of the coupling constants, and the peak intensities.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 20
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$^3J(P,C)$ COUPLINGS IN 3-PHOSPHABICYCLO[3.1.0]HEXANE 3-OXIDES

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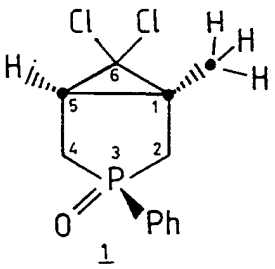
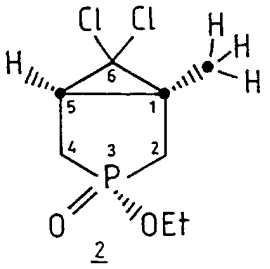
Vicinal phosphorus-carbon couplings ($^3J(P,C)$) measured for 3-phosphabicyclo[3.1.0]hexane 3-oxides (1 and 2) of known geometry have been studied. With one exception (see below), the dependence of the $^3J(P,C)$ constants on the torsion angles (Ø) followed the Karplus-equation ($^3J(P,C)=A\cos^2Ø+B\cos Ø+C$).



1



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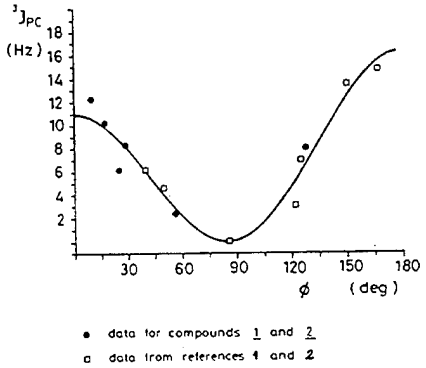

On C_6 coupled through two vicinal paths by the phosphorus atom, extremely large constants (ca. 12 Hz) have been observed in 1 and 2 (Ø~77°). According to our explanation, "through space" coupling is responsible for the extraordinary large splitting.

The 176°-12.7 Hz and 111°- 0 Hz data pairs obtained for 8-chloro-5,6-di(methoxycarbonyl)-4,7-dimethyl-2-ethoxy-2-phosphabicyclo-[2.2.2]octa-5,7-diene 2-oxide also fit the Karplus curve.

This work was supported by OTKA (grant no.: T 014917).

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 21
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DIRECT CHROMATOGRAPHIC RESOLUTION OF P-CHIRAL ORGANOPHOSPHORUS COMPOUNDS AT ANALYTICAL AND PREPARATIVE LEVELS.

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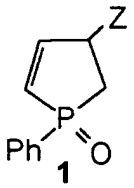
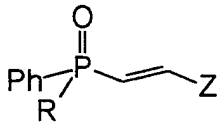
and Maria Curie-Skłodowska University, ul. Gliniana 33, 20-031 Lublin, Poland.

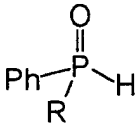
High-performance liquid chromatography utilizing chiral stationary phases (CSPs) is well established as a very simple and efficient method for obtaining discrete amounts of optically active compounds with high e.e., as well as for determining their enantiomeric composition. We wish to demonstrate in the present work that a totally synthetic brush-type π-acidic CSP based on a bis(*N,N'*-3,5-dinitrobenzoyl) derivative of (*R,R*)- or (*S,S*)-*trans*-1,2-diaminocyclohexane as selector can be used successfully to resolve variety of chiral organophosphorus compounds containing stereogenic centers at phosphorus.



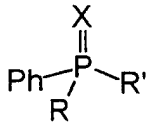
1
Z = H, OH



2
Z = H, Ar, $S(O)_nPh$



3



4
X = O, S, Se, BH_3

Ample examples of resolutions include: a) resolutions of tertiary vinyl phosphine oxides including cyclic and terminally substituted ones of type **1** and **2**, b) preparative resolutions of secondary phosphine oxides **3**, c) miscellaneous P-chiral thiophosphoryl derivatives, and d) studies of the influence of structural modifications of the analyte on the enantioselectivity of the resolution process in the model series of phosphine oxides, sulfides, selenides and boranes of type **4**.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 22
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OPTICALLY ACTIVE PHENYL-t-BUTYLPHOSPHINOTHIOIC ACID AS A USEFUL CSA FOR THE ENANTIOMERIC EXCESS DETERMINATION OF ALCOHOLS, AMINOALCOHOLS AND RELATED COMPOUNDS

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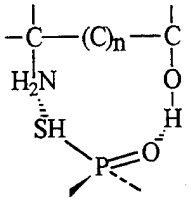
There are rather few methods for determination of the enantiomeric excess of chiral alcohols, amines, thiols and related compounds.[1] All these methods consist in the formation of diastereomeric derivatives of the samples investigated with various chiral derivatizing agents (the CBA method) followed by the quantitative determination of their diastereomer composition using NMR or other techniques.

We have now found that the easily available optically active t-butylphenyl-phosphinothioic acid forms diastereomeric solvates (the CSA method) with a series of alcohols, amines and related compounds such as aminoalcohols, diols and hydroxyacids.

The values of chemical shift differences of diastereomeric solvates ($\Delta\delta$) are in the range between 0.003 and 0.08 ppm. A particularly large $\Delta\delta$ is observed for the proton attached to the C(OH) group in nor-ephedrine (0.3 ppm). This fact and the lack of nonequivalence for N,N-dimethyl 1-phenylethylamine can be explained in terms of the formation of bidentate-type complexes.



The presented procedure can be a valuable complement of the methods existing up to now to its simplicity and a possibility of a recovery of the substrates.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 23
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SIMULATION OF 1-AMINOPROPANEPHOSPHONIC ACIDS WITH CONSIDERATION OF AQUEOUS SOLUTIONS

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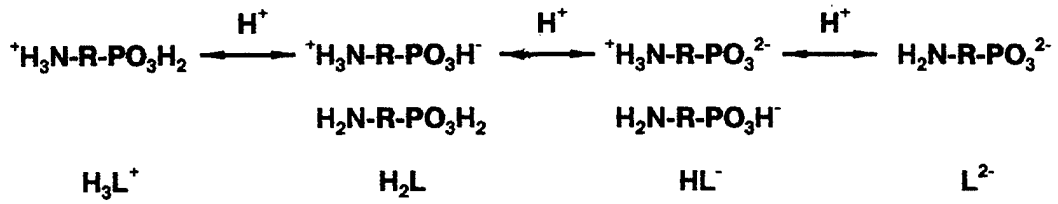
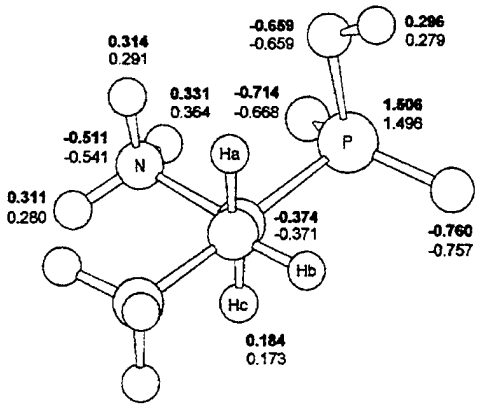
While solid state structures of aminophosphonic acids are well characterised by X-Ray methods only few informations are available concerning the solution state structures. We have attempted to simulate the structures of acids and corresponding cations and anions in aqueous solutions. It proved to be difficult to describe correctly the electrostatic interactions of solute and solvent by theoretical methods.

As a model system we used the 1-aminopropanephosphonic acid, well-known from basic research in the London group of. The protonation equilibrium of $CH_3CH_2CH(NH_2)PO_3H_2$ is described by the following scheme:



The structures of ionic species in aqueous solutions may help to interprete biological activities. The atomic partial charge contribution is important to discriminate between the micro-dissociation species of LH_2 and LH^-.

Results from ab-initio calculations with 3-21G** and 6-31+G** basis sets confirm the protonation sequence.



As example the molecular structure and the calculated atomic partial charges for the zwitter ionic form of the LH_2 species with GAUSSIAN 92 (3-21G**) for the gasphase (normal font) and in a polar medium (bold font) using the SCRF method with ε=78.36 for H_2O are given in the figure.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 24
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P-ANALOG OF CARBAMIC ACID: CRYSTAL STRUCTURE OF $(CO)_5CRH_2P$-COOH AND *AB INITIO* CALCULATIONS

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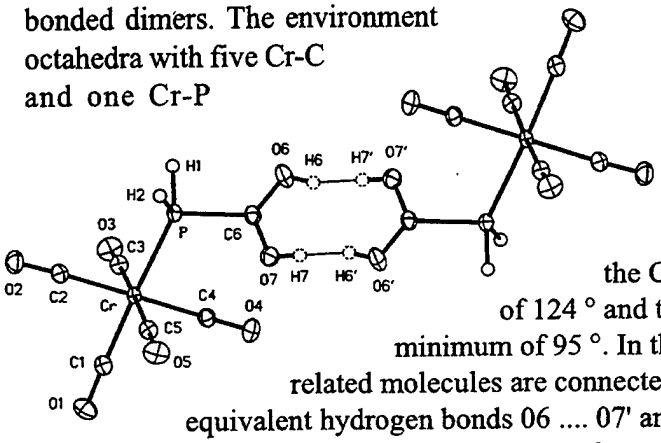
Phosphinoformic acid is unstable like the N-analogue carbamic acid. We found however that the acid can be stabilized by coordination via P to a $(CO)_5Cr$-moiety [1]. In accordance with the conclusions of Leiserowitz [2] about solid carboxylic acids the **crystal structure** of complex-stabilized phosphinoformic acid consists of hydrogen bonded dimers. The environment of the Cr atom is a distorted octahedra with five Cr-C bonds between 1.881 and 1.928 Å and one Cr-P bond of 2.335 Å. The angular distortion is small as shown by a maximum deviation of about 2.3 ° from the ideal geometry. At the P atom all bonding angles involving the Cr atom are widened to a maximum of 124 ° and the other ones are reduced to a minimum of 95 °. In the crystal structure two symmetry-related molecules are connected to each other by means of two equivalent hydrogen bonds 06 .... 07' and 07 .... 06' of 2.660 ç length between the carboxylic groups. Because of a twofold disorder along the bond P-C6, proven by bond lengths of 1.269(2) Å for C6-06 and 1.264(2) Å for C6-07 as well as by the localization and refinement of two H atoms with an occupancy factor of 0.5 bonded to each of the O atoms, no distinction can be made between the C=O double and the C-O single bond.



ab initio The structures were optimized without symmetry constraints [3]. The harmonic vibration frequencies were calculated analytically at the HF/3-21G* level of theory in order to characterize the stationary point on the potential hypersurface as a minimum. The calculation clearly shows that the hydrogen bonded dimer is energetically favoured by 63 kJ/mol at the HF/6-31G** level over two distinct monomers in the gas phase. This value is in the typical range for conventional acids (formic acid: 59 kJ/mol). Considering the bond lengths it can be stated that dimerization does not effect the P-C-bond length (186.0 pm HF/6-31G** level). However, the C-O bond lengths change significantly: the C-O double bond stretches (119.9 pm vs. 118.5 pm in the monomer), while the single bond shortens (130.5 vs. 132.8 pm). The O-H-O bridge is 278.7 pm long.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 25
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POLAROGRAPHIC INVESTIGATIONS OF FUNCTIONALIZED ALKANEPHOSPHONIC ACIDS. PART II

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In this presentation we attempted to verify the enigmatical problem of the polarographical activity of the phosphonic function, especially its electrochemical reduction.
Thus, the first report on the polarographic activity of the nitro substituted phenylphosphonic acid was presented by Kosolapov and Jenkins in 1957 [2].
However, the first and still single report on the polarographic reduction of the phosphonic function was published by Tomilov and co-workers in 1975 [3]. They observed that at the half-potential $E_{1/2}$ = - 1.62 V vs. SCE (aqueous solutions of potassium or lithium chloride as supporting electrolytes) the cathodic wave of phosphorous acid appeared. On the basis of this observation the occurrence of the polarographic reduction of the phosphonic function expressed by eq. 1 was postulated:

$$HP(O)(OH)_2 + 2H^+ + 2e \;=\; H_2P(O)(OH) + H_2O \qquad \text{(eq. 1)}$$

Occurrence of this electrochemical reaction would posses particular value (e.g. for the synthesis of polarographically active complexones or functionalized alkanephosphinous acids). Such a conversion, however, although possible in aprotic solvent does not occur in aqeuous solutions on a mercury cathode.
The results indicating reluctance of the phosphonic function to the polarographical reduction in aqueous solutions were presented in this communication.

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[1] For Part. I see:: Z.H. Kudzin, S.W. Skrzypek, R. Skowronski, Phosphorus, Sulfur and Silicon, 77 (1993) 206.
[2] G.M. Kosolapov, J. Jenkins, J. Chem. Soc., 1957, 3430.
[3] A.P. Tomilov, I.M. Osadchenko, L.M. Kisil, G.A. Ayuyan, Elektrokhimiya, 11 (1975) 1213.

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POLARITY AND CONFORMATIOS OF PHOSPHORYLETHYLENES AND PHOSPHORYLACETATES IN SOLUTION.

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ELEONORA A. ISHMAEVA AND K. MICHAEL PIETRUSIEWICZ[a]
Kazan State University, Kazan 420008, Russia;
[a]Centre of Molecul. and Macromolecul. Studies PAS, Lodz

A series of derivatives $R^1R^2P(X)R^3$, where R^1=R^2=Ph, R^3= -CH=CH-Me, X=O(I); R^1=Me, R^2=Ph, R^3= $-CH=CH_2$, X=O(II); R^1=R^2=Ph, R^3= $-CH=CH_2$, X=Se(III) and $R^1R^2P(O)-CH_2C(O)OX$, where R^1=Ph, R^2= $-CH=CH_2$, X=Ment*(IV); R^1=Ph-2-OMe, R^2=Ph, X=Ment*(V); R^1=R^2=CH_2Ph, X=Et(I), were investigated by means of dipole moments method. The problem of conjugation in phosphorylethylenes and conformation behaviour of phosphorylacetates was considered. DM (exp.) of (I-IV), determined in CCl_4 solution are 4.48(I), 4.27(II), 4.97(III), 4.21(IV), 5.21(V) and 4.02 D (VI). The intramolecular electronic interactions of phosphoryl group with unsaturated fragment did not displays in polarity properties of compounds (I-III). The experimental dipole moments of derivatives (I-III) are equal to the calculated values of DM. DM (IV-VI) is very sensitive to orientation of the P=O and C=O polar bonds. Because DM (exp.) of these compounds very sensitive to its orientation. DM (calc.) for cis- and trans- orientation of P=O and C=O dipoles are really different, that allows to drow the conclution that, in the contrast to the crystal state, the corresponded dipoles prefer an anti array in solution.

This work is realized by financial support of Russian Fond of Fundamental Investigations.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 27
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POLARITY AND CONFORMATIONS OF PHOSPHAZACOMPOUNDS IN SOLUTION

ZHANNETA R. GULYAEVA, IGOR I. PATSANOVSKY,
ELEONORA A. ISHMAEVA, LECH STEFANIAK[a],
AND WOJCIECH DOMALEWSKI[a]
Kazan State University, Kazan 420008, Russia;
[a]Institute of Organic Chemistry PAS, Warshawa, Poland

A series of iminophosphoranes o-X-C_6H_4-N=PPh_3, where X=H(I), Me (II), Et (III), OMe(IV), OEt(V) were investigated by means of dipole moments method. Because of an orientation of aromatic fragment determines intramolecular interactions in the system (benzene ring - double N=P bond), the problem of internal rotation of N-C_{ar} bond is important. DM (exp.) of molecules (I-V), determined in dioxane are 4.30(I), 4.34(II), 4.53(III), 4.75(IV), 4.79 D(V), respectively.

The bond polarity P=N was determined from the experimental DM of iminophosphorane (I), using as the model; m (P=N) = 3.60 D.

The analysis of dipole moments of the derivatives (II-V) on vector-additive scheme as function of rotation angle (φ) of aryl radical at N atom, at the zero angle of rotation corresponds the protection of the P=N bond and X- $C_{ar.}$ fragment was realized. This fact allows to conclude, that for compounds (II and III) realizes the bissectoral conformations (rotation angle $\varphi \sim 0\text{-}30^0$; the structure of alkoxy - substituted derivatives (IV,V) are characterized by angle $\varphi \sim 90^0$.

This work is realized by financial support of Competition Centre of Fundamental Natural Science (S.-Petersburg)

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 28
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TRANSITION METAL COMPLEXES OF (AMINOMETHYL)PYRIDYL-SUBSTITUTED CYCLOTRIPHOSPHAZENES;

THERMAL DEPOLYMERIZATION OF PHENOXY(AMINOMETHYL)-PYRIDYL PHOSPHAZENE COPOLYMERS

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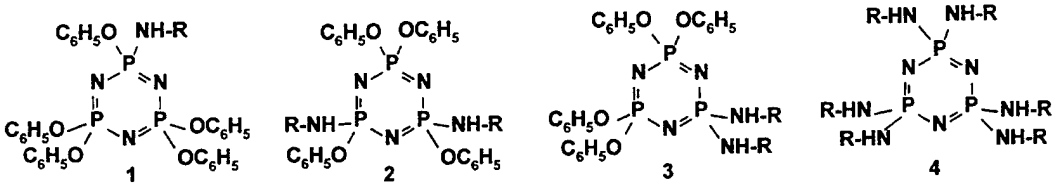
Different types of phosphazenes with (aminoalkyl)pyridyl side groups were synthesized. Mono- and cis-non-geminal disubstituted species **1** and **2** are formed when the remaining chlorine atoms of penta- or tetraphenoxy-substituted cyclotriphosphazenes are replaced by the pyridyl groups. Geminal di- and hexasubstituted compounds **3** and **4** can be obtained from reactions of hexachlorocyclotriphosphazene with the pyridine derivative.



R = alkylpyridine

Metal complexes of the general formula $CuL_2(NO_3)_2$, $CoL(NO_3)$, and $PtLCl_2$ were prepared using 2-(aminomethyl)pyridylpentaphenoxycyclotriphosphazene **1** as a multi-functional N-donor ligand. Copper and platinum are bonded to the ligand via the nitrogen of the pyridine and the amine group of the substituent whereas the cobalt is attached to the pyridine and one of the phosphazene N-atoms.

Thermal studies of homo- and mixed-substituent copolymers with 3-(aminomethyl)-pyridyl and phenoxy groups on the phosphazene chain $[NP(NHCH_2pyr)_x(OC_6H_5)_y]_n$ show that depolymerization occurs above 250° C to yield six- and eightmembered cyclic species when 50% or more of the substituents are phenoxy groups. Polymers with higher amounts of pyridyl substituents form an insoluble residue when heated.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 29
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AMINOBIS(DIORGANYLAMINO)PHOSPHANES: VERSATILE REAGENTS IN HYDRIDOPHOSPHAZENE CHEMISTRY

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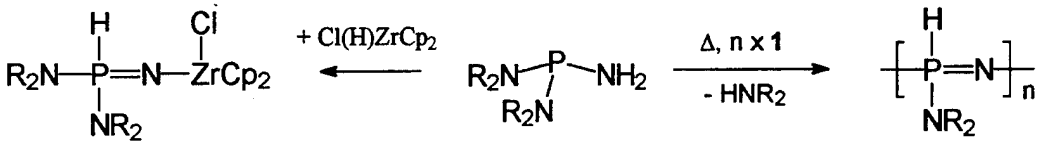
Abstract: The synthesis, crystal structure, polymerisation and metal complexation of aminobis(diorganylamino)phosphanes are discussed.

Aminobis(diorganylamino)phosphanes have hitherto only been postulated as reaction intermediates in the synthesis of hydridophosphazenes [1].

By treatment of bis(diorganylamino)chlorophosphanes with lithium amide the title compounds **1a,b** are obtained. The crystal sructure of **1b** is discussed.

At room temperature **1a,b** react via amine elimination to oligomeric and polymeric hydridophosphazenes, from which the *cis* and *trans* isomers of the cyclotriphosphazene **2a** and the cyclotetraphosphazene **3** can be isolated as stable products.



4a **1a,b** **2a**: n = 3
a: R = iPr, **b**:R = Ph **3**: n = 4

2a can be synthesized in much higher selectivity by cleavage of the Zr-N bond in **4a** which is obtained by reaction of **1a** with $Cl(H)ZrCp_2$.

Furthermore the reaction behaviour of **1a** with main group and transition metal compounds is reported.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 30
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UNUSUAL REGIOSELECTIVITY IN THE REACTIONS OF CHLOROCYCLOPHOSPHAZENE-CONTAINING CROWN ETHERS WITH DINUCLEOPHILES

Krystyna Brandt, Iwona Porwolik, K. Placha, T. Kupka, A. Olejnik, Robert. A .Shaw, David. B. Davies**
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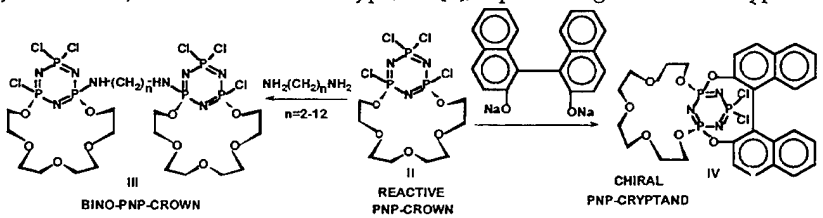
Abstract: New macrocyclic ligands with cyclophosphazene sub-units, representing geminally diamino-bridged derivatives of BINO-crown type (III), and bisansa-cyclosubstituted ones of chiral PNP cryptand type (IV) have been obtained by the regioselective substitution reactions of mono-ansa(oxytetraethylenoxy) reactive PNP-crown, $N_3P_3Cl_4[O(CH_2CH_2O)_4]$ **(II)** with the dinucleophiles, like alkylenediamines or sodium diarylates.The supramolecular control of these processes is discussed.

Key Words: *regioselective substitution, cyclophosphazenes, crown ethers, bis-crowns, cryptands*

Only a few phosphorus cryptands and bimacrocycles are reported [1]. Therefore there is a need to develop synthetic routes to these systems which might present interesting complexation properties.

A new class of functional macrocyclic ligands with cyclophosphazene sub-units has been obtained in our laboratory by cyclosubstitution reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ **(I)**, with tetraethylene glycol in the presence of NaH, the resp. mono-ansa(oxytetraethylenoxy) derivative, $N_3P_3Cl_4[O(CH_2CH_2O)_4]$, **(II)** being a major product of this reaction [2]. Owing to the incorporation of a 3-membered **-P=N-P=** fragment of the N_3P_3 ring into the macrocyclic polyether skeleton, the crown **II** is capable of forming coordination complexes both with alkali and transition metal cations.

The presence in PNP-macrocycle **II** of 4 reactive chloride functions enables the condensation of this compound with dinucleophiles, like alkylenediamines, or sodium diarylates, leading to the formation of the respective geminally diamino-bridged derivatives of BINO-crown type, **III**, or geminally cyclobis(dioxysubstituted) ones of the bis-ansa type, **IV** [3], representing chiral PNP cryptand:



Unusual regioselectivity of geminal substitution of chlorine atoms in **II** with the aforementioned dinucleophiles has been ascribed by us to the formation of the intermediate complexes of **II** with the resp. reagents; in the case of diamines a *"sandwich"*-type complex structure has been assumed. Without the supramolecular control the course of the given dinucleophilic substitution reactions would be determined by the respective steric and/or thermodynamic factors, that should yield structures different than III or IV: non-geminally bridged BINO-PNP-crowns (when reacting II with longer-chain diamines, n>4), or spiro-substituted PNP-ansa-macrocycles (in the reactions of **II** with shorter-chain diamines (n=2,3) and bis-β-naphthol). The formation of spiro structures in the reaction of I with bis-β-naphthol has been previously reported [4]. Studies on elucidating the phenomenon of supramolecular control in dinucleophilic substitution reactions of **II** are under way.

This work has been supported by the European Commission (grant CIPA-CT93-0019) and the Polish State Research Council (grant 2 P303 068 06).

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STUDIES ON POLY(DIALKOXYPHOSPHAZENES) FOR THE MEDICAL APPLICATIONS

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Key words: poly(dichlorophosphazene), poly(dialkoxyphosphazenes),substitution, physicochemical properties, medical application, NMR studies, dielectric properties

INTRODUCTION

The presence of trace of chlorine in poly(diorganophosphazenes) $[-N=P(OR)_2-]_n$, where R = C_2H_5, CH_2CF_3, C_2F_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$, $CH_2C_6H_5$ in many cases leads to the substantial changes of their physicochemical properties and limits application possibilities of this class of polymers especial for the medical materials. Despite the optimization of reaction conditions for each nucleophilic alkoxy substituent, the obtained poly(dialkoxyphosphazenes) exhibited some physicochemical anomalies.

RESULTS AND DISCUSSION

The molecular motions investigation of poly(dialkoxyphosphazenes) by means of the dielectric and pulsed NMR methods indicated in some cases the presence of anomalies in the dependence of the spin-lattice relaxation time T_1 and the tangent of dielectric loss angle (tan δ) upon the temperature for the polymer fractions of similar molecular weights, obtained in different syntheses. The ^{31}P NMR of the fractions indicates that the anomalies are connected with the presence phosphazene fragments containing asymmetrically substituted phosphorus atoms in the polymer [1,2].

The presence of trace of chlorine and poly(dialkoxyphosphazenes) fraction limits their application as the polymeric implants.

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A STEPWISE SYNTHESIS OF DIVERSIFIED PHOSPHAZENE OLIGOMERS

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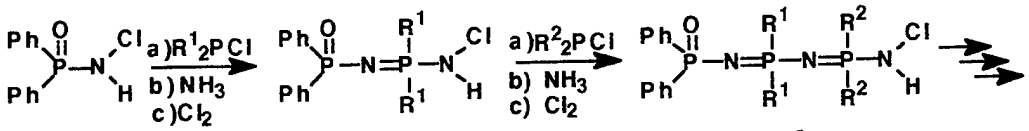
Abstract A stepwise approach to oligophosphazenes in which substituents at each phosphorus of the backbone can be diversified is described, through new N-chloroaminophosphorus compounds. Heterophosphazenes have also been obtained.

Key Words: phosphazene, N-chloroamino phosphorus compound, oligomer.

In the aim to synthesize oligophosphazenes **2** in which substituents at each successive phosphorus of the main chain should be preselected, preventing so the further hazardous distribution which is usually encountered during the thermal copolymerization of monomer precursors (Neilson [1]) or the substitution reactions on high polymeric halophosphazenes (Allcock [2]), we selected a stepwise recurrent strategy, based on the reactivity of N-haloamino^{IV}P-phosphorus compounds.



1 $R^1 = R^2$ (ou $= R^2$) = Ar, OAr, OAlk, NR_2, Cl... **2**

Examples are given, starting from the newly synthesized N-chlorodiphenylphosphinamide **1**, for the obtention of new compounds in which side groups are attached to the second phosphorus either through phosphorus-carbon bonds (P-Ph, P-*p*.Tol, P-*n*.Bu) or *via* oxygen (P-OPh, P-OEt), or nitrogen (P-NMe_2) linkages. P-Cl compounds have also been obtained. Even more, insertion of arsenic instead of phosphorus in the inorganic backbone is obtained, allowing the access to polymer precursors for specific applications.

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NEW CYCLOTRIPHOSPHAZENES WITH P-C_{Ar} BONDS.

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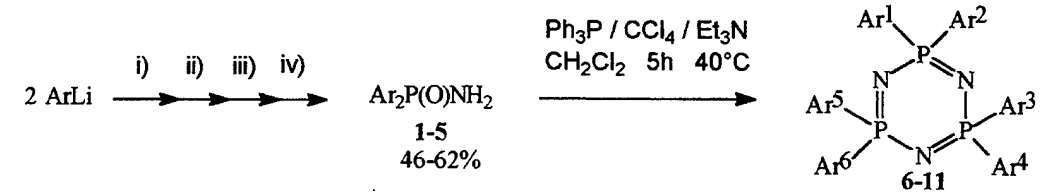
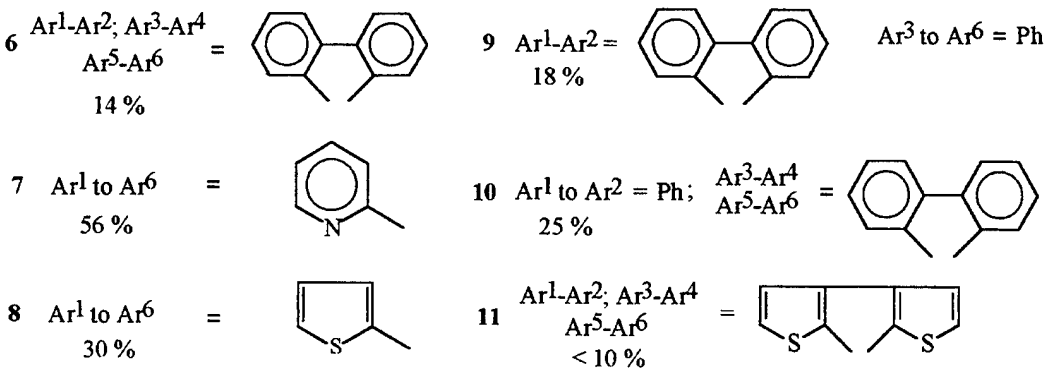
Abstract We describe some new cyclotriphosphazenes in which the phosphorus substituents are either free rotating aromatic or heteroaromatic groups, or rigid spirobiaryl units.

Key words *Arylcyclotriphosphazenes ; Phosphinamides.*

As compared with cyclotriphosphazenes having P-O or P-N side groups, cyclotriphazenes having P-C bonds are much less currently described[1]. However, both better chemical and thermal stabilities[2] and, in the case of spirocyclic phosphazenes, interesting physico-chemical properties, as solid-state inclusion[3] or magnetic field effects, could be expected for these P-C compounds.
The new compounds **6-11** are obtained through phosphinamide precursors **1-5** which are synthesized from aryllithium species.





i) $Et_2NP(O)Cl_2$ or Et_2NPCl_2 then H_2O_2 ii) HCl 37% iii) PCl_5 or SO_2Cl_2 iv) NH_3 aq or gaz

[1] ALLEN C. W., *Chem. Rev.*, **91**, 119 (1991)
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PREPARATION OF ORGANIC-INORGANIC POLYMERS: REACTION OF FUNCTIONALIZED CYCLOTRIPHOSPHAZENES WITH DIISOCYANATES

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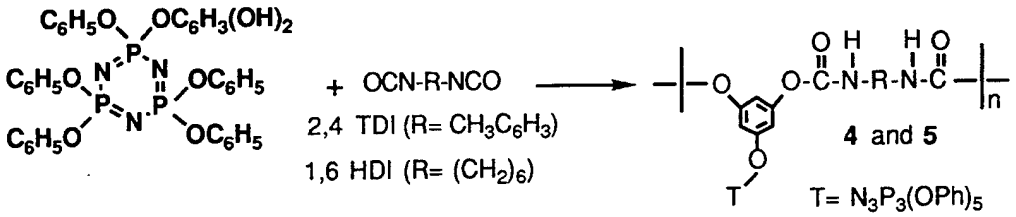
Abstract Synthesis of new urethane-phosphazene polymers: reaction of cyclotriphosphazenes containing hydroxyl functions with diisocyanates.

Key words : (3,5-dihydroxyphenoxy)(pentaphenoxy)cyclotriphosphazene - Urethane phosphazene polymers

The objective of this work was to prepare organic-inorganic polymers from hydroxy derivatives and diisocyanates. The first step consists of the reaction of (hexachloro) cyclotriphosphazene with sodium phenolate to give chloro(pentaphenoxy) cyclotriphosphazene 1; the second, the reaction of 1 with sodium 3,5-dimethoxy phenolate to obtain (3,5-dimethoxyphenoxy)(pentaphenoxy)cyclotriphosphazene 2; the third, the deprotection of hydroxyl functions in 2 with BBr_3/H_2O as [1] to give the (3,5-dihydroxyphenoxy)(pentaphenoxy)cyclotriphosphazene 3. As illustrated below, 3 reacts with 1,6-hexamethylene or 2,4-tolylene diisocyanates to give polymers 4, 5 [2] .



The structures of both classes of compounds were investigated by ^{31}P, ^{13}C, ^{1}H NMR, infrared spectroscopies, mass spectrometry and elemental analysis. The molecular weights of polymers were determined by SEC analysis with the use of THF as solvant.

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POLY(ORGANOPHOSPHAZENES) : USE IN THE IMPROVEMENT OF STANDARD MATERIALS. APPLICATION TO THE MODIFICATION OF SURFACE PROPERTIES OF POLY(VINYL ALCOHOL)

LYDIE PEMBERTON*, ROGER DE JAEGER*, LEON GENGEMBRE**
*L.A.S.I.R. (CNRS UPR A 2631 L) et **Laboratoire de Catalyse Hétérogène et Homogène (CNRS URA 402), Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

Abstract Modification of surface properties of poly(vinyl alcohol) by grafting of poly(organophosphazenes).

Key words : Surface modification - Poly(organophosphazene) - Poly(vinyl alcohol)

If the gas-barrier properties of poly(vinyl alcohol) PVA are among the best of any synthetic polymer when dry, they are poor under high humidity conditions, and therefore it is desirable to reduce this moisture sensitivity [1]. The great variety of structures of poly(organophosphazenes) POPZ gives rise to very diverse physical and chemical properties. For instance, these compounds can be hydrophobic or hydrosoluble, electrical conductors or insulators, photodegradable or photoresistant [2]...Therefore, our objective was to confer to PVA some of these properties, especially hydrophobicity, while conserving its bulk properties. We have reported two methods of grafting POPZ polymers onto PVA films surface.The first consists in a chemical reaction between PVA and the poly[(phenoxy)(p-ethylphenoxy)phosphazene] fonctionalized with maleic anhydride, the second in free-radical initiated grafting of the poly[(phenoxy)(p-ethylphenoxy)(o-methoxy p-allylphenoxy)phosphazene]. The surfaces of the modified polymer films have been studied by FTIR-ATR and UV spectroscopies, contact angle measurements, and XPS analysis. In both cases, a great enhanced hydrophobicity of the film surfaces has been observed.

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THERMOCHEMISTRY OF VAPORIZATION AND SOLVATION OF SOME THREE- AND TETRACOORDINATED ORGANOPHOSPHORUS COMPOUNDS

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Abstract The vaporization and solvation enthalpies about 100 P(III)- and P(IV)-compounds of different acyclic and cyclic space structure have been determined and analysed.

Thermochemistry of vaporization and solvation of P(III)- and P(IV)-compounds is not studied enough. The vaporization enthalpy values of such kind of compounds could be easy determined using the Equation (1) [1]:

$$\Delta H_{vap}\ (kJ\ mol^{-1}) = \Delta H_{soln}(C_6H_{14}) + 4.39 + 1.05\ MR_D \qquad (1).$$

This circumstance gives us the possibility [2] to determine and analyse for ethers (A_i) of phosphoric, phosphonic, phosphorus and thiophosphorus acids of different structure the non-specific and specific solvation enthalpies in any mediums (S) (Eqn.2):

$$\Delta H_{solv}^{A_i/S}(obs) = \Delta H_{solv}^{A_i/S}(non\text{-}spec.) + \Delta H_{spec.solv}^{A_i/S} \qquad (2).$$

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THE FEATURES OF ORGANOELEMENT COMPOUNDS CONFORMATIONAL ANALYSIS

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Conformational analysis of organoelement compounds (OEC) has anumber of features. There are some common characteristics of OEC electronic structure to be of importance:

1. The appearance of polar bonds in OEC. Both the C-E and E(1)-E(2) bonds (e.g. P-N,Si-Hlg,As-O) are polar, in contrast to the C-C and H-C bonds in carbon compounds. Especially, this is about of semipolar bonds N -> O (3.5D), P -> O (2.5-3.5D) and others having very strong assimetry of electron density distribution.

2. The greater element and bond (C-E and E-E) polarizabilities, especially in OEC, containing heavy atoms. Owing to this, fact the direction of bond polarization is not enough to prediction and conversion of bond polarity is often observed with the variation of substituents in OEC.

3. The presence of element lone electron pairs and low-lying unoccupied molecular orbitals in OEC. These factors (along with polar bond spesifity) form as a rule the all variety of "conformational effects" connected with mutual lone pairs and polar bonds orientation and hyperconjugation-type interactions.

This work is realized by financial support of International Science Foundation

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 38
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UNSATURATED PHOSPHORUS COMPOUNDS: SPATIAL AND ELECTRONIC STRUCTURE ON THE BASE OF ELECTRICAL AND ELECTROOPTICAL METHODS.

IGOR I. PATSANOVSKY AND ELEONORA A. ISHMAEVA
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The influence of classical systems connected with phosphorus atom: >P(Y)-C(R)=C<, >P(Y)-C≡C- and unusual ones, -P=E and P≡C- on spatial and electronic structure of organophosphorus compounds has been considered. On the complex analysis ground of polarity and polarizability data, obtained for model olefines, imines, acetylenes and nitriles the existence of nonformal similarity between this compounds classes has been demonstrated. It is reflected in analogy of conformational behaviour and electron effects, realized with participation of multiple carbon, nitrogen and phosphorus bonds:

a). Rotation isomery about P-C and P-N bonds are characterized by stabilization of bissectoral forms for the structural types with usual and low-coordinated phosphorus.

b). Introduction of -C(R)=C< or -C≡C- fragments to phosphorus atom not changes the principal rotation picture isomery about another simple phosphorus bonds.

c). In low-coordinated phosphorus and arsenic compounds and in corresponding unsaturated carbon and nitrogen derivatives, classical multiple bonds and ones formed by trivalent phosphorus and arsenic demonstrate the available analogy as a partners for conjugation.

This work is realized by financial support of International Science Foundation.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 39
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THEORETICAL ASPECTS OF CYCLOADDITION REACTIONS OF PHOSPHORYLNITRILE OXIDES TO UNSATURATED COMPOUNDS.

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Abstract. Ab initio (4-31G*) and semiempirical (MNDO, AM1) quantum-chemical calculations of phosphorus-functionalized and non-phosphorylated nitrile oxides have been done. In approximation of general multielectronic perturbation theory, all nitrile oxides, including trifluoroacetonitrile oxide and dialkoxyphosphorylnitrile oxides, by type of orbital interactions qualify as electron-donor dipoles.

The following based on a comparison of energies and structure of $p\pi$-bondying and $p\pi$-antibondying orbitals of phosphorylnitrile oxides and the most characteristic non-phosphorylated nitrile oxides and an evaluation in approximation of the general multielectronic perturbation theory [1] the contributions of orbital interactions of frontal molecular orbitals (FMO's) into the stabilization energy (Est) of transition state of reaction systems of "nitrile oxide - dipolarophile" type conclusions have been made.

(Dialkoxyphosphoryl)nitrile oxides, despite the lowering energy of HOMO as compared with benzonitrile oxide by approximately 1.75 eV, should be classified with electron-donating agents in which the interactions with participation of LUMO under condition of dissimilerity of HOMO constitution on reaction centres of dipolarophile can influence regioselectivity of cycloaddition. In the competition of electronic and steric interactions determining are the last. (Dialkoxyphosphoryl)nitrile oxides both for character of orbital interactions and for chemical properties are close to trifluoroacetonitrile oxide.

The electron-donating property of phosphorylnitrile oxides is the consequence of the inertness of phosphoryl moiety rather, then its influence. This follows from the fact that the separation of phosphoryl group and nitrile oxide fragment by methylene link in dimethoxyphosphorylacetonitrile oxide has a little influence on changing the character of FMO's [2] and chemical properties of nitrile oxides [3,4].

It is represented correct to speak about differentiation of all nitrile oxides in cycloaddition reactions on a degree of electron-donation.

Calculated energy of orbital interactions "HOMO of nitrile oxide - LUMO of dipolarophile" and Est for the given systems that react by "head to tail" type are somewhat less than those for the systems reacting by "head to head" type. It testifies about high sensitivity of cycloaddition reactions to steric hindrances. As in the case of reaction of (diisopropoxyphosphoryl)nitrile oxide with isopropylpropiolate (which under the electronic characteristics is analogue of methylpropiolate, but stericaly is more loaded) is observed formation the only 5-substituted cycloadducts, while the reaction with methylpropiolate results to formation 4- and 5-substituted cycloadducts [3].

In (*bis*aminophosphoryl)nitrile oxides HOMO and adjacent to it molecular orbital are formed unshared electronic pairs of amino groups. Therefore, in view of marked above electron-donating character of all nitrile oxides, should be expected strong secondary-orbital interactions for potential reaction systems and low activity of (*bis*aminophosphoryl)nitrile oxides in reactions [2+3]-cycloaddition.

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THE PHENYLPHOSPHINIDENE C_6H_5P IS STABLE UNDER UNIMOLECULAR CONDITIONS - A THEORETICAL PREDICTION

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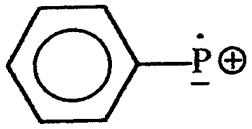
As members of the family of low-coordinated phosphorus compounds, the phosphinidenes (**RP**) containing subvalent phosphorus (σ^1,λ^1-P) are of current interest. Until now, no **Organophosphinidene RP** (R=Alkyl, Aryl) is known to be stable in the condensed phase. As the results of trapping experiments are questioned, the formation of **RP** as intermediates is still doubtful [1]. The mass spectrometric decay of some organophosphorus compounds yields radical cations $[C_6,H_5,P]^{+\bullet}$ m/z 108. For these species structures **1** and **2** are conceivable:



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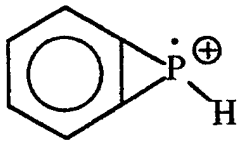

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Using *ab initio* MO-calculations we were able to show that both ions correspond to minima on the potential surface of $[C_6,H_5,P]^{+\bullet}$. Surprisingly, **1** proved to be more stable than its counterpart **2** by 87,8 kJ/mol (HF/6-31G** basis set incl. ZPVE correction). The potential barrier was calculated to be 153,4 kJ/mol. In case of the corresponding neutrals, the phosphinidene form was evaluated to be 132,6 kJ/mol more stable. Thus, **1** should be a suitable precursor for generating phenylphosphinidene in the rarefied gas phase by Neutralization-Reionization mass spectrometry. **Latest Results**: In cooperation with **J. K. Terlouw** (McMaster University, Hamilton, Canada) we found that the ion m/z 108 generated by electron impact on $C_6H_5PBr_2$ has the connectivity **1** according to the observed structure diagnostic decays. By NRMS the ion can be neutralized and C_6H_5P has proved to be stable in the dilute gas phase.

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ON THE ELECTRONIC STRUCTURES OF METAPHOSPHATE $PX_3^{(-)}$ AND METAPHOSPHITE $PX_2^{(-)}$ ANIONS, X = CH_2, SIH_2, NH, PH, O, S

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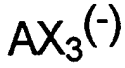
Abstract Quantum chemical calculations at RHF/6-31+g(d,p) with electron correlation and vibrational energy corrections are reported on the metaphosphate and metaphosphite series, indicating a facile second-order Jahn Teller distortion of the planar geometries.

Since the first detection of the metaphosphate anion, 1 (X = O)[1] in the gas phase, this species has been the subject of detailed discussion. Structural investigations are hitherto



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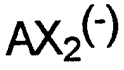

2

known on 1 (X =CR_2, R = $SiMe_3$)[2] and recently on the imino derivative, 1 (R = NR)[3]. On the whole series of metaphosphates, 1 (X = CH_2, SiH_2, NH, PH, O, S) and corresponding metaphosphites, $PX_2^{(-)}$ quantum chemical investigations at RHF/6-31+g(d,p) level with MP4SDTQ and zero-point vibrational energy corrections are reported[4]. They reveal for the metaphosphates various symmetry coupled distortions from total planarity in 1, as the consequence of a second-order Jahn-Teller effect. Corresponding group transfer reactions relate the stabilities of the metaphosphates with respect to the metaphosphites.

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ORBITAL ISOMERISM IN THE 1.3-DIPHOSPHACYCLOBUTANE-2.4-DIYL, QUANTUM CHEMICAL INVESTIGATIONS AT MCSCF LEVEL

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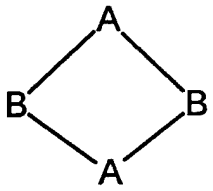
Abstract Quantum chemical calculations at open shell level (MCSCF, MP2, CISD) indicate the strong biradical nature of the title compound which is isoelectronic to the well known S_2N_2.

The delocalization of six π-electrons in a four-membered ring heterocycle has been well documented for disulfur nitride S_2N_2 , 1 (A = S, B = N). Likewise for isoelectronic compounds structures have been discussed which appear to allow π-electron delocalization[1]. The first species of this type was recently synthesized and structurally characterized[2], 1 = A_2B_2 [A = Cl, B = PR, R = 2,4,6-tri-tert-butyl-phenyl].



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Quantum chemical calculations at ab initio level and explicit electron correlation treatment (MCSCF, MP2) on the title compound, phosphetane and 1,3-diphosphetane reveal sizable energy barriers for inversion at phosphorus, making a conjugative π-delocalization of the lone pair at phosphorus within the ring system unlikely. Considerable biradical character is assigned to the energy lowest singlet state (C_i symmetry, ^1A_g), slightly below in energy with respect to the triplet state (^3A_u) and depending on the basis set and the chosen CI level (MRCI, MP4SDTQ etc., $\Delta E < 10$ kcal/mol). Substituent effects cause only a slight variation of energy differences. The title compound is an orbital isomer[2] to its bicyclic structural isomer diphosphabicyclobutane, which is lower in energy. An orbital crossing inhibits facile ring closure reaction of the former to the latter structural isomer.

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AB INITIO CALCULATIONS SHOW HOW ^{31}P NMR CHEMICAL SHIFTS IN PXYZ PHOSPHINES CORRELATE WITH SUBSTITUENT ELECTRONEGATIVITY.

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Letcher and Van Wazers suggestion[1] that the ^{31}P NMR chemical shifts of phosphines might be related to the substituent electronegativity, EN(X)[2], has not been verified subsequently by the available experimental data[3,4]. We now have explored this relationship systematically by means of reliable[5] *ab initio* magnetic property calculations[6] on a comprehensive set of molecules: PXY_2 (Y= H, F, CH_3, Cl) and PXYZ (Y= H, Cl and Z= F) with X= H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl.

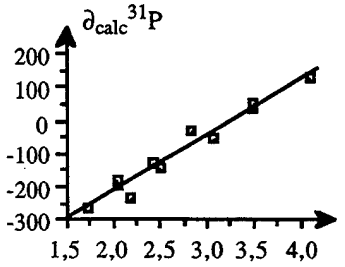

Fig.1: H_2P-X

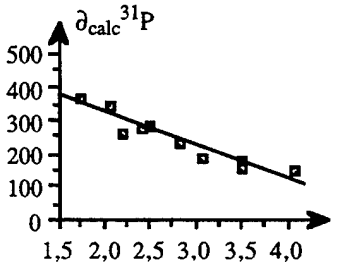

Fig.2: F_2P-X

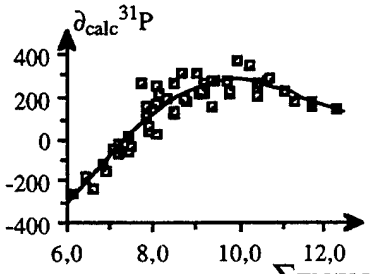

Fig.3: PXYZ

$\partial_{calc}{}^{31}$P of monosubstituted phosphines, PH_2X (Fig. 1), correlates with EN(X) as do those for the difluorophosphines, PF_2X (Fig. 2). However, the slopes are opposite ! Data for a more varied set of phosphines, PXYZ, when plotted against the electronegativity sum, ∑EN(X,Y,Z), reveals a general pattern (Fig. 3) which combines both these trends. Using a simple MO model, Letcher and VanWazer predicted similar behavior for hypothetical PX_3 models with increasing ∑EN(X,Y,Z) from 3.0 to 12.0 .[1]

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[6] $\partial_{calc}{}^{31}$P: SOS-MBPT/BIII //RMP2/6-31+G** with DeMon93© and GAUSSIAN92©.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 44
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COMPLEXES OF THIOPHOSPHORYL COMPOUNDS WITH $AgNO_3$.

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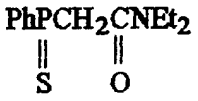
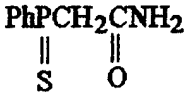
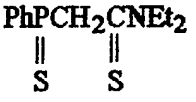
Under conditions of interphase catalysis complexing agents L^1, L^2 and L^3 have been synthesized[1] . Using spectral and X-ray methods complex formation of thises ligands with $AgNO_3$ has been studied.



L^1



L^2



L^3

Each ligand forms a complex with Ag^+ ion by means of two donor centers: S and O atoms (two S atoms in case of L^3). First of all in a solution P=S group of the ligands is coordinated by Ag ion. Crystalic complex $[AgL^1NO_3]_2$ is a center symmetric dimer, in which S atoms are bridging and Ag ion has tetrahedral environment (X-ray data)[2]. Complex $Ag\,L^2NO_3$ is stabilized by H-bonds. In contradistinction to L^1 and L^2 ligand L^3 forms a soluble complex $[Ag(L^3)_2]NO_3$, lgK=3.9 (spectrophotometric measuring in CH_3CN).

This work was supported by Russian Fundamental Research Foundation (project 93-03-04351).

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ON THE REACTION OF TRIPHENYLTRITHIOPHOSPHITES WITH COPPER (I) AND COPPER(II) HALIDES

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Abstract Reactions of triphenyltrithiophosphite $(PhS)_3P$ with copper (I) and copper (II) halides (CuHal, $CuHal_2$, where Hal=Cl, Br) have been investigated.

Key words triphenyltrithiophosphite, copper halides, complex, coordination

Reactions of the triphenyltrithiophosphite with CuHal and $CuHal_2$ (Hal=Cl, Br) have been studied. Triphenyltrithiophosphite and copper(I) halides form crystalline polymeric complexes with metal coordination via phosphorus and sulphur atoms of the thiophosphite ligand. The structure of the complex was established by X-ray data.

The reaction between triphenyltrithiophosphite and copper(II) halides is accompanied by the reduction of the copper (II) to copper(I) and the evolution of the free halogen, which, in the case of $CuCl_2$, is takes place, or, as in the case of $CuBr_2$, reacts with trithiophosphite with the formation of diphenyldithiobromphosphite and diphenyldisulfide.

$$2P(SPh)_3 + 2CuCl_2 \longrightarrow 2(PhS)_3P{\cdot}CuHal + Cl_2$$
$$4P(SPh)_3 + 2CuBr_2 \longrightarrow 2(PhS)_3P{\cdot}CuBr + (PhS)_2PBr + PhSSPh$$

The influence of the nature of the solvent on the course of these reactions has been studied. While uncoordinated $(PhS)_3P$ is unreactive towards ethanol, its 1:1 complex with Cu (I) was found to react with boiling ethanol with the formation of diethylphosphoric acid. It was established that CuCl catalyzes the reaction of $(PhS)_3P$ with ethanol.

ACKNOWLEDGEMENTS
The authors wish to express their sincere thanks to Prof. P.G.Jones and Dr. A.Fischer for X-ray inverstigations and to Deutscher Akademischer Austauschdienst for their sponsorship of these investigations.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 46
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STRUCTURE AND PHYSICAL PROPERTIES OF COORDINATION COMPOUNDS OF 2-AMINOINDAN-2-PHOSPHONIC ACID WITH SOME d-ELECTRON ELEMENTS

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Many complexes of 1-aminoalkylphosphonic acids have been obtained and their structures have been studied [1-3]. On the other hand, 2-aminoindan-2-phosphonic acid (2-AIP), the phosphonic conformationally restricted cyclic analogue of phenylalanine, has been recently obtained [4]. We undertook a study of interaction of cobalt(II), nickel(II), and copper(II) with 2-AIP, to learn how the rigid ligand structure influences the complexes structure.

Based on of elemental analyses, reflectance spectra in the visible region, infrared spectra (IR, FIR), and magnetic susceptibility measurements (295-4.2 K), the compositions of complexes were determined and their structures were suggested.

Only $[Cu(OH)(2\text{-AIP})]_2 \cdot H_2O$ is a dimer in which copper atoms are bound by the hydroxy bridge [5]. $[Ni(2\text{-AIP})(H_2O)_3] \cdot 2H_2O$ and $[Co(2\text{-AIP})(H_2O)_3] \cdot 2H_2O$ are polymers in which the bridging role between the neighbouring metal atoms is played by the phosphonic groups. The amino group of 2-AIP takes part in coordination of metals, too. Copper(II) is four-coordinated and form distorted tetrahedral structure. Cobalt(II) and nickel(II) are six-coordinated and form distorted octahedral structures. The cobalt(II) complex exhibits metamagnetism at low temperatures.

The structure of the copper(II) and cobalt(II) complexes with 2-AIP can be compared with structure of copper(II) and cobalt(II) complexes with racemic 1-amino-2-phenylethylphosphonic acid as well as 1-aminocyclopentenyl-1-phosphonic acid.

Acknowledgements This work was partialy supported by grant 3 T09A 158 08 from the Polish State Committee on Scientific Research.

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ALKYLATION, OXIDATION AND DECARBONYLATION OF TRIFERRIOPHOSPHINE $\{CpFe(CO)_2\}_3P$

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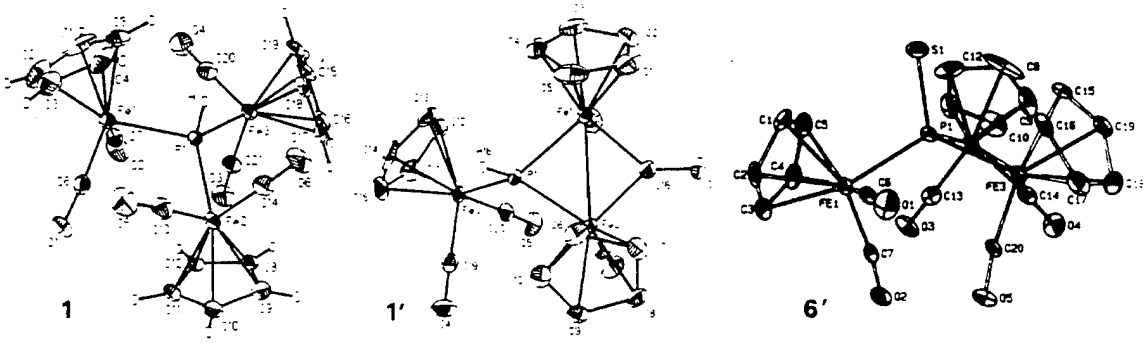
Abstract The syntheses and structures of PH-, PCl-, POR- and PR-triferriophosphonium salts, -phosphines and -chalkogenophosphoranes are discussed.

According to the isolobal analogy we regard the phosphorus atom as a coordination center and the 17-electrons complex fragments like $CpFe(CO)_2$ (= Fp = ferrio substituent) as coordinating ligands.

The reaction of $CpFe(CO)_2X$ (X = Cl, Br) with $P(SiMe_3)_3$ yields the open PH-triferriophosphonium salt $[Fp_3PH]_2FeX_4$ (**1**)[1] which can be decarbonylated to the closed analogue $[\{(\mu\text{-}CO)Fp'_2\}FpPH]_2FeX_4$ (**1'**). In CCl_4 they undergo a hydrogen-halogen exchange reaction giving the PCl-derivatives $[Fp_3PCl]_2FeX_4$ (**2**) which can be decarbonylated to $[\{(\mu\text{-}CO)Fp'_2\}FpPCl]_2FeX_4$ (**2'**). **2** is protolysed by ethanol to the POEt-compound $[Fp_3P(OEt)]_2FeX_4$ (**3**). Both PH-triferriophosphonium salts **1, 1'** are deprotonated by DBU to give the open and closed triferriophosphines Fp_3P (**4**) and $\{(\mu\text{-}CO)Fp'_2\}FpP$ (**4'**). The alkylation reaction is only possible for **4** and affords the open PR-triferriophosphonium salts $[Fp_3PR]Cl$ (**5a-c**)[1]. The directed P-oxidation of **4, 4'** by sulfur or selenium leads to the corresponding chalkogenophosphoranes $Fp_3P{=}E$ (**6**) and $\{(\mu\text{-}CO)Fp'_2\}FpP{=}E$ (**6'**)[1]. Further decarbonylation of **6'** yields the interesting spiro compound $\{(\mu\text{-}CO)Fp'_2\}Fp'P{=}E$ (**7'**) which seems to be the first η^2-P=S complex of a transition metal.



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FERROCENE AS SUBSTITUENT IN ORGANOPHOSPHORUS CHEMISTRY

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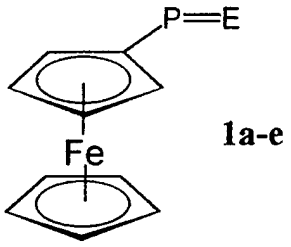
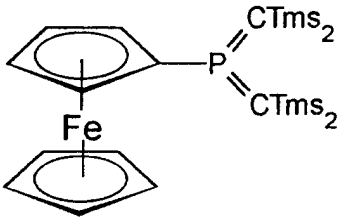
Abstract Synthesis and spectroscopic properties of ferrocenyl phosphanes and phosphoranes in low coordination are presented and discussed.

One of the most interestimg features of the ferrocenyl substituent is its remarkable ability to stabilize a positive charge on an adjacent atom. Therefore the subject of our investigations is the synthesis of neutral ferrocenylphosphanes in low coordination in order to examine the influence of the ferrocenyl group on the P=E system.

Following common procedures we synthesized a ferrocenyldiphosphene [1] **1a**, ferrocenyliminophosphanes **1b,c** and ferrocenylmethylenephosphanes **1d,e**. Moreover we extended our investigations also to $\sigma^3\lambda^5$-ferrocenylphosphoranes and gained **2a** as well as the related phosphirane depending on temperature.



1a-e



2a

E: **1a** =P-Mes*, **1b** =N-Mes*, **1c** =N-Tms, **1d** =C(OTms)*t*Bu, **1e** =C(OTms)Fc

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LANTHANIDE AND TRANSITION METAL COMPLEXES OF DIALKYL α-HYDROXYIMINOPHOSPHONATES

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α-Hydroxyiminophosphonic acid derivatives are widely known not only as intermediates in the synthesis of the important aminophosphonic acids,[1,2] but also as phosphorylating agents,[3] potential metalloenzyme inhibitors,[4] and as compounds having fungicidal activity.[5] In this work the scope of these compounds has been extended considerably by the synthesis of a number of novel dialkyl derivatives. Novel lanthanide (La^{III}, Pr^{III}, Nd^{III}, Gd^{III} and Dy^{III}) and transition metal (Co^{II} and Ni^{II}) complexes of dialkyl α-hydroxyiminophosphonates $(RO)_2P(O)C(R')N(OH)$ where R = Et, Pr^i and R' = Me, Et have been prepared and the NMR shift properties of the Pr^{III} complex (R = Et; R' = Et) indicate the potential of these compounds as NMR shift reagents for the analysis of geometric isomers.[6,7] *X*-ray crystal structure analysis of $[Ni(L^1)_2Cl_2]$ (L^1: R = Et; R' = Et) shows a distorted *cis*-octahedral coordination at the nickel atom giving two symmetry related diethyl-(*E*)-α-hydroxyiminopropanephosphonate ligands and two chlorine donors, and those of $[Pr(L^2)_3Cl_3]$ and $[Nd(L^2)_2(NO_3)_3(H_2O)]$ (L^2: R = Pr^i; R' = Et) show nine-coordination geometries with asymmetric bidentate and monodentate L^2 bonding respectively. Thus the metal complexes show unusual coordination ambivalence, changing from symmetrically bidentate to asymmetrically bidentate and then to monodentate bonding modes, to accommodate the different steric requirements of the coordinating anions in facilitating neutral complex formation.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 50
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HEMILABILE PHOSPHONATE-PHOSHANE COMPLEXES OF RHODIUM AND IRIDIUM - SYNTHESIS AND CATALYTICAL PROPERTIES

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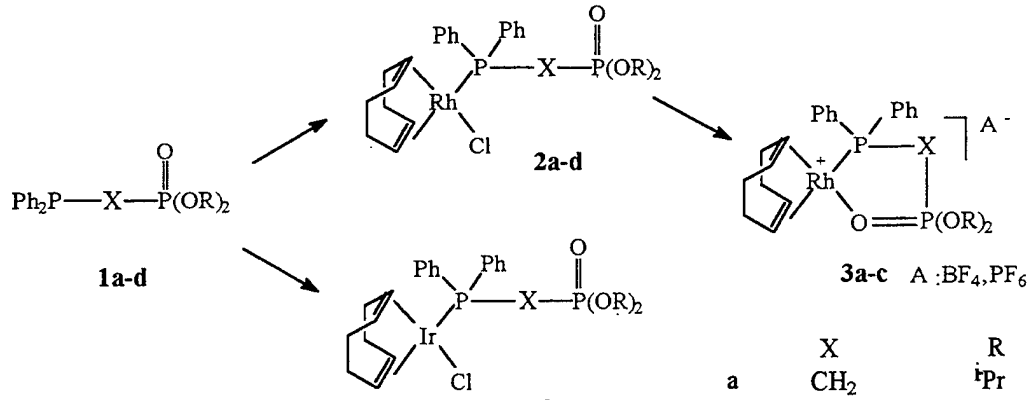
New phosphonate-phosphane ligands **1a-d**[1] were converted into the Rh and Ir complexes **2a-d** and **3a-c**. The open-chain Rh complexes **2a-d** are more effective catalysts for liquid-phase MeOH-carbonylation with respect to known bisphosphane and phosphane-monoxide phosphane complexes $[Rh(CO)L_1]_n$, $[Rh(cod)L_2]$ (L_1: $Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$; L_2: $Ph_2P(CH_2)_2PPh_2$).
While attempts of preparing stable complex-catalysts fixed on silica or alumina for slurry and vapour-phase reactions failed, active carbon was found widely superior concerning the leaching problem. Phosphonate-phosphane-Rh complexes **2a-c** are also able to act as hemilabile ligands on supported catalysts, as shown by catalytic measurements and IR-spectroscopic investigations. **2b** formed very stable monocarbonyl-species, which are easily converted into dicarbonyl-species with increasing CO partial pressure.
In case of Ir the phosphonate-phosphane ligands did not enhance the carbonylation activity compared with Rh complexes.



	X	R
a	CH_2	^{i}Pr
b	CH_2CH_2	Me
c	$CH_2CH_2CH_2$	^{i}Pr
d	1,4-C_6H_4	^{i}Pr
e	CH_2CH_2	Me

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REACTIONS OF BIS(TRIFLUOROMETHYL)PHOSPHINE AND TETRAKIS(TRIFLUOROMETHYL)PHOSPHINE WITH RUTHENIUM CARBONYL CLUSTERS

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Abstract The reaction of $(CF_3)_2P\text{-}P(CF_3)_2$ with $[Ru_3(CO)_{12}]$ yielded compounds : $[Ru_4(CO)_{13}\{\mu\text{-}P(CF_3)_2\}_2]$ **(1)**, $[Ru_4(CO)_{14}\{\mu\text{-}P(CF_3)_2\}_2]$ **(2)**, and $[Ru_4(CO)_{11}\{\mu\text{-}P(CF_3)_2\}_4]$ **(3)**; reaction with $[(\mu\text{-}H)_4Ru_4(CO)_{12}]$ yielded **(1)** and $[(\mu\text{-}H)_3Ru_4(CO)_{12}\{\mu\text{-}P(CF_3)_2\}]$ **(4)**. The reaction of $(CF_3)_2PH$ with $[Ru_3(CO)_{12}]$ yielded compounds **(1)** and **(4)** and compounds **(1)** and **(2)** using cluster : ligand ratios of 1:1 and 1:2 respectively. All the compounds have been characterised by X-ray crystallography; a schematic diagram of their structures is shown in Figure 1. The fluxional behaviour of the hydrides in **(4)** was studied using variable temperature ^1H NMR spectroscopy (see Figure 2). The result of this study was used in the assignment of hydride positions of **(4)** in the solid state.

Key Words Tetraruthenium clusters, Bis(trifluoromethyl)phosphine, Tetrakis(trifluoromethyl)phosphine.

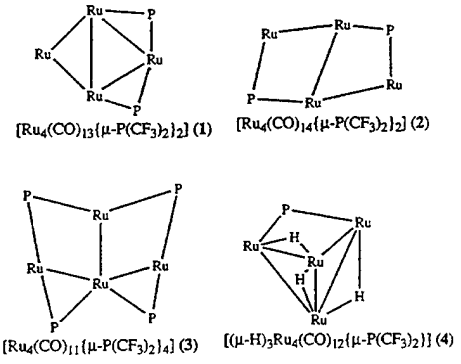

Figure 1. Schematic Diagram of Compounds (1), (2), (3) and (4) showing only the Ru-P Framework.

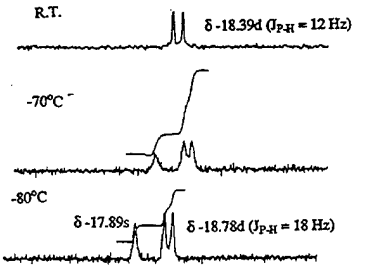

Figure 2. Variable Temperature ^1H NMR Spectra of (4)

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TRIPHOSPHA-FERROCENES AS LIGANDS. CRYSTAL STRUCTURES OF $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2{}^tBu_2P_3)M(CO)_5]$, (M= Cr, Mo, W) AND THE NOVEL RUTHENIUM AND NICKEL COMPLEXES $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2{}^tBu_2P_3)Ru_3(CO)_9]$ AND $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2{}^tBu_2P_3)Ni(CO)_2]_2$

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and PETER G. JONES
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Abstract Syntheses and structures of penta- and hexaphosphorus analogues of ferrocene have been described recently [1]. Unlike their simple ferrocene analogues, these complexes have further ligating potential towards other transition metal centres by virtue of the availability of the ring phosphorus lone-pair electrons that are not involved in the η^5-coordination. We now describe the first exampies of coordination compounds of the triphospha-ferrocene $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2{}^tBu_2P_3]$. In the ruthenium complex $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2{}^tBu_2P_3)Ru_3(CO)_9]$ **2** two adjacent phosphorus atoms of the $\eta^5\text{-}C_2{}^tBu_2P_3$ ring are interlinked by a ruthenium carbonyl cluster in which all three ruthenium atoms interact with the phosphorus atoms. The tetrametallic nickel complex $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2{}^tBu_2P_3)Ni(CO)_2]_2$ **3** represents the first example of intermolecular interlinkage of two phospha-ferrocene systems by two metal centres.

Key Words: Metal complexes, phospha-ferrocenes, 31P NMR spectroscopy, X-ray crystal structure analysis

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DIPHOSPHIRENIUM SALT: A NEW VERSATILE LIGAND

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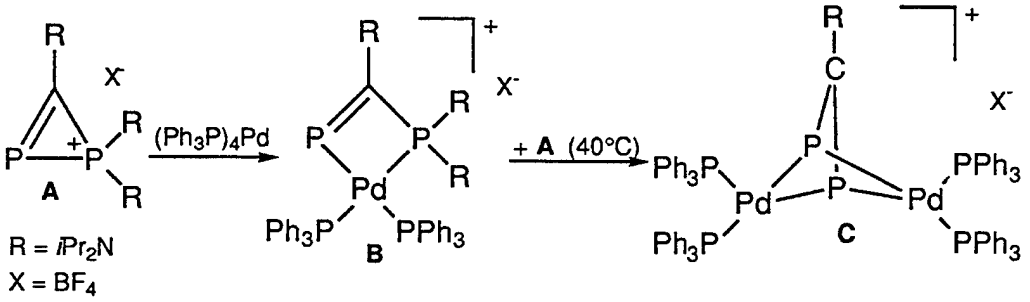
Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cédex (France)

Strained aromatic cyclopropenylium cations are versatile ligands for transition metal complexes: η^1-, η^2- and η^3-coordination modes have been observed. Here we report on the ligand properties of the related diphosphirenium salt **A**[1]. Treatment of a dichloromethane solution of diphosphirenium salt **A** with an equimolar amount of palladium tetrakis(triphenylphosphine) afforded 1,3-diphospha-2-bis(triphenylphosphine)pallada(II)cyclobutene **B** in 70% yield. Exchange of the triphenylphosphine ligands occurs with various phosphines, and the structures of these new diphosphametallacyclobutenes have been elucidated by NMR and in one case by a single X-ray diffraction study[2].



Surprisingly, when a dichloromethane solution of complex **B** was refluxed overnight in the presence of diphosphirenium salt **A** a new complex **C** was formed. This cationic 1,3-diphospha-2,4-dipallada(II)tricyclo[1.1.1]pentane is the first compound featuring pyramidal μ^2-phosphinidene units.

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1-PHOSPHA- AND 1-AZA-3-PHOSPHAALLYLIC ANIONS

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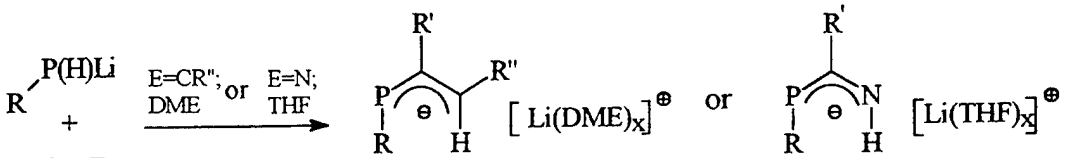
Institut für Anorganische Chemie der Universität, Gerhard-Domagk-Str. 1,
D-53121 Bonn, Germany

Abstract Synthesis, structure and reactivity of 1-phospha- and 1-aza-3-phosphaallyl anions are discussed.

Heteroallyl anions containing nitrogen or phosphorus are rather well explored and found to be remarkable chelate ligands for main group and transition metals.

We were able to realize a convenient synthesis of various 1-phosphaallylic systems **1** by treatment of lithium aryl- or alkylphosphanides with different C-C-triple bonds [1a,c]. **1** exhibits versatile reactivity, e. g. in cycloaddition reactions [1d] or intramolecular cyclization [1b]. Application of the synthetic route for 1-phosphaallyl anions to nitriles instead of acetylenes makes the 1-aza-3-phosphaallylic systems **2** accessible, which can be protonated to the corresponding NH_2-substituted phosphaalkenes [2]. The x-ray structures of the latter two types of compounds are discussed.



1 **2**

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BIORELEVANT PHOSPHONIC ACIDS - PROTONATION AND COMPLEXFORMATION EQUILIBRIA

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and K. KELLNER#

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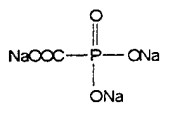
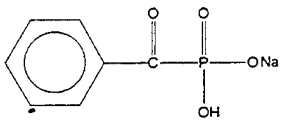
\# Dr. Felgenträger & Co. Öko-Chem. and Pharma GmbH, Seminarplatz 3, D-06846 Dessau, Germany

Various methods of NMR- and PC-controlled titrations were developed in our laboratories. In addition to the by now well-investigated ^{31}P- we applied ^{13}C-, ^{1}H-, ^{19}F- and ^{113}Cd-NMR controlled titrations. Here we report about the methodical progress and results obtained from acylphophonic acids and corresponding hydroxyimino derivatives - as shown below - which gained interests as potentially anti-viral agents:
Tri-sodium-phosphono-formiate (FOSCARNET) **1**, Sodium-benzoyl-phosphonate **2**, Di-sodium-1,6-hexane-bis-phosphonate **3**, Di-sodium-1,8-di-oxo-1,8-octane-bis-phosphonate **4**, Di-sodium-1,8-bis-hydroxyimino-1,8-octane-bis-phosphonate **5**:



1



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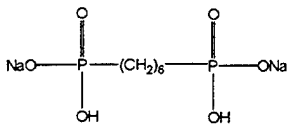

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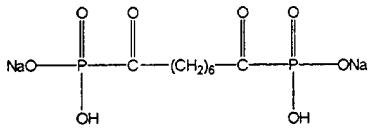

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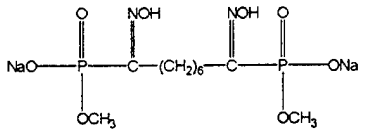

5

Particular attention was drawn towards the novel bis-acylphosphonates and corresponding hydroxyimino structures. By PC-guided high precision titrations and $^{31}P\{^{1}H\}$-NMR purity, decomposition, protonation and stability constants for the formation of calcium complexes were monitored.

Further applications concern the concept of micro dissociation equilibria of amino phosphinic acids and phosphino carboxylic acids.

This work was supported by the German-Israel-Foundation for Scientific Research and Development.

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New Directions in the Development of Water-Soluble Phosphines and Transition Metal Compounds

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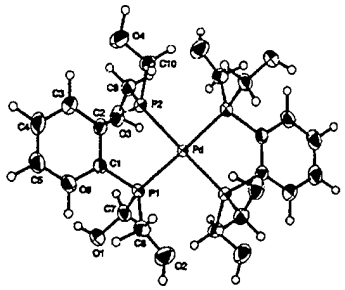
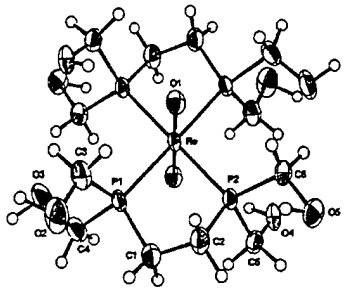
Charles J. Smith, Wynn A. Volkert and Alan R. Ketring
Center for Radiological Research and MU Research Reactor
University of Missouri, Columbia, Missouri 65203, USA.

The water-soluble bisphosphines, *1,2*-bis(bis(hydroxymethyl)phosphino)benzene ("HMPB") (**1**) and *1,2*-bis(bis(hydroxymethyl)phosphino)ethane ("HMPE") (**2**) were synthesized in near quantitative yields by the catalytic hydroformylation of $H_2PC_6H_4PH_2$ and $H_2PCH_2CH_2PH_2$ in the presence of formaldehyde in aqueous media.[1,2] The reactions of these chelating bisphosphines **1** and **2** with $Pt(COD)Cl_2$ and $Pd(PhCN)_2Cl_2$ produced water-soluble Pt(II) and Pd(II) complexes $M[(HOH_2C)_2PC_6H_4P(CH_2OH)_2]_2Cl_2$ (M = Pt, **3**; Pd, **4**) and $M[(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2]_2Cl_2$ (M = Pt, **5**; Pd, **6**) respectively. The reactions of **1** and **2** with $Re(O)_2I(PPh_3)_2$ and $[Re(O)_2(NHC_5H_5)_4]Cl$ to produce new water-soluble Re(V) complexes are also described. All the new compounds were characterized by ^1H and ^{31}P NMR spectroscopy. X-ray structures of representative Pd(II) and Re(V) complexes as shown below confirmed the chemical constitution of this new generation of water-soluble metal complexes.





[1] Reddy, V. S., Katti, K. V. and Barnes, C. L., Inorg. Chim. Acta., *In Press*
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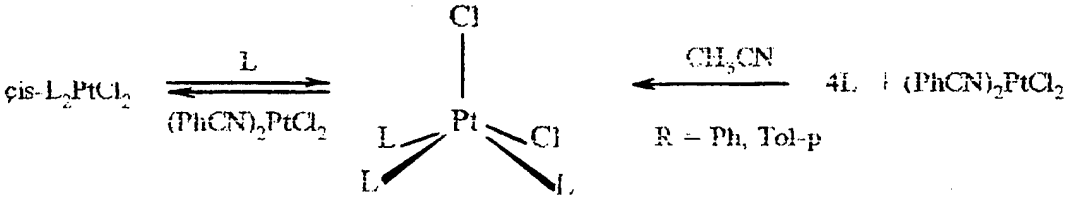
1,3,5-DIAZAPHOSPHORINANES ON THE Pt-GROUP METAL TEMPLATES. CONFORMATIONAL BEHAVIOUR OF THE HETEROCYCLIC LIGANDS AND STABILIZATION OF UNUSUAL COORDINATION OF Pt(II) ION.

S.V.BOBROV, A.A. KARASIK, G.N.NIKONOV
A.E.Arbuzov Institute of Organic and Physical Chemistry,
Russian Academy of Sciences, Kazan Scientific Center, Kazan, Russia

Structure and reactivity of square-planar phosphine complexes are greatly depended from the repulsion of the $P(\alpha C\equiv)_3$ units and neighbouring ligands. The conformational behaviour of heterocyclic phosphines (in particular 1,3,5-diazaphosphorinanes) on the metal templates determines the special features of structures of the corresponding complexes.

It has been shown that 1,3,5-diazaphosphorinanes formed cis-P-complexes of Pt(II) and Pd(II). X-ray analysis of the obtained complexes demonstrated that the phosphine ligands possess chair conformation with diaxial orientation of aryl substituents on P and N atoms. This conformation is stabilized by attractive dispersion interaction of diaxial aryl groups. It has been shown on the base of NMR ^1H data that the less sterically demanded conformer with equatorial orientation of P-M bonds predominates in solutions of all complexes.

The phosphine Pt(II) complexes L_2PtCl_2 in the presence of free ligand excess formed 5-coordinated species L_3PtCl_2. The physical properties and behaviour of L_3PtCl_2 in solutions are probably determined by the ligand sterical demands.



In the solid state the complex L_3PtCl_2 (R=Tol-p) has usual yellow color and it NMR ^{31}P spectrum appears as A_2B spin system. At the same time complex L_3PtCl_2 (R=Ph) has unusual deep red color and it NMR spectrum is consistent with fast cis- to trans- L_2PtCl_2 isomerization catalyzed by free phosphine. Thus, isolated complex L_3PtCl_2 (R=Ph) is probably a low stable intermediate of cis-trans isomerization.

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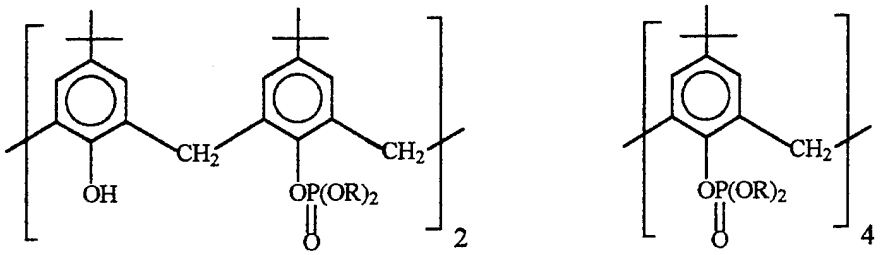
SYNTHESIS AND CATION TRANSFER PROPERTIES OF ALKYL CALIX[4]ARYL PHOSPHATES. A NEW SERIES OF MOLECULAR RECEPTORS.

I.S.ANTIPIN, A.A.KHRUSTALEV, A.I.KONOVALOV
Kazan State University, Kazan, 42008, Russia

Abstract Synthesis, structure and metal ion extraction ability of the new series of host molecules: alkyl calix[4]arylphosphates, are discussed.

Macropolycyclic architectures are particularly well suited for design of synthetic molecular receptors. Calixarenes received much interest as building block for the constraction of new host systems. Our attention has focused on functionalization of phenolic OH groups (lower rim) of calix[4]arene. Bearing in mind a very strong complexation of phosphoryl P=O group with various metal cations we have prepared a series of calix[4]arene derivatives containing two or four phosphate functions, and their ion-binding properties were investigated.



New series of host systems were obtained by the reaction of tetra-tert-butylcalix[4]arene with dialkyl (from methyl to octyl) chloro(bromo)phosphates in the presence of potassium carbonate as a base in refluxing acetonitrile in 60-80% yield. The structure of obtained compounds was confirmed by ^{1}H , ^{31}P NMR and mass spectroscopy. To examine the complexation characteristics of new compounds the liquid-liquid extraction of metal ions from water into chloroform by these podands was studied. It was observed extraction efficiency and selectivities which are absent for parent calixarene. Such behaviour suggests the strong participation of phosphoryl groups in the formation of complexes with metal cations.

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ZIRCONIUM PROMOTED RING OPENING. A NEW ROUTE TO PHOSPHINITES AND POLYPHOSPHINITES

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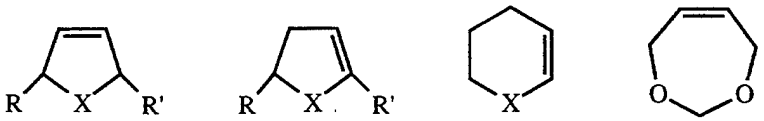
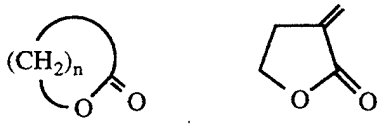
b Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
Sienkiewicza 11290-362 Lodz,Poland

Ring opening reactions involving various heterocycles, the Schwartz reagent $[Cp_2ZrHCl]_n$ and a number of chlorophosphines or phosphenium salts will be presented. Scope and limitations of this useful methodology will be discussed.

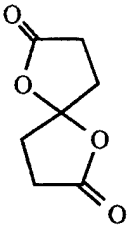


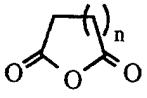
X = -P , -N , O , -B , $\diagdown$ Si , ...

R, R' = H, Me, OMe

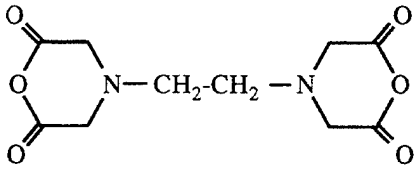


n = 2,3,4





n = 1,2



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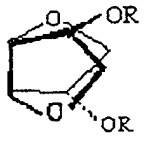
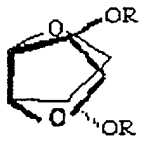
CHIRAL OLIGO- AND POLYPHOSPHITES (PHOSPHONITES, PHOSPHINITES) ON THE BASE OF SPECIFICALLY ORIENTATED IN SPACE HYDROXYLCONTAINING COMPOUNDS. SYNTHESIS, STRUCTURE, AND INVESTIGATION OF COMPLEXATION.

VERA YU. MISHINA, MIKHAIL K GRATCHEV, KONSTANTIN L.ANFILOV, IL'DAR G.MUSTAFIN, ANNA R.BEKKER AND EDWARD.E.NIFANTYEV
Moscow Pedagogical State University, 1 M.Pirogovskaya, Moscow 119882, RUSSIA

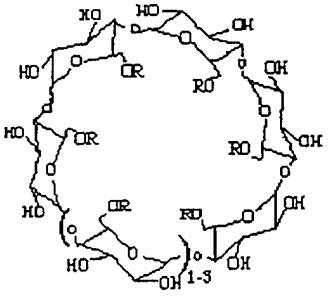
The effective methods of phosphorylation of complex systems with specifically orientated in space hydroxyl groups,namely dianhydro-D-mannitol(A), -D-sorbitol(B), cyclodextrines(C), and cellulose(D) (A-D, where R=H), have been elaborated.



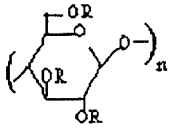
A,E



B,F

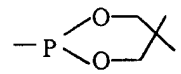


C,G



D,H

Where A-D : R=H; E-H : R=residue of P(III)-derivative, for example:



, $-P(NAlk_2)_2$, -P(OAlk)Ph, $-PPh_2$ and some others.

The factors effecting on the efficiency and the direction of phosphorylation of the indicated compounds were investigated. It was shown, that in the case of shortage of phosphorylation agent the closed in space hydroxyl groups may be subjected to the competitive bis- and cyclophosphorylation because of intramolecular hydroxyl group assistance. P(111)-Azolides turned out to be the most effective phosphorylation means which reduced to minimum the undesirable cyclophosphorylation.

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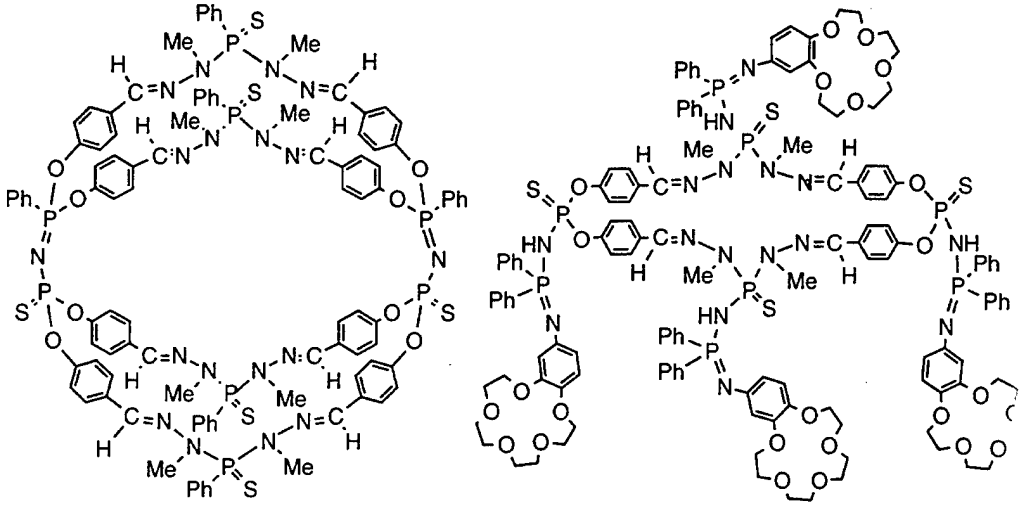
PHOSPHORUS-CONTAINING MULTIMACROCYCLES AND CRYPTANDS

Anne-Marie CAMINADE, Joëlle MITJAVILLE and Jean Pierre MAJORAL*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cédex, France

Numerous well established methodologies are known for the synthesis of organic cryptands and multimacrocycles. However, in most cases, these synthetic pathways are not appropriate to the synthesis of phosphorus containing analogues. We present several methods which allowed us to isolate in high yield original phosphorus derivatives such as the cryptand and the multimacrocycle depicted below [1-4].



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SYNTHESIS AND NMR SPECTROSCOPIC PROPERTIES OF C-FLUORINATED BISPHOSPHONIC ACIDS

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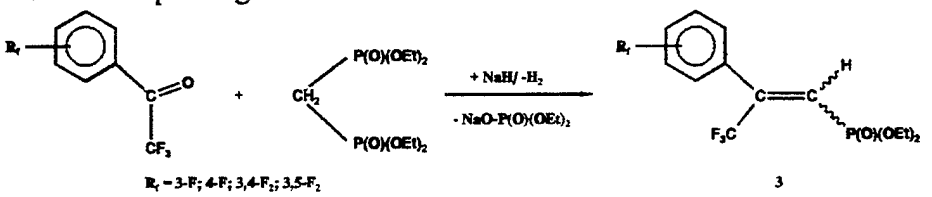
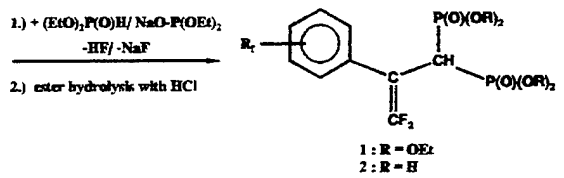
INTRODUCTION

Fluorinated and halogenated bisphosphonates have gained widespread interests in chemistry, pharmacy and medicine. The concept of biochemical activity with metal-chelating agents has encouraged our research team to study synthesis, NMR and analytic chemistry of fluorinated aromatic and olefinic geminal bisphosphonates.

RESULTS AND DISCUSSION

We have developed a reaction pathway for a novel type of fluorinated bisphosphonic acid esters **1** and corresponding acids **2**:





Fluorinated acetophenones and methylenediphosphonic acid ester react under the conditions of the Wittig-Horner-Emmons-Reaction to yield the vinylphosphonates **3**, which add diethyl phosphite. After the nucleophilic addition of the phosphonate group a fluoride ion elimination takes place leading to the bisphosphonic acid esters **1**, which are cleaved by hydrochloric acid to the parent acids **2**. The bisphosphonates **1** and **2** are characterised by 1D-, 2D-, DR- and NOE spectroscopic methods using nuclei ^{1}H, ^{13}C, ^{19}F and ^{31}P. Variable temperature $^{31}P\{^{1}H\}$- and ^{19}F-NMR deduced the dynamic behaviour of the model compounds.

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SYNTHESES OF NOVEL BISPHOSPHONO-PYRIMIDINEDIONES VIA PENTACOVALENT ORGANOPHOSPHORUS METHODOLOGY

CYNTHIA K. McCLURE*, ROBERT C. HAUSEL, KARL B. HANSEN, CHRISTOPHER W. GROTE, KANG-YEOUN JUNG¥
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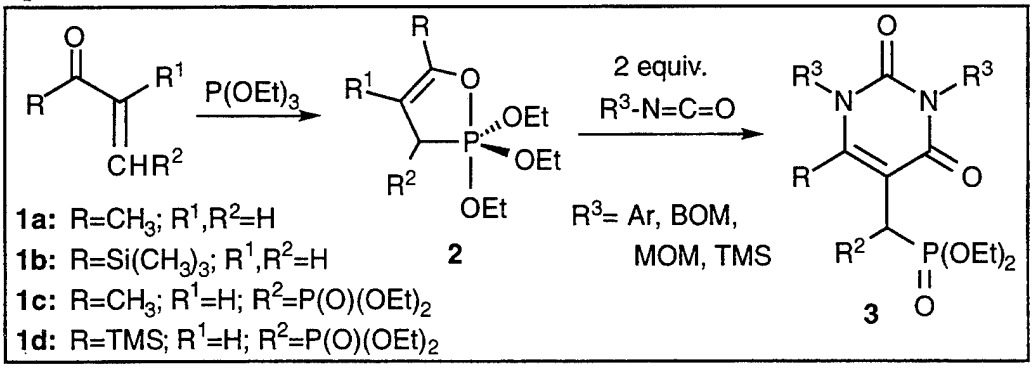
Abstract The synthesis of bisphosphono-pyrimidinediones from the condensations of pentacovalent oxaphospholenes with isocyanates is discussed.

Geminal bisphosphonic acids and their salts are known to be effective inhibitors of bone resorption and mineralization, symptoms of diseases such as osteoporosis and Paget's disease.[1] The active antiresorptive compounds are composed of a "bone hook" portion and a "bioactive moiety". Compounds with a nitrogen or nitrogen-based heterocycle in the "bioactive moiety" are among the more potent antiresorptives.[2] Using our pentacovalent organophospholene methodology, we can readily access mono- and bis-phosphono-pyrimidinediones, **3a-d** in moderate to excellent yields.[3] Molecular modeling has indicated that the deprotected bisphosphonates **3c,d**, could have antiresorptive activity.[4] These compounds are curently being synthesized, and the deprotected heterocycles will be tested for antiresorptive activity.



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THE SYNTHESIS AND EVALUATION OF QUATERNARY PYRIDINIUM BISPHOSPHONATES AS POTENT ANTI-RESORPTIVES

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Departments of Chemistry and Molecular Biology, Sheffield University, Sheffield, S3 7HF, UK.; Procter & Gamble Pharmaceuticals Inc. Cincinnati, Ohio, USA.

Abstract. Several novel quaternary pyridinium bisphosphonates have been synthesised and their efficacy as potential anti-resorptive bone agents have been tested in *Dictyostelium discoideum*. This assay has been shown to accurately reflect the potency of a bisphosphonic acid as an anti-resorptive compound. All the quaternary bisphosphonates are very potent growth inhibitors but results indicate that the more potent compounds are those containing hydrophobic, bulky groups.

Key Words: Bisphosphonate, Anti-resorptive, Dictyostelium, quaternary pyridinium.

INTRODUCTION

A hypothesis that the nitrogen functionality of the more potent N-heterocyclic bisphosphonate anti-resorptives should be positively charged for activity was tested by comparing the potency of the methyl quaternary pyridinium analogue of Risedronate with Risedronate itself in a rat model.[1]

This result indicated that quaternary pyridinium bisphosphonic acids were possible candidates as potent anti-resorptive agents. We thus set out to synthesise a range of quaternary pyridiniumbisphosphonates varying the nature of the quaternary group.

The potency of the bisphosphonates was estimated in our *Dictyostelium discoideum* growth inhibition assay. The inhibition of growth of this slime mould by bisphosphonic acids has been shown to correlate with the anti-resorptive potency of the compounds as estimated by other means.[2,3]

IC_{50} values of the bisphosphonic acids were estimated from growth and dose-response curves of the incubated mould.

CONCLUSION

All the quaternary analogues synthesised were potent growth inhibitors of *Dictyostelium*, and were substantially more potent than most of the early bisphosphonate anti-resorptives tested in the same assay.

The results show an increase in potency on increasing the size (and subsequently hydrophobicity) of the quaternary group e.g. $-(CH_2)_3Ph$. The least potent analogues were those with only small quaternary groups e.g. $-CH_2CH_3$ or $-(CH_2)_3SH$.

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THIAZOLIUM-SUBSTITUTED GEM-BISPHOSPHONATES.

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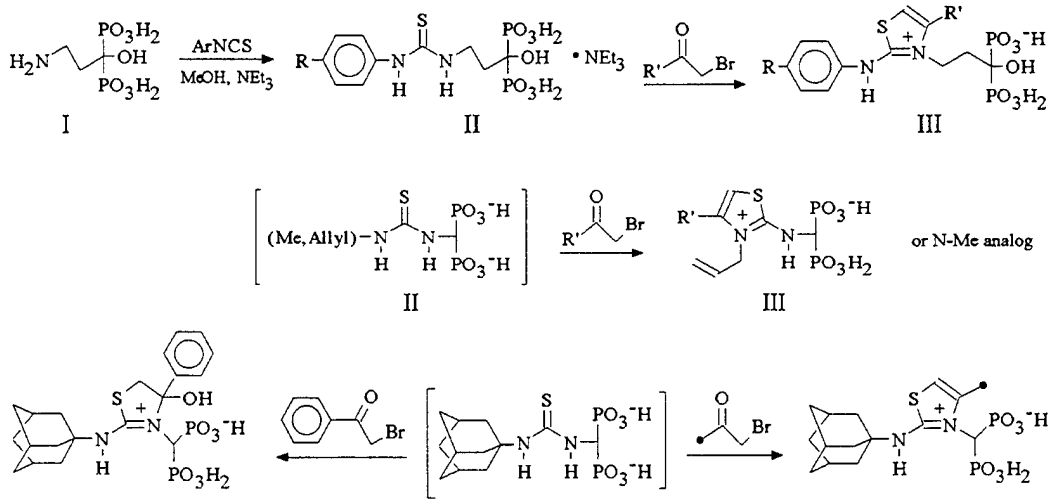
Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Str. 5, Kiev 253660, Ukraine

Heterocyclic derivatives of gem-bisphosphonates exhibit various biological activities. We have found that thiazolium substituted bisphosphonic acids can be obtained by two-step synthesis from amino-bisphosphonates (I). Reaction of (I) with isothiocyanates in alkohol in the presence of triethylamine led to corresponding thioureas (II) obtained as natrium or triethylamonium salts [1]. Further treatment of (II) with α-bromoketones give aminothiazoles (III) with a good yield. As a rule only less hindered nitrogen atom is involved into the cyclization with formation of one from two of possible isomers.



Obtained thiazoliumalkylidene-1,1-bisphosphonic acids are colourless high-melting substances easily convertable in water soluble (if R'=Me) Na salts.

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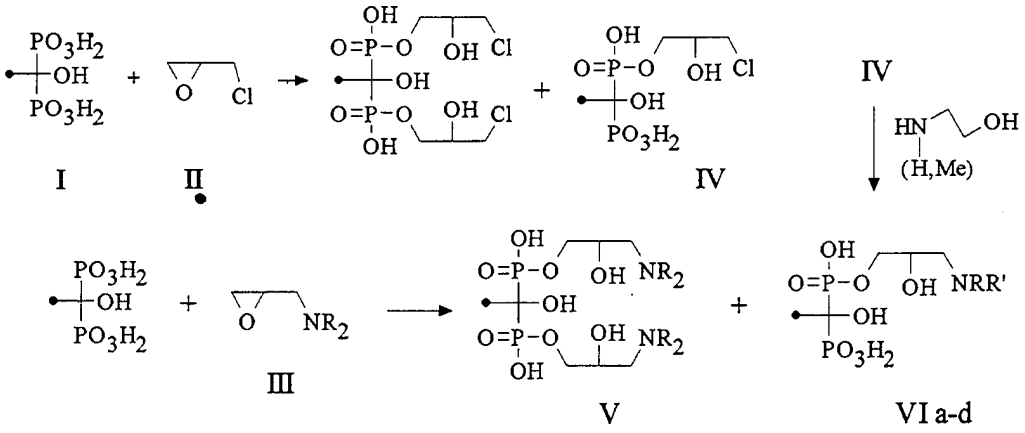
AMINOHYDROXYPROPANE ESTERS OF HYDROXYETHYLIDENEBISPHOSPHONIC ACID.

CHUIKO ALEXEY, PHILONENKO LUDMILA, BORISEVICH ANATOLY, LOZINSKY MIRON
Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Str. 5, Kiev 253660, Ukraine

The 1-hydroxyethylidene-1,1-bisphosphonic acid (HEDP) (I) reacts with epichlorohydrine (II) and aminoepoxypropanes (III) in water. Optimum pH for the esterefication is 6-7. The reaction completes in 20-30 h on 60°C at this pH and leads to the mixture of the original HEDP with the mono- and diesters. The mixture of di-Na salts of HEDP and the monochloroester (IV) in ratio 1:1.7 was precipitated from the reaction solution on using of the epichlorohydrine (II). This mixture was used for synthesis of aminoesters (VI a,b) unavailable by direct reaction of HEDP with corresponding aminoepoxides.



VI) RR'= H,C_2H_4OH (a), Me,C_2H_4OH (b), $(C_2H_4)_2O$ (c), Et_2 (d).

The aminoesters (V, VI) was isolated by ion-exchange chromatography on KU-2-8 (analog Dowex-50X8) ion-exchange resin.

Obtained aminoesters (V and VI) are glassy or crystalline hygroscopic substances. Any precipitate doesn't appear in the water solution of (VI) when Ca^{2+} salts are added.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 67
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SYNTHESIS OF NOVEL BISPHOSPHONATE INHIBITORS OF PHOSPHOGLYCERATE KINASE (3-PGK) (E.C.2.7.2.3)

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Chemistry Dept., University of Sheffield, Brook Hill, Sheffield, UK, S3 7HF

Abstract Novel, aromatic bisphosphonates have been synthesised as non-systematic analogues of 1,3-*bis*phosphoglyceric acid (1,3-BPG). These incorporate non-scissile α-halo and α-methylene phosphonates and have submicromolar K_i values for 3-PGK.

Keywords: halogenation, isopolar, isosteric, spectrophotometric assay, aromatic.

INTRODUCTION

3-PGK converts 1,3-*Bis*phosphoglycerate (1,3-BPG) into 3-phosphoglyceric acid (3-PGA), forming ATP. In a minor alternative process, 1,3-BPG is converted into 2,3-BPG by *bis*phosphoglycerate mutase, (BPGM), and this is then hydrolysed to 3-PGA by 2,3-BPG phosphatase. The selective inhibition of the kinase but not of the mutase is a significant medical target. Crystallographic analysis of these two enzymes shows that the active site of 3-PGK [1] is larger than that of BPGM.[2, 3] Thus, it should be possible to identify inhibitors of 3-PGK which are excluded from the site of the mutase. We have synthesised 'non-systematic' inhibitors whose structures are generally based on 1,3-BPG and are 1,4- or 1,5-bisphosphonates with an aromatic spacer.

SYNTHESIS AND RESULTS

Our need for isopolar and isosteric mimics of bisphosphates calls for synthesis of a range of bisphosphonates and their monochloro, dichloro, monofluoro and difluoromethylene analogues. We have used pyridine and benzene as the aromatic spacer and are working on use of pyrrole and thiophene cores. All the bisphosphonic acids are made as their tetraalkyl esters and deprotected using trimethylsilylbromide or 6N hydrochloric acid. They are purified and tested as their cyclohexylammonium salts. The testing of the bisphosphonic acids was carried out using 3-PGK isolated from human blood and the K_i values were obtained spectrophotometrically by monitoring NAD^+ at 340 nm for the back reaction. The general order of the results was checked by a luminometric assay for the forward reaction. The α-chloro and fluoromethylene bisphosphonates tested showed submicromolar K_i values. The K_i values for the α-hydroxy and methylene phosphonates were around 100μM.
These results clearly show good leads on strong, competitive inhibitors for 3-PGK. Routes to the dichloro and difluoromethylene phosphonates have now been established. Also, routes are being investigated to bisphosphonates with thiophene and pyrrole cores.

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A HAPTEN FOR THE GENERATION OF ANTIBODY PHOSPHATASES

JASON BETLEY, G. Michael Blackburn
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Abstract A series of hydroxymethylene and α,β-unsaturated aminophosphinic acids was prepared, modelled on the 'exploded' transition state proposed (Herschlag [1]) for the chemical hydrolysis of phosphate monoesters. They exhibit the dual utility of being transition state analogues for the chemical hydrolysis of phosphate monoesters and having the potential for inhibition of phosphatase enzymes. (**1**) was chosen to be utilised as a hapten molecule for the generation of catalytic antibodies.

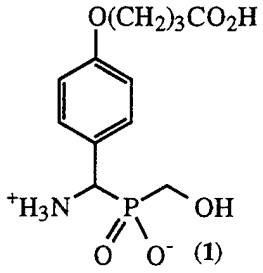
Key Words: Catalytic, Antibodies, Phosphatase, Hapten, Abzymes

PHOSPHATE MONOESTER HYDROLYSIS

A large number of abzymes has been reported capable of the cleavage of aliphatic esters. Examples of antibody phosphatases, however, are few and show rather small rate enhancements (Scanlan [2]). By examining the proposed transition state for chemical hydrolysis, it is hoped to elicit antibodies that are both prolific and specific.

Modelling the Transition State

The enzymic process occurs *via* enzyme serine phosphorylation. The chemical process, however, proceeds *via* a 'metaphosphate-like' transition state. The well-developed leaving group positive charge and the negatively charged 'metaphosphate' are mimicked in hapten molecule (**1**) by a zwitterionic amino phosphinic acid moiety. The hydroxymethylene unit serves as a model for an incoming nucleophilic water molecule. The overall hapten dimensions serve to imitate the large amount of bond breaking and small amount of bond making present in the 'exploded' transition state.



(**1**)

The synthesis of the hapten (**1**) is achieved in 7 steps from 4-hydroxybenzaldehyde. Williamson ether addition appends the linker moiety, followed by formation of the aldehyde bisacetamide with acetamide in refluxing acetic acid/acetic anhydride. Treatment with hypophosphorous acid in refluxing acetic acid affords the N-acetyl phosphonous acid, which is not isolated, but hydrolysed and protected to yield the CBZ-amino acid. Hydroxymethylation with gaseous formaldehyde /TMSCl/Et_3N and subsequent deprotection furnishes hapten (**1**) ready for conjugation to carrier protein.

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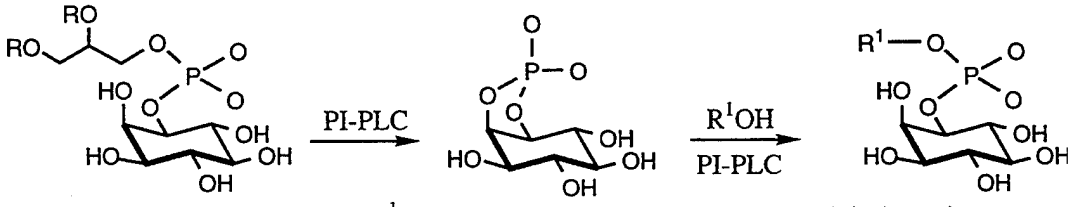
ENZYMATIC SYNTHESIS OF INOSITOL PHOSPHODIESTERS USING PHOSPHATIDYLINOSITOL-SPECIFIC PHOSPHOLIPASE C

GUAN ZHIWEN & KAROL S. BRUZIK*
Department of Medicinal Chemistry and Pharmacognosy, University of Illinois at Chicago, Chicago, IL 60612

Abstract Transesterication of inositol 1,2-cyclic phosphate with primary alcohols in the presence of phospholipase C produces alkyl inositol phosphates.

Cleavage of phosphatidylinositol (PI) by the specific phospholipase C (PI-PLC) produces inositol 1,2-cyclic phosphate (IcP) [1]. Bacterial PI-PLC further hydrolyze IcP into inositol 1-phosphate (IP) at low rates. We have found originally that incubation of IcP with PI-PLC in the presence of the Tris-HCl buffer and glycerol produced several by-products. These products were identified as acyclic diesters containing Tris and glycerol, respectively.



R = palmitoyl, R^1 = 1° alcohols, diols, aminoalcohols, alditols, serine

Application of other primary alcohols showed that this reaction is of a very general scope. Transesterification of IcP proceeded with a wide spectrum of alcohols such as primary alkanols and alkenols, diols, polyols and 2- and 3-amino alcohols, diacetyl glycerol and serine, but not with acyclic or cyclic secondary alcohols. The presence of the branching point at the carbon atom β- with respect to the hydroxyl group did not hamper the reaction. With polyols derived from monosaccharides only the primary hydroxyl groups participated, and the presence of inositol was inhibitory. The attempts at transesterification with long chain-, bromo-, epoxy- and mercapto- alcohols were unsuccessful. The reaction was completely nonstereospecific with respect to configuration of an alcohol, and thus both pro-*R* and pro-*S* hydroxyl groups of prochiral diols and *R*- and *S*-enantiomers of chiral diols reacted with equal rates. The obtained acyclic diesters undergo further transesterification in water to produce IcP. The final product of a prolonged incubation with PI-PLC was always IP, however, monitoring the reaction time courses by means of high performance anion exchange chromatography coupled with pulsed amperometric detection, or by ^{31}P NMR, allowed determination of the optimal point for stopping the transesterification process. The obtained yields were in the range 20-80% depending on the nature of an alcohol and its concentration. The starting IcP can be conveniently obtained in a single step by treatment of soybean phospholipid with small amounts of PI-PLC.

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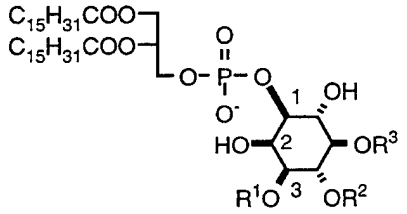
GENERAL SYNTHESIS OF PHOSPHATIDYLINOSITOL PHOSPHATES

ROBERT J. KUBIAK & KAROL S. BRUZIK*
Department of Medicinal Chemistry & Pharmacognosy, University of Illinois at Chicago, Chicago, Illinois 60612

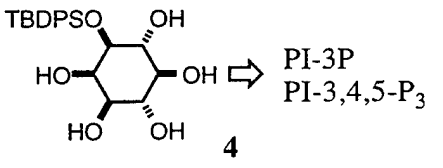
Abstract A general method for synthesis of 3-phosphorylated phosphatidylinositols is described.

Phosphatidylinositol (PI) and phosphatidylinositol phosphates (PIP_n), such as PI-4-P, PI-4,5-P_2 undergo receptor-mediated cleavage by phosphatidylinositol-specific phospholipase C, and are precursors of second messengers important in diverse cellular signaling pathways. In contrast, the 3-phosphorylated phosphatidylinositols, such as PI-3-P (**1**), PI-3,4-P_2 (**2**) and PI-3,4,5-P_3 (**3**), which are formed in response to signals of growth factors, are resistant to hydrolysis by this enzyme, and their cellular function is only beginning to emerge [1,2]. These compounds are formed in minute quantities, and therefore have to be synthesized for many practical applications.

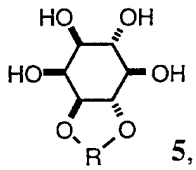


1, $R^1 = PO_3^{2-}$, $R^2 = R^3 = OH$
2, $R^1 = R^2 = PO_3^{2-}$, $R^3 = OH$
3, $R^1 = R^2 = R^3 = PO_3^{2-}$

Here, we describe the first general approach to all 3-phosphorylated phosphatidyl-inositols starting from easily accessible intermediates **4** and **5** [3]. This approach could also be extended to all inositol phospholipids and their phosphorothioate analogs. The common difficulty associated with syntheses of PI phosphates is the necessity to discern between phosphorylation sites leading to phosphomono- and phosphodiesters. Using precursors **4** and **5** these sites were differentiated by regioselective low temperature benzoylation of inositol hydroxyl groups. Depending on the starting compound selective benzoylation at 3, 3,4- and 3,4,5-positions could be achieved. Further redesign of protective groups led to several enantiomerically pure precursors of phospholipids featuring the same protective groups and differing only in their number and positions in the inositol ring.



PI-3P
PI-3,4,5-P_3



PI-3,4-P_2

4

5, R = tetraisopropyldisiloxanedi-1,3-yl

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LONG-RANGE ^{31}P-^{31}P SPIN COUPLING CONSTANTS IN THE ^{31}P NMR SPECTRA OF PHOSPHITE TRIESTERS

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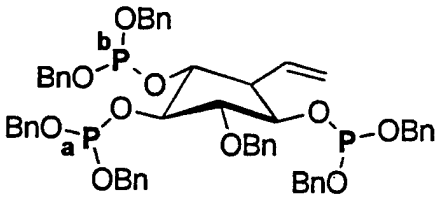
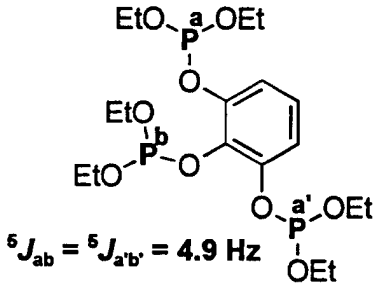
Department of Medicinal Chemistry, School of Pharmacy and Pharmacology,
University of Bath, Claverton Down, Bath BA2 7AY, UK.

Abstract. Data are presented on the magnitudes of $^5J_{PP}$ and $^6J_{PP}$ spin-spin coupling constants in the ^{31}P NMR spectra of a variety of novel polyphosphite triesters.

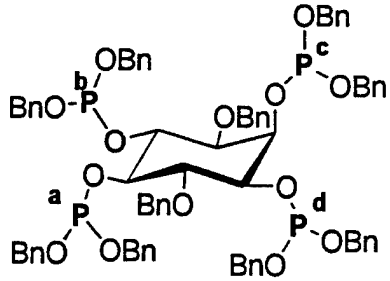
During our investigations into the synthesis of polyphosphate analogues of the ubiquitous second messenger D-*myo*-inositol 1,4,5-trisphosphate, we have reacted many different polyhydroxy compounds with phosphitylating reagents. The ^{31}P NMR spectra of the resulting polyphosphite triesters often display ^{31}P-^{31}P spin couplings over five[1] or six bonds. We have collected data on the magnitudes of the coupling constants in a range of molecular frameworks, and some examples are given here.



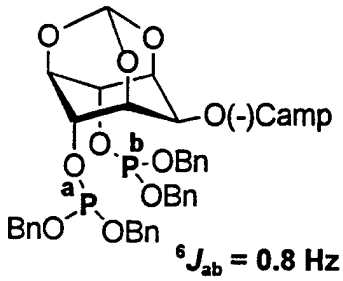
$^5J_{ab}$ = 6.7 Hz



$^5J_{ab} = {}^5J_{a'b'}$ = 4.9 Hz



$^5J_{ab}$ = 3.7 Hz, $^5J_{cd}$ = 1.8 Hz



$^6J_{ab}$ = 0.8 Hz

Bn = benzyl, Et = ethyl, (-)Camp = (-)camphanate .

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 72
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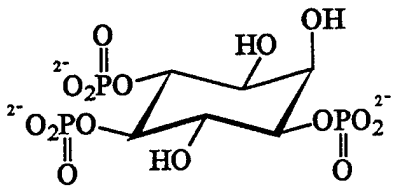
THE SYNTHESIS OF CHIRAL *MYO*-INOSITOL TRISPHOSPHATE ANALOGUES

STEPHEN J. MILLS AND BARRY V. L. POTTER
Department of Medicinal Chemistry, School of Pharmacy and Pharmacology, University of Bath, Claverton Down, Bath BA2 7AY, UK.

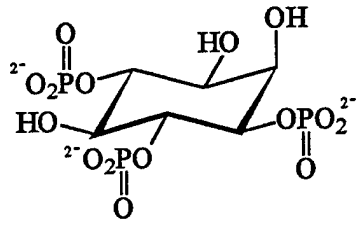
Abstract D- And L-Ins(1,4,6)P_3 and D-Ins(1,4,6)PS_3 were synthesised and evaluated for their ability to mobilise Ca^{2+}.

D-*myo*-Inositol 1,4,5-trisphosphate [Ins(1,4,5)P_3**(1)**] is a ubiquitous water soluble second messenger, which releases Ca^{2+} from non-mitochondrial stores. It is generated by activation of GTP-binding proteins, which are coupled to phospholipase C-catalysed cleavage of the minor membrane lipid phosphatidylinositol 4,5-bisphosphate.

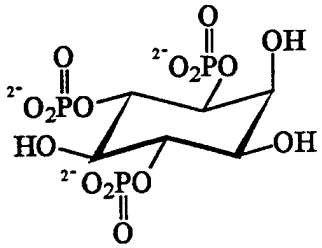
We have synthesised three chiral Ins(1,4,5)P_3 analogues. These include, D-Ins(1,4,6)P_3 **(2)**, L-Ins(1,4,6)P_3 **(3)** and D-Ins(1,4,6)PS_3 **(4)**. The latter **(4)** is a very low intrinsic partial agonist at the platelet Ins(1,4,5)P_3 receptor, releasing only 17% of the preloaded Ca^{2+}. **(2)** Is a full agonist for Ca^{2+} release, but **(3)** is essentially inactive.



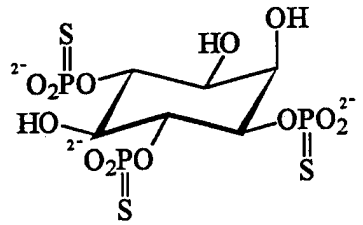
D-Ins(1,4,5)P_3 (1)



D-Ins(1,4,6)P_3 (2)



L-Ins(1,4,6)P_3 (3)



D-Ins(1,4,6)PS_3 (4)

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 73
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SYNTHESIS OF NOVEL POLYPHOSPHATE ANALOGUES OF INOSITOL 1,4,5-TRISPHOSPHATE

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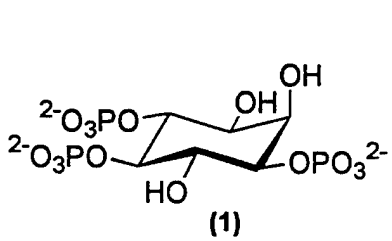
University of Bath, Claverton Down, Bath BA2 7AY, UK.

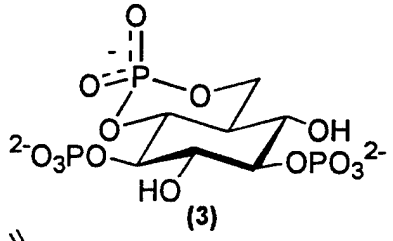
Abstract The synthesis of novel polyphosphate mimics of inositol 1,4,5-trisphosphate, including ring-contracted and conformationally restricted analogues is reported.

The binding of many hormones, neurotransmitters and growth factors to their extracellular receptors results in production of the second messenger D-*myo*-inositol 1,4,5-trisphosphate [Ins(1,4,5)P_3 (**1**)] *via* activation of phosphoinositidase C. Ins(1,4,5)P_3 interacts with a family of intracellular receptor-operated Ca^{2+} channels to mobilise non-mitochondrial Ca^{2+} stores in a vast array of cell types, and the synthesis of analogues of Ins(1,4,5)P_3 offers the prospect of pharmacological intervention in this ubiquitous signalling pathway. Recently, we have synthesised a number of novel polyphosphate mimics of Ins(1,4,5)P_3, including the cyclopentane-based "Pentagon IP3" (**2**).[1]

The conformationally restrained racemic analogue **3** was a full agonist at the platelet Ins(1,4,5)P_3 receptor, but 40-fold weaker than Ins(1,4,5)P_3. Racemic **4**, which bears an equatorial hydroxymethyl group, was found to be equipotent with Ins(1,4,5)P_3.



(1)



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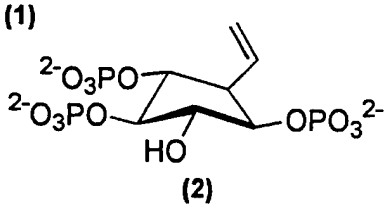

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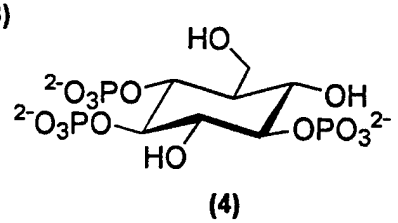

(4)

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 74
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PATHWAYS FOR THE PRODUCTION OF PHARMACEUTICAL GRADE SYNTHETIC PHOSPHOLIPIDS

D. J. HARRIS, E. R. LEE, C. S. SIEGEL, I. R. DAVISON, C. B. JACKSON, R. D. BROWN, J. BEAUMONT, H. C. PINKARD, R. PROBST* AND H. EIBL.**
Genzyme Corp., One Kendall Square, Cambridge, MA 02139, USA, *Sygena LTD., Eichenweg 1, CH-4410 Liestal, Switzerland and **Max-Planck-Institut für Biophysikalische Chemie, D-37077 Göttingen, FRG.

Abstract Two routes are described for the synthesis of pharmaceutical grade phospholipids at the multi-kilogram scale.

Key Words: phospholipid synthesis, biocatalytic synthesis, asymmetric synthesis

In the past, kilogram and multi-kilogram amounts of phospholipids were only available by isolation from natural sources. Recently, developments in synthetic phospholipid chemistry have resulted in the creation of effective methods for the large scale production of lipid and phospholipid molecules well defined in structure and configuration.

The Sygena route was based on the work of H. Eibl [1] with D-mannitol as the source of chirality. The intermediate diacylglycerols were phosphorylated with phosphorous oxychloride and the resulting diacylglycerolphosphorous oxydichlorides were converted to the respective phospholipids by reaction with different alcohols (or protected alcohols) such as choline, ethanolamine, glycerol etc.

Genzyme [2] has developed a route based on the biocatalytic enantioselective phosphorylation of glycerol by glycerol kinase to give sn-glycerol-3-phosphate. Sn-glycerol-3-phosphate was then converted to a variety of phosphatidic acids via acylation with fatty acid anhydrides. The respective phosphatidylcholines were prepared by a chemical phosphate esterification step. Mixed chain phosphatidylcholines were prepared by the phospholipase A_2 catalyzed preparation of lyso-phosphatidylcholines followed by acylation with the appropriate fatty acid anhydride. Phospholipids with other head groups were prepared from phosphatidylcholines via phospholipase D catalyzed transesterification. Both the Sygena and Genzyme pathways are being used to prepare a range of pharmaceutical grade phospholipids at the multi-kilogram or greater scale.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 75
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AMIDOTHIONOPHOSPHATES: NOVEL ANTIOXIDANT MOLECULES.

Oren Tirosh^, Yehoshua Katzhendler[#], Yechezkel Barenholz[@], Isaac Ginsburg[&] and Ron Kohen^
^Department of Pharmacy, [#]Department of Pharmaceutical Chemistry, School of Pharmacy, [@]Department of Biochemistry, Faculty of Medicine, and the [&]Department of Oral Biology, The Hebrew University of Jerusalem Israel.

This work describes the synthesis and characterization of a new family of antioxidants. The molecules have the same active group, but different oil-to-water and octanol-to-water partition coefficients due to different substituents. Three new molecules were synthesized based on the chemical structure of the primary amide attached to a thiophosphate group forming an amidothionophosphate. The amidothionophosphate molecules were exposed to the oxidative stress of hydrogen peroxide and sodium hypochlorite, and the chemical changes following the exposure were monitored by ^{31}P NMR. The reaction constants with reactive oxygen species such as hydroxyl radical and superoxide radical were also calculated and found to be $1.5*10^9$ $M^{-1}S^{-1}$ and $8.1*10^2$ $M^{-1}S^{-1}$, respectively. In order to elucidate the ability of amidothionophosphates to act as antioxidants in protecting lipids and proteins, we examined damage prevention in Bovine serum albumin, egg phosphatidyl choline liposomes and lipid emulsions following oxidative stress.Amidothionophosphate showed unique protection properties in these models. In contrast to other antioxidant molecules (ascorbic acid, cystine, and a-tocopherol) the new group did not have any pro-oxidative effects as measured by oxygen consumption from buffer solutions containing amidothionophosphates and cupric sulfate as a redox-active metal. Amidothionophosphates reduced significantly and in a dose-dependent manner the oxidative burst in human neutrophils as measured by luminol-dependent chemiluminescence, and they also markedly depressed the killing of human fibroblasts by mixtures of glucose oxidase and streptolysin S. The toxicity of these molecules was tested by i.p. injection of up to 1000 mg/kg to white Sabra mice. No mortality was observed 30 days after administration of up to 500 mg/kg.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 76
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MICROTUBULES FROM FLUORINATED PHOSPHORYLATED AMPHIPHILES IN AQUEOUS/ALCOHOLIC AND NON-AQUEOUS SOLVENTS

MARIE PIERRE KRAFFT, FRANÇOISE GIULIERI, AND JEAN G. RIESS
Laboratoire de Chimie Moléculaire, Unité Associée au CNRS, Université de Nice-Sophia Antipolis, Faculté des Sciences, 06108 Nice Cédex 02, France

Phospholipids are known to self-organize into bilayer membranes and liposomes. Recently, much attention has also been focussed on highly ordered cylindrical, bilayer-based hollow microstructures usually called tubules, that form, for example, from diacetylenic phosphatidylcholines [1]. However, despite the potential of these new supramolecular architectures in both fundamental and applied area, only few tubule-forming surfactants have been reported yet. We have shown that the driving force required to form and stabilize coiled membranes in water can be brought by fitting amphiphiles with a single fluorinated chain, without need for rigid segments, hydrogen bonding between polar head or chiral centers [2,3].

We now report the formation of multilayered tubular edifices from perfluoroalkylated dimorpholinophosphoramidates, $C_nF_{2n+1}(CH_2)_2OP(O)[N\square O]_2$, n = 8, 10, in ethanol or methanol or glycerol/water mixtures, as well as in dimethylformamide. Well-developed tubules, as shown phase contrast optical microscopy and negative staining transmission electron microscopy (10-20 μm, Φ: 0.5-2 μm, fig. 1), are obtained, for example, using a 2/1 ethanol/water ratio. These tubules are very robust and retain their morphology after centrifugation, drying and resuspension in an alcohol/water mixture. In DMF, it was possible to monitor the formation of isolated tubules by progressive rolling-up of planar bilayer sheets. Reversible interconversion of the tubules into giant multilayered vesicles was observed upon heating.

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[3] J. G. Riess, *J. Drug Target* 1994, **2**, 455-468.

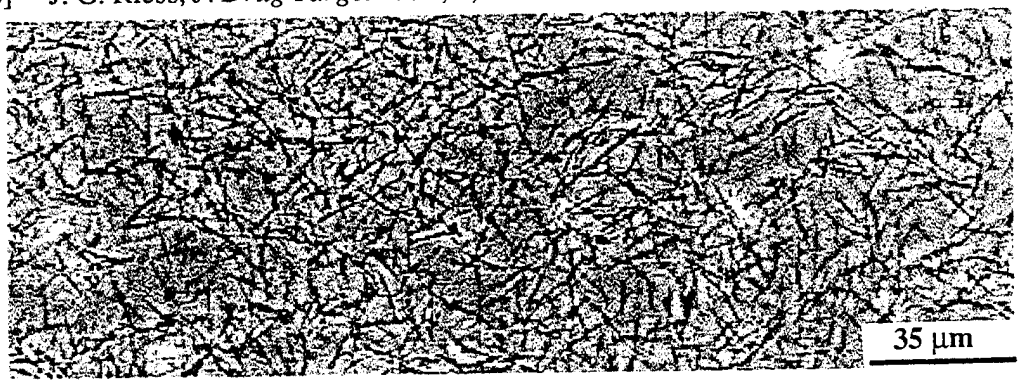

FIGURE 1: Fluorinated tubules obtained from $EtOH/H_2O$ medium.

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SYNTHETIC STUDIES TOWARD THE PREPARATION OF PHOSPHONATE ANALOGS OF SPHINGOMYELINS AND CERAMIDE 1-PHOSPHATE USING PENTACOVALENT ORGANOPHOSPHORUS METHODOLOGY

CYNTHIA K. McCLURE*, PRANAB K. MISHRA
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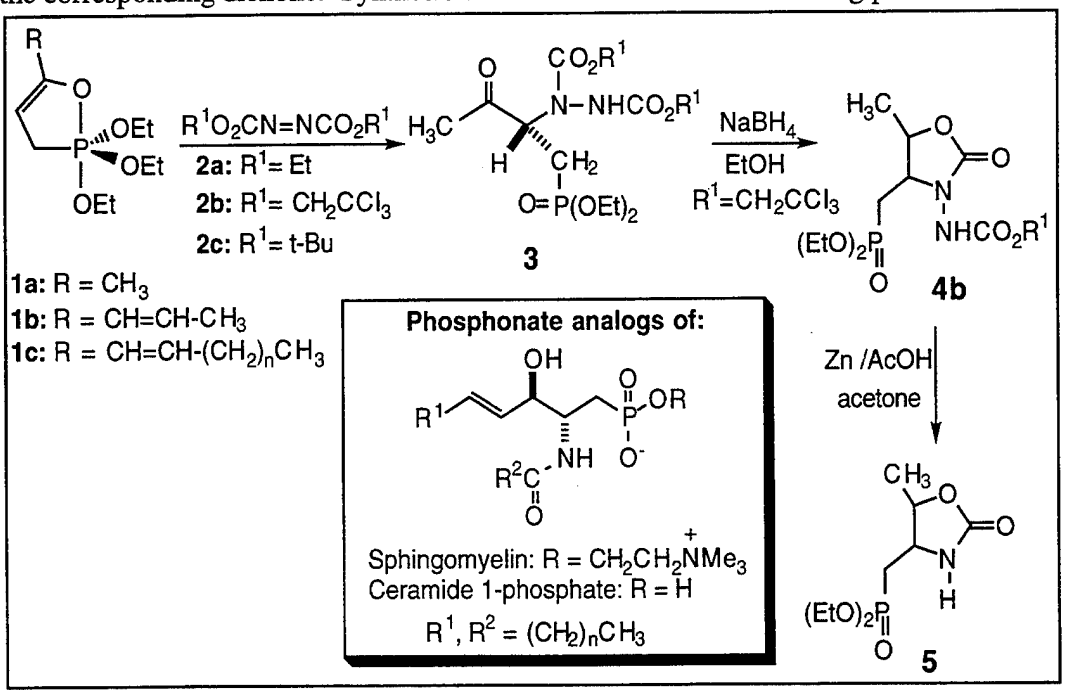
Abstract Non-isosteric phosphonate analogs of sphingomyelin and ceramide 1-phosphate are being synthesized from the condensation product of a pentacovalent oxaphospholene and azodicarboxylates. Model studies are initially described.

Model studies for the syntheses of phosphonate analogs of sphingomyelins and ceramide 1-phosphate are being pursued. The pentacovalent oxaphospholene **1a** readily condenses with dialkyl azodicarboxylates **2a-c** to form the hydrazido-keto-phosphonates **3a-c** in excellent yields.[1] Upon reduction with $NaBH_4$, **3b** produced the oxazolidinone **4b** in high yield (3:1, cis major). Treatment of **4b** with Zn/HOAc/acetone readily cleaved the N-N bond to form **5**. Standard N-N cleavage conditions failed with R = Et, t-Bu. The relative stereochemistry in both diastereomers of **5** was determined by NOE studies. The syntheses of the sphingomyelin and ceramide 1-phosphate derivatives require the use of the P(V) **1c**. We have been successful preparing **1b** from the corresponding dienone. Synthesis of the dienone to form **1c** is being pursued.



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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 78
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MOLECULAR INTERACTIONS OF OLIGONUCLEOTIDES IN ORGANISM- A SOURCE OF BROAD SPECTRUM OF BIOLOGICAL ACTIVITIES

VALENTIN VLASSOV, LEONID YAKUBOV, MARINA NECHAEVA, LUDMILA PAUTOVA, ELENA RYKOVA, PAVEL LAKTIONOV, INNA VLASSOVA and LARISSA BALAKIREVA

Institute of Bioorganic Chemistry, Novosibirsk 630090 Russia.

Abstract Oligodeoxynucleotides interact with a few proteins at the cell surface and in the bloodstream. These interactions determine cellular uptake, biodistribution and some nonspecific antiviral and immunomodulating effects of oligonucleotides.

Key Words oligonucleotides, nucleic acid -protein interaction

Perspective therapeutics, derivatives of oligonucleotides, affect functions of the complementary target nucleic acids and can cause some sequence independent effects, including nonspecific antiviral effects, inhibition of cell proliferation and activation of immune system. The sequence independent effects may be explained by interaction of oligonucleotides with some nucleic acid- related proteins. We investigated nucleic acid binding proteins in the blood plasma and at the cell surface. The method was affinity modification with radiolabeled oligodeoxynucleotides bearing an alkylating group, 4-[(N-2-chloroethyl-N-methyl)amino]benzylphosphamide residue at the terminal phosphate.

We have found that at the surface of eucaryotic cells, oligonucleotides bind to a specific nucleic acid binding receptor and to receptor CD4. Binding of oligonucleotides to cells stimulates incorporation of phosphorus into phosphatidic acid and increases production of diacylglycerol suggesting that the oligonucleotide binding receptor functions as a typical receptor coupled to cellular signaling system. Binding to specific receptors plays an important role in cellular uptake and transcytosis of oligonucleotides through biological barriers. We have found that oligonucleotides can enter organism through mucosa and skin. Using electron microscopy we have observed spontaneous cellular uptake of oligonucleotides and fast transportation of the compounds to the cell nucleus. Interaction of oligonucleotides with receptor CD4 explains sequence-independent anti-HIV effects of the compounds.

In the serum, oligonucleotides were found to bind to epidermal growth factor, immunoglobulins M and G and serum albumin. It was shown, that specific antigens interfere with the oligonucleotide- immunoglobulin interaction. Covalent attachment of oligonucleotides to immunoglobulins yields crosslinked complexes similar to the antigen-antibody complexes in the ability of binding to the Fcγ receptor at the lymphocyte surface. Binding of oligonucleotides to proteins should affect the fate and bioavailability of the compounds in organism. The interaction with immunoglobulins may affect polyclonal activation of immune system. Further investigation of the proteins interacting with oligonucleotides may result in identification of the targets of therapeutic value.

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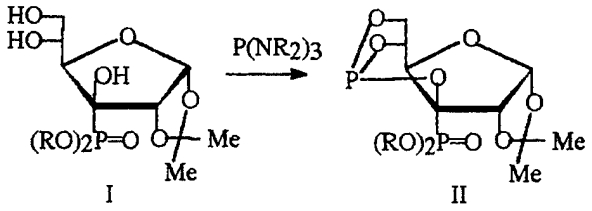
FURANOSE BICYCLOPHOSPHITES AS SYNTHONS OF MODIFIED NUCLEOSIDE DIPHOSPHATES

MIKHAIL P. KOROTEEV, VITALII K. BELSKII, ANNA R. BEKKER, and EDUARD E. NIFANTYEV
Moscow Pedagogical State University, M. Pirogovskaya, Moscow 119882, Russia

Previously we synthesized and examined in detail 1,2- alkylideneglucofuranose 3,5,6-bicyclophosphites; mono- and bicyclophosphates with peculiar chemical and physiological activity were obtained on their base [1]. During the study of their structural dependence, we modified the hydrocarbonic moiety, synthesiz-ed 1,2,3- and 3,5,6-bicyclophosphites and cyclophosphates of gulofuranose, and correlated their features with those of glucose analogues. Furthermore, an additional phosphonate moiety (obtained by a stereoselective reaction of an appropriate ketonic sugar with silylphosphites) was introduced into the glucofuranose 3,5,6-bicyclophosphite molecule to the third carbon atom. As a result, the monosaccharide matrix gained two functional groups containing tri- and fourcoordinated phosphorus.



I II

The synthesized compounds make optically active ligands for enantioselective metallocomplex catalysts and can be synthons of modified nucleotides inhibiting tyrosinekinase and proteinkinase C. For example, on interaction of glucofuranose phosphito-phosphonates with hydrogen peroxide and other homolytic agents, the bicyclophosphite group undergoes a regioselective change to 3,5- or 3,6-cyclophosphate moiety. Thus, we obtained new modified analogues of cyclic nucleotides and 3'-nucleoside-phosphates in high yields.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 80
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DEOXYRIBONUCLEOSIDE CYCLIC 3',5'-PHOSPHOROFLUORIDATES

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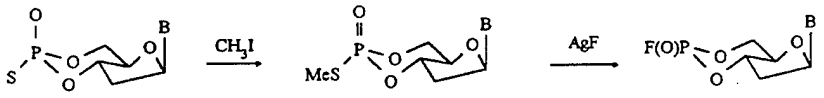
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Department of Bioorganic Chemistry, Sienkiewicza 112, 90363 Łódź, POLAND

The synthesis of nucleoside cyclic 3',5'-phosphorofluoridates, so far not described compounds in the chemical literature, have been performed. As a key substrate we used 2'-deoxyribonucleoside cyclic 3',5'-phosphorothioates (**1**) which have been obtained in this Laboratory several years ago.[1]

Alkylation of the triethylammonium salt of **1** with methyl iodide and subsequent treatment of 2'-deoxyribonucleoside cyclic 3',5'-(S-methyl)phosphorothioates (**2**) with aqueous silver fluoride[2] (Scheme 1) gave **3**.



1a, b **2a, b** **3a, b**

a : B = Thy
b : B = Cyt

The reaction progress was monitoring by means of ^{31}P nmr. If pure [Sp]-**1a** was used as the substrate, crude **3a** consisted of the mixture of diastereoisomers absorbing at -7.3 ppm and -9.0 ppm (CD_3CN) with $^1J_{P\text{-}F}$ 923 and 948 Hz, respectively in the ratio 9:1. Pure [Rp]-**1a** under analogues condition gave as the product **3a**; the ratio of diastereomer absorbing at -7.3 ppm and -9.0 ppm equal 2:1. Treatment of this mixture with concentrated aq. NH_3 caused epimerization process leading exclusively to **3a** resonating at -7.3 ppm ($^1J_{P\text{-}F}$ 923 Hz). When we performed the conversion of phosphorothioate into phosphorofluoridate starting from diastereomeric mixture of deoxycytidine cyclic 3',5'-phosphorothioates (**1b**, Sp:Rp=2:1, Scheme 1) exclusively one diastereomer of **3b** (δ_{31P} -7.9 ppm, $^1J_{P\text{-}F}$ 950 Hz) was obtained.

Acknowledgments: This project was financially assited by the State Committee of Scientific Research, Grant No. 500-02-01-5.

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DINUCLEOSIDE (5'→3')-O,S-PHOSPHORODITHIOATES - NEW CLASS OF DINUCLEOTIDE ANALOGUES

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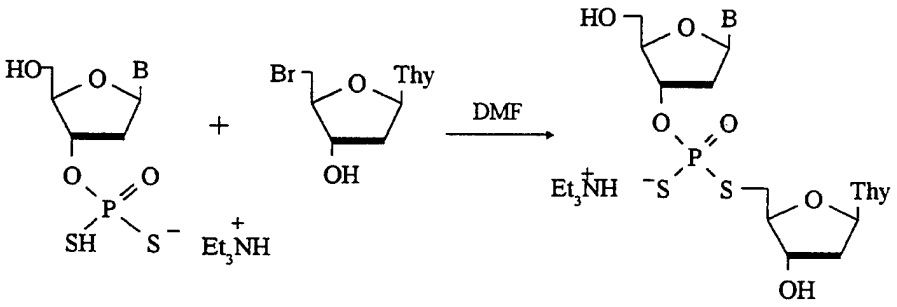
Nucleoside 3'-O- and 5'-O-phosphorodithioates have been recently described by Caruthers *et al.*[1] as a new type of nucleotide analogues. These compounds have also been obtained in our Laboratory by one-pot dithiaphospholane approach.[2] We now report on the transformation of some of these derivatives into new class of dinucleotide analogues. We have found that nucleoside 3'-O-phosphorodithioates (**1**) react in DMF solution with 5'-bromo-5'-deoxythymidine to give in high yield corresponding dinucleoside (5'→3')-O,S-phosphorodithioates (**2**) - first examples of a new class of dinucleotide analogues possessing the internucleotide phosphorothioate linkage with one of the sulfur atoms in a 3'-bridging position.



1a, B=Thy
1b, B=Cyt

2a, B=Thy, δ ^{31}P NMR =72.9, 73.6ppm
2b, B=Cyt, δ ^{31}P NMR =72.8, 73.5ppm

The products **2a,b** were isolated by ion exchange chromatography as a mixture of diastereomers by virtue of asymmetry of internucleotide phosphorus as evidenced by ^{31}P NMR and HPLC. Their structure was confirmed by characteristic ^{31}P NMR chemical shift and by LSIMS mass spectrometry.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 82
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SYNTHESIS OF DODECA(THYMIDINE PHOSPHATE) CONTAINING (*o*-CARBORAN-1-YL)METHYLPHOSPHONATE INTERNUCLEOTIDE LINKAGE

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Laboratory of Biochemical Pharmacology, Department of Pediatrics, Emory University School of Medicine and VA Medical Center, Decatur, GA 30033, USA.

Abstract The synthesis of dodeca(thymidylic phosphate) containing 3'-end (*o*-carboran-1-yl)methylphosphonate group instead of natural phosphodiester internucleotide linkage is described.

The use of boron-containing compounds in the treatment of malignancies is based on the property of boron-10 nuclei delivered to neoplastic cells in the form of a boron carrying drug, to absorb low-energy neutrons. The ensuing micronuclear reaction releases about 100 million times more energy than that of the neutron used, resulting in cancer cell destruction. Boronated oligonucleotides were designed as specific boron rich trailers for boron neutron capture therapy (BNCT) and antisense oligonucleotide technology (AOT).[1,2,3] A solid phase synthesis of oligonucleotides containing modified (*o*-carboran-1-yl-methyl)phosphonate groups at 3'-end of the oligonucleotide chain was accomplished. A standard β-cyanoethyl cycle and automated DNA synthesizer was used for the unmodified phosphodiester linkage formation. The phosphotriester method using the monomer 5'-O-monomethoxytritylthymidine 3'-O-[O-methyl(*o*-carboran-1-yl)methylphosphonate][1] was successfully applied to produce modified *o*-carboran-1-yl-methylphosphonate internucleotide linkage.

ACKNOWLEDGMENTS
Supported by the NIH grant RO1-CA 53892 and R44-CA 65434 and the Department of Veterans Affairs.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 83
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SYNTHESIS AND ANTI-HIV-1 REVERSE TRANSCRIPTASE ACTIVITY OF TRIPHOSPHATES OF PENCICLOVIR AND β-D-DIOXOLANE-GUANINE

ZBIGNIEW J. LESNIKOWSKI,[1] AMY S. JUODAWLKIS,[1] ROBERT M. LLOYD, JR.,[1] CHUNK K. CHU[2] AND RAYMOND F. SCHINAZI[1]*

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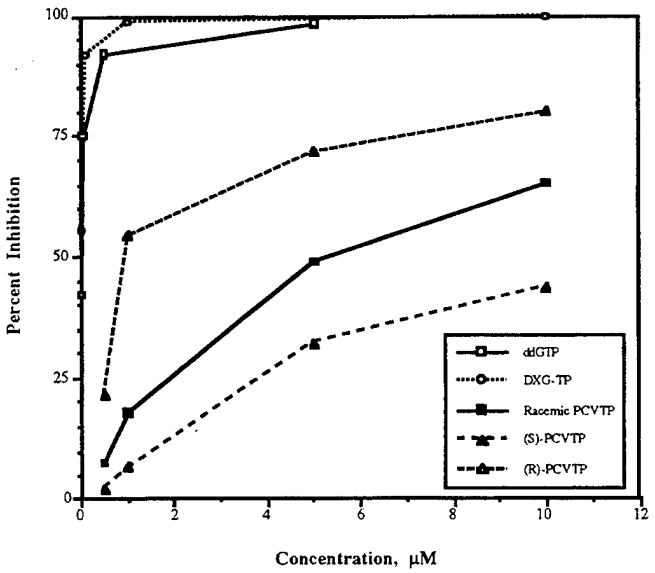
Abstract The synthesis of *R*- and *S*-9-(4-Hydroxy-3-hydroxymethyl-but-1-yl)guanine (PCV) and (-)-β-D-dioxolane-guanine (DXG) triphosphate and their enzyme inhibitory activity is descibed.

Penciclovir (PCV) and (-)-β-D-dioxolane-guanine (DXG) are selective antiviral agents against certain herpesviruses and human immunodeficiency viruses (HIV), respectively. The triphosphate forms inhibit viral replication by acting as substrates for viral polymerases.[1] To test the activity of nucleotide analogues against HIV-1 reverse transcriptase (RT) *in vitro*, the suitable triphosphates were synthesized.



Phosphorylation of *O*-monoisobutyryl-PCV (*R*-, *S*- or racemic form) with 2-chloro-4*H*-1,2,3-dioxaphosphorin-4-one followed by reaction with tri-*n*-butylammonium pyrophosphate, oxidation,[2] and removal of isobutyryl protection produced the desired PCV-triphosphates. Similarly DXG-triphosphate was synthesized. Enzymatic assays using a poly(rC)$_n$.oligo(dG)$_{12-18}$ template primer revealed potent activity of PCV- and DXG-triphosphates against HIV-1 RT.

ACKNOWLEDGMENTS. Supported by the NIH grant RO1-AI 25899 and the Department of Veterans Affairs.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 84
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A ^{31}P NMR STUDY OF THE STABILITY OF CARBOXYIFOSFAMIDE AND CARBOXYCYCLOPHOSPHAMIDE, TWO METABOLITES OF IFOSFAMIDE AND CYCLOPHOSPHAMIDE

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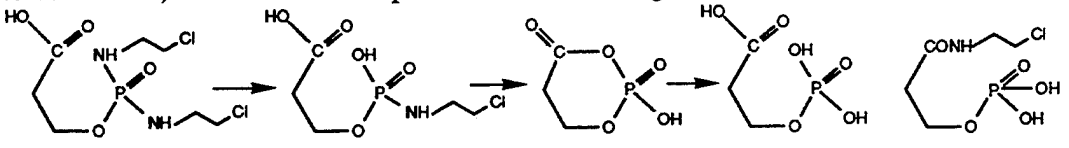
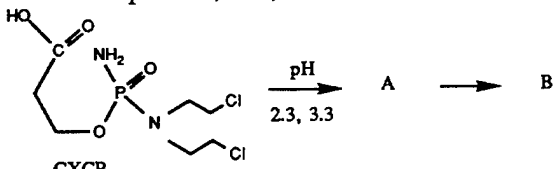
Ifosfamide (IF) and cyclophosphamide (CP) are two phosphorated anticancer agents used in the treatment of solid tumours. Several phosphorated metabolites, among them carboxyifosfamide (CXIF) and carboxycyclophosphamide (CXCP), were detected and quantified by ^{31}P NMR in urine from patients treated with IF or CP. In agreement with other authors [1], we observed a great inter-patient variability in the urinary excretion of CXIF in patients treated with IF [2]. This variability was attributed to a genetic polymorphism of aldehyde dehydrogenase, the enzyme responsible for the formation of CXCP or CXIF [1,3]. Since CXCP and CXIF are unstable, we thought that the inter-individual variability could also be due to a degradation during the storage of urine samples. A ^{31}P NMR study of the stability of CXIF and CXCP in urine as a function of time, pH (7 and 5.5) and storage temperature (25°C, 8°C, -20°C, -80°C) demonstrated that (i) CXCP and CXIF are more stable at pH 7 than at pH 5.5, (ii) CXCP is more stable than CXIF at both pH, (iii) the degradation decreases with temperature but still occurs at -20°C and even -80°C. For an accurate quantification of these compounds, the storage of urine samples must be done at -80°C immediately after collection and not exceed 1 month at pH 7 whereas, at pH 5.5, the assay must be carried out in the few days following the sampling. To identify the degradation products of CXCP and CXIF, the time course of hydrolysis (between pH 2 and 7) of these compounds was monitored by ^{31}P NMR. The structure of each compound formed was determined by mass spectrometry and ^{1}H and ^{13}C NMR after their isolation (except compound A too unstable to be isolated). The results are reported in the following schemes.



CXIF D A B C

B was detected at all pH (2.3, 3.3, 4.2, 5.6, 7.0), D only at pH 4.2, 5.6 and 7.0, A at pH 2.3, 3.3, 4.2, 5.6 and C at pH 3.3, 4.2, 5.6.



CXCP

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, pp. 85
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HERBICIDAL ACTIVITY OF PHOSPHONIC, PHOSPHINIC AND PHOSPHINOUS ACID ANALOGUES OF AROMATIC AMINO ACIDS

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Over 40 phosphonic, phosphinic and phosphinous acid analogues of phenylglycine and phenylalanine were synthesized and screened for their herbicidal activity on *Lepidium sativum* (crest) and *Cucumis sativus* (cucumber). The most active appeared to be 2-amino-1-hydroxy-3-phenylpropylphosphonic acid which was equipotent with popular herbicide glyphosate. Also aminobenzylphosphonic acids, analogues of phenylglycine, exhibited notable herbicidal activity and thus represent a group of the most active herbicides found among simple aminophosphonic acids. Other compounds showed moderate herbicidal activity. Preliminary results indicate that analogues of aromatic amino acids display their activity as effectors of biosynthesis of aromatic amino acids.

Synthesis of enantiomerically pure 2-amino-1-hydroxy-3-phenypropylphosphonic acids were achieved by simple addition of diethyl phosphite to enantiomers of N-blocked phenylalaninals. This reaction was found to be highly stereoselective. Since the obtained compounds may be also considered as phosphonic acid analogues of statine their inhibitory potency towards cytosolic (EC 3.4.11.1) and microsomal (EC 3.4.11.2) aminopeptidases was evaluated. Both stereoisomers, however, were found to be the weak inhibitors of the enzymes.

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THE USE OF LYPOLITIC MICROORGANISMS *Pseudomonas fluorescens* AND *Penicillium citrinum* FOR THE PREPARATION OF OPTICALLY ACTIVE 1-HYDROXYALKYLPHOSPHONATES.

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Lipases are perhaps the most widely used biocatalysts in organic synthesis. In this study lipases were found to catalyse the acetylation of diethyl 1-hydroxyalkylphosphonates, as well as 1-aminoalkylphosphonates. Unfortunately the lack of enantioselectivity was observed despite of the source of enzyme, as well as the type of organic solvent used as the reaction medium. Also the use of lipases for the enantioselective hydrolysis of diethyl O-butyryloxyalkylphosphonates in aqueous media was unsuccesful. Quite oppositively the hydrolysis of these substrates by wide-type strain of *Pseudomonas fluorescens* yielded optically active diethyl 1-hydroxyalkylphosphonates with moderate or good yields and of satisfactory optical purity, as determined by means of n.m.r. analysis of Mosher derivatives. The use of other lypolitic microorganism - *Penicillium citrinum* - was also succesful providing enantiomeric forms of the products obtained from the reaction catalyzed by *Pseudomonas fluorescens*. The substrate specificity of these two microorganisms, is discussed in some detail.

The exogenous lipase produced by *Pseudomonas fluorescens* did not catalyze the hydrolysis of diethyl O-butyryloxyalkylphosphonates . This indicates that some cellular enzymes are most probably resposible for the observed enantioselective hydrolysis

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THE INTERACTION OF THIOETHYNYL ESTERS OF THIOPHOSPHORIC ACIDS WITH CYTOCHROM P 450

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We have shown that thioesters of phosphoric acids of general formula $(RO)_2P(X)C{\equiv}CR^1$, were X=O or S, containing an acetylenic bond in α-position of the S-ester group has unugually high destructive effect on some isoforms of cytochrome P 450 of arthropods and mammals. These isoforms probably , participate in the process of inactivation of the acetylenic thioesters. We assume that this process may be thought as being a rupture of rhe P-S bond, which leads to the formation of killer particles - alkylthioketenes.

$$(RO)_2P(X)SC{\equiv}CR^1 \longrightarrow (RO)_2P(X)OH + R^1CH{=}C{=}S$$

The latter possess high reactivity and can destruct cytochrome P 450. This idea was supported by studying of the direct interaction of rat liver microsomes with lithium hexynyl mercaptide, which is readily hysrolyzed in medium under conditions of incubation with cytochrome P 450 to form the same killer particle - butylthioketene

$$C_4H_9C{\equiv}CSLi \longrightarrow C_4H_9CH{=}C{=}S$$

This effect is not observed for the saturated analogues since their interaction results in the formation of metabolites which cannot be isomerized into thioketenes.

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Effect of Phosphate Fertilization on Micronutrient Content of Maize Plant

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The effect of fertilization and irrigation on phosphate and metal content in maize was studied in an arable land plot experiment on fertilization effects. A field plot experiment was carried out at the Látókép Farm 15 km from Debrecen. Each treatment consisted of 46 m^2 plots, arranged in a randomized block design with four replication, where the basic treatment was fertilization; the additional treatments were crop rotation, irrigation and cultivation. The soil is Calcareous Chernozem with 2.8-3.0% humus content. The depth of the humus layer is 70-90 cm. The N-content and original P-content of the soil is average, but it is rich in K. Besides macroelements, there is no shortage of trace elements. The element content of maize was determined with a Labtam 8440M inductively coupled plasma atomic emission spectrometer after digestion. A relationship between phosphate and microelement contents in plant was studied. A linear relationship between phosphate and magnesium, and some microelement contents can be found. Linear correlation in P and Mg content of maize was found strongest (Fig 1.).

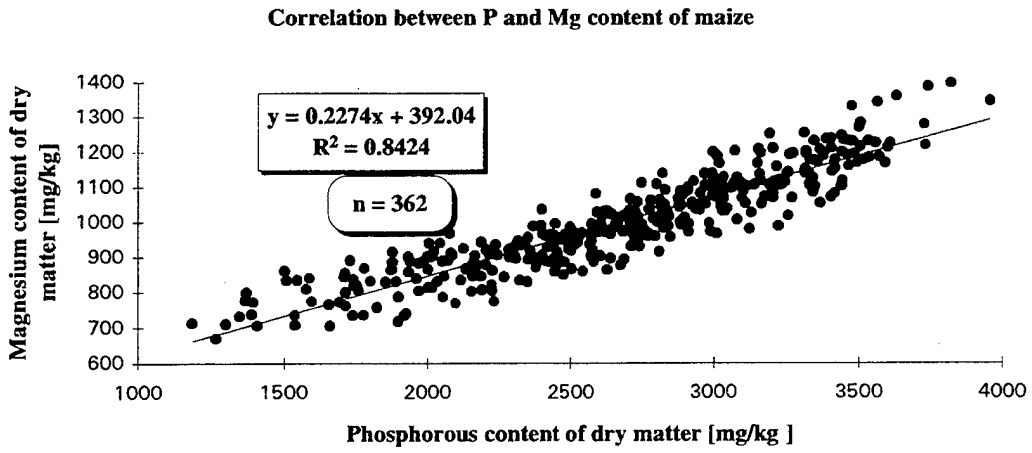

Figure 1.

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THE USE OF PHOSPHINE AS AN AGRICULTURAL FUMIGANT

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Abstract Problems associated with using a phosphine /CO_2 mixture as a fumigant include oxidation and contamination with P_4

Phosphine is an extremely toxic gas and at low concentrations provides an efficient fumigant for stored grain where insect infestations, if unchecked, can cause severe losses. Fumigation has become increasingly important as stricter regulations are placed on pesticide residues in foodstuffs. Phosphine is ultimately converted to environmentally and biologically benign oxidation products and as it is commercially inexpensive, it is an attractive proposition as an industrial chemical. Insects develop resistance to PH_3 but effective control is possible by maintaining a toxic concentration over a lengthy period (1-3 weeks) either in a sealed enclosure or by continuous injection of gas to make up for loss.

Phosphine itself is too dangerous to handle and is replaced by a 2% w/w mixture with CO_2 (Phosfume, USP 4,889,708; GBP 2177004) which is non inflammable. Pure PH_3 is not spontaneously inflammable but it is too expensive. Originally the gas was generated by the slow hydrolysis of crude calcium phosphide

This paper describes difficulties which arose in using the CO_2/PH_3 system in the field, namely fires when dismantling the apparatus and clogging of pipes leading to cessaation of gas flow. The fire problem proved to be due to residual P_4 in the PH_3 and analytical techniques (NMR and GC) were developed to determine it. The clogging, by a yellow-brown solid, apparently a P_nH_x polymer was more difficult to trace and appears due to inadvertent oxidation in the cylinder filling process. Polymer formation can be demonstrated experimentaly. The mechanism is obscure but is presumably a free radical chain reaction The polymeric solid on prolonged exposure to air affords a mixture of phosphonic, phosphinic, and phosphoric acids and an air stable high melting solid which analyses for $CO_2 \cdot P_2H_4$, an apparently unique example of a $PH_3 + CO_2$ reaction.We have been unable to detect P_2H_4 or other spontaneously inflammable higher hydrides unequivocally in either PH_3 or Phosfume

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DESIGN AND ENANTIOSELECTIVE SYNTHESIS OF PHOSPHONATES AS ENZYME INHIBITORS

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The serine proteases [1] form an important group of hydrolytic enzymes essential to a variety of biological activities ranging from food digestion to blood clotting. However their uncontrolled activity is also known to be implicated in a number of pathological conditions including emphysema, cystic fibrosis, cancer and myocardial infarction. Their selective control is therefore an important goal and could offer a basis for the rational design of therapeutic agents.

Recent studies [2] involving the phosphonate analogues of peptidyl amino acids have shown that the diphenyl esters behave as potent specific irreversible inactivators of targeted members of the serine protease group e.g. chymotrypsin and elastase. We have also more recently prepared fluoro- and chloro- substituted phenyl esters of these analogues and have found considerable enhancement in inhibitory activity over the unsubstituted analogues, (e.g. m-chlorophenyl esters show k_i/K_i values up to 10^3x greater than the corresponding phenyl esters).

We have also successfully extended our synthetic approach to the preparation of a number of basic amino acid analogues e.g. cbz-Orn^P(OPh)$_2$, cbz-Lys^P(OPh)$_2$ etc.,[3] and using a guanidation reaction elaborated these to arginine and related analogues e.g. cbz-Arg^P(OPh)$_2$ and cbz-*homo*-Arg^P(OPh)$_2$ etc. These have been targeted as inhibitors of trypsin and trypsin-like serine proteases. Preliminary biological results suggest they are selective for these and also show specificity towards individual members of the trypsin group.

The dependence of biological interactions on absolute configuration imposes limitations on results obtained using racemic materials. As a result we have developed a convenient enantioselective synthesis for individual isomers of a wide range of α-aminophosphonous and phosphonic acids [4] and the corresponding phenyl esters. The biological properties of these compounds are currently being investigated.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 91
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ARYLBENZYLPHOSPHONATES - A NEW CLASS OF IRREVERSIBLE PENICILLIN ACYLASE INHIBITORS

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Abstract Anionic phosphonates are shown to inactivate penicillin acylase via phosphonilation of active site with simultaneous release of appropriate phenol.

Phosphorus-containing inhibitors are valuable tools for understanding the properties and physiological role of hydrolytic enzymes. Previously derivatives of benzylphosphonic acid have been investigated as reversible inhibitors of penicillin acylase from *E. coli* (EC 3.5.1.11). On the contrary, compounds with general structure (I) have quite different mode of action and are irreversible competitive inhibitors of enzyme:

$$\underset{\text{(Ia-d)}}{C_6H_5CH_2P(O)(O^-)\text{-}O\text{-}C_6H_4\text{-}R} + E(Ser)OH \longrightarrow E(Ser)OP(O)(O^-)\text{-}O\text{-}CH_2C_6H_5 + R\text{-}C_6H_4OH$$

where R=CO_2H, CO_2CH_3, $CO_2CH_2C_6H_5$, NO_2 for the compounds (Ia-d) respectively. Now only β-lactamase is known to have such types of inhibitors. Inactivation process involves formation of an intermediate before the chemical stage. Second order rate constants have been determined (k_2=1,78x10^3 $M^{-1}min^{-1}$, 40x10^3 $M^{-1}min^{-1}$, 200x10^3 $M^{-1}min^{-1}$, 1220x10^3 $M^{-1}min^{-1}$ for compounds Ia-d, respectively). The effectiveness of these compounds varies in a very broad range and depends on the nature of R-group. There is strong correlation between inactivation activity and phenolic fragment properties as a good leaving group. It indicates general mechanism of enzyme interaction with anionic arylbenzylphosphonates: the greater acidity of phenol is accompanied with greater inhibitors effect. The enzyme's inactivation by compound (Ia-d) is accompanied by stoichiometric release of appropriate phenol even when large excess of inhibitor is used. The reactivation of the inactivated enzyme has not been observed both in water solution and in presence of 6-aminopenicillanic acid. Apart from kinetic stability of the inactivated enzyme, the most striking feature of these inhibitors is the high rate phosphonylation itself. Based on obtained results we suggest that catalytic activity loss take place due to phosphonilation of active site serine hydroxyl with simultaneous release of appropriate phenol.

Thus, the phosphonates include in their mode of action an admixture of transition-state analogue and mechanism based inhibitor characteristics. They are thought to be used as convenient active site titrants, as sources of fresh insight into the chemical properties of enzyme active site.

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SEARCH ON ENZYME INHIBITORS OF THE GLUTATHIONE METABOLISM : SYNTHESIS OF PHOSPHONOPEPTIDES

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In a program designed to prepare peptide derivatives with altered biological activity, methods for incorporating α-amino phosphonic acids at the "C-terminal" position were investigated.

Replacement of one amino acid residue in a peptide chain with an aminoalkanephosphonic acid, to give a phosphonopeptide offers numerous structural possibilities to study particular biological mechanisms. This replacement leads to P-analogs of peptides possessing substrate activity or inhibitory power against certain enzymes.

We report here simple methods for the synthesis of di and tripeptides related to glutathione and ophthalmic acid.

$$H_2N\text{-}CH(COOH)\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}\mathbf{X}\text{-}NH\text{-}CH_2\text{-}COOH$$

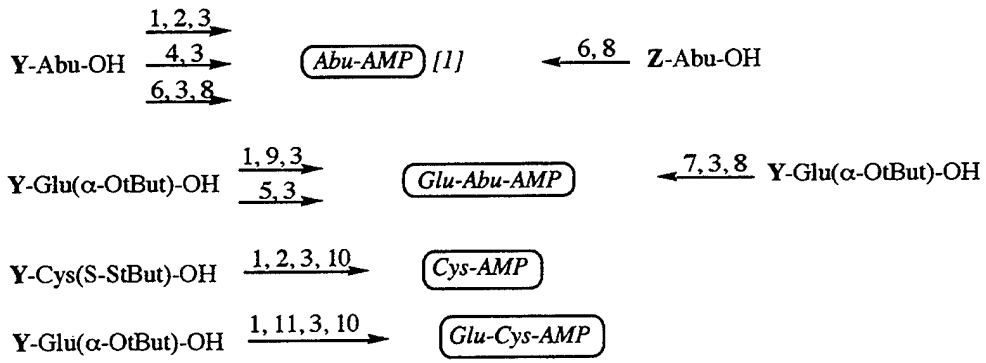
L-γ-glutamyl residue (Glu) — *glycyl residue*

X = -NH-CH(CH_2-CH_3)-CO- = L-α-aminobutyryl residue (Abu) → Ophthalmic acid

X = -NH-CH(CH_2-SH)-CO- = L-cysteinyl residue (Cys) → Glutathione

In these compounds the terminal carboxylic group of the natural compounds (Glycyl residue) is replaced with a terminal phosphonic group (aminomethyl phosphonic residue, AMP).

To realize the preparation of these phosphonic analogs, we have used conventional methods of the peptide chemistry adapted to the particular characteristics of the new products :



Y = $(CH_3)_3C$-O-CO- ; **Z** = C_6H_5-CH_2-O-CO- ; 1 : N-hydroxysuccinimide (SuOH) ; 2 : AMP ; 3 : CF_3COOH ; 4 : iButOCOCl + AMP ; 5 : iButOCOCl + Abu-AMP ; 6 : EDCI + $AMP(OEt)_2$; 7 : EDCI + $Abu\text{-}AMP(OEt)_2$; 8 : HBr + CH_3COOH ; 9 : Abu-AMP ; 10 : PBu_3 ; 11 : Cys(S-StBut)-AMP

All molecules have been characterized by IR and ^{31}P, ^{13}C, ^{1}H NMR spectroscopy.

From these results it is apparent that N-ethyl-N'-(3-dimethylamino-propyl)carbodiimide hydrochloride (EDCI) is an excellent coupling agent between esters of aminomethylphosphonic acid and N-carbobenzoxy or N-*t*butyloxyamino acids.

In the same way we obtained satisfactory results with the mixed carbonic-carboxylic anhydride and N-hydroxysuccinimide active ester methods using free amino-phosphonic acids as substrates.

This work describes a new synthetic entry to a range of phosphonopeptides which may be considered as phosphono analogs of glutathione. The latter is implicated in biologically important processes and the interest of these parent compounds which possess structural relationships arises from their possible interaction with enzymes of the glutathione metabolism. Enzymatic tests which these mimetic compounds are under investigation in this field.

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-Molecular Engineering of P(V)porphyrin-

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Molecular Engineering, tailor-made systematization of functional molecule is an important research subject for functional molecular materials. In principle, some of the multi-porphyrin systems are considered to be converted into the elements of molecular photo-electronic devices. Especially, their systematization with appropriate electron mediators into large polymeric systems is one of the feasible approaches to the molecular systems based on the electron transfer. Phosphorus (V)porphyrin has an unique structure, 3 centers 4 electrons, covalent bond in axial direction, and many interesting derivatives were synthesized.

They are; a donor-sensitizer-acceptor triad molecule (A) for an efficient photo-induced electron transfer, a cyclodextrin substituted P(V)porphyrin (B) for efficient photo-chemical transducing catalysis, 1-D and 2-D porphyrin arrays connected with conjugating molecular wire (C,D) for molecular electronics, an 1-D porphyrin arrays connected with insulating molecular wire (E) for molecular photonics, and an oligonucleotide shackled with porphyrin (F) for artificial photo active restrictive enzyme. They all showed their specific attractive functions as the authors had expected.

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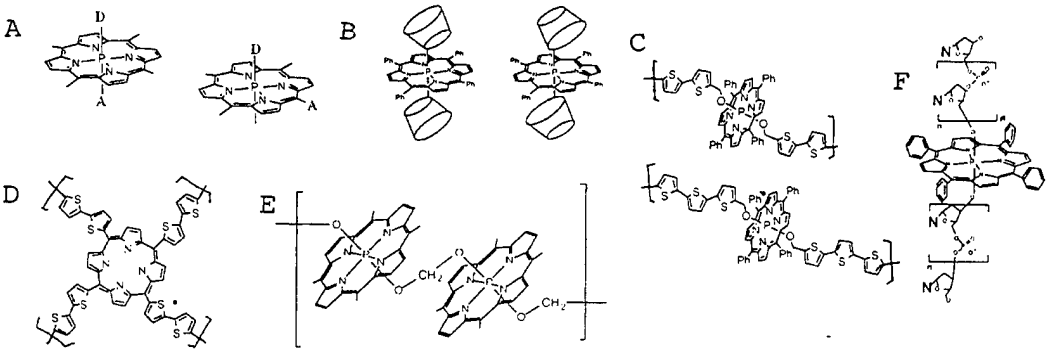

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 94
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INFLUENCE OF IODINE ON REACTIVITY OF PHOSPHORUS SULFIDES AND HOMOLOGUES OF DAVY'S REAGENT IN ORGANIC REACTIONS

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Abstract The use of iodine results in reactivity enhancement of phosphorus sulfides and homologues of Davy's reagent in the reactions with disulfides, aminals and thioacetals. The reactions β-diiodotetraphosphorus trisulfides with disulfides, aminals and thioacetals were studied.

INTRODUCTION

Phosphorus sulfides and $(RSPS_2)_2$ react with dialkyl disulfides, aminals and thioacetals under severe conditions (100-200°C) with the formation of some novel organothiophosphorus compounds.

RESULTS AND DISCUSSION

The application of iodine in the reactions of P_4S_3, P_4S_5, P_4S_7, P_4S_{10} and $(RSPS_2)_2$ with dialkyl disulfides leads to a significant improvement in yields of trialkyl tetrathiophosphates at 20-60°C. These reactions proceed via the intermediate formation of S,S'-dialkyl S'',S''-alkyltetrathiolothionophosphates. The products of (1-dialkylamino)- and (1-alkylthio)alkyl thionophosphonate structure were obtained in the reactions of P_4S_3, P_4S_5 and P_4S_7 with aminals and thioacetals in the presence of iodine at 20°C. The reaction of P_4S_{10} with thioacetals which leads to (1-alkylthio)alkyl tetrathiophosphates is also facilitated when iodine is employed (20°C).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 95
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SYNTHESIS AND CRYSTAL STRUCTURE OF HALOMETHYLTRIPHENYLPHOSPHONIUM HALIDES AND BROMOTRIPHENYLPHOSPHONIUM TRIBROMIDE

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The phosphonium salts have been prepared by the reaction of triphenylphosphine with the corresponding halomethanes (eq. (1)) and bromine (eq.(2)), respectively.

$$(C_6H_5)_3P + RX \longrightarrow [(C_6H_5)_3PR]^+ X^- \quad (1)$$

[R = CH_2I X = I (**I**); R = CBr_3 X = Br, (**II**); R = CBr_3 X = Br; Br_3 (**III**); R = CH_2Br X = Br_3 (**IV**)]

$$(C_6H_5)_3P + 2\,Br_2 \longrightarrow [(C_6H_5)_3PBr]^+ Br_3^- \text{ (V)} \quad (2)$$

The crystal and molecular structures of **I - V** have been determined by X-ray structure analysis. The crystals are orthorhombic ($Pca2_1$ (**I**)), triclinic ($P\bar{1}$ (**II**)), and monoclinic (C2/c (**III**); $P2_1/n$ (**IV**); $P2_1/c$ (**V**)). In the solid state all compounds consist of discrete monomeric $(C_6H_5)_3PR^+$ cations and X^- anions with halogen halogen interactions between the halogens bonded in the cations and the halogen anions. The cations of **I - V** have a slightly irregular tetrahedral geometry around the P atom. The Br_3^- anions are nearly linear with symmetrical (**III**) or asymmetrical (**IV, V**) Br Br bonding distances.

(**I**) is the first compound in which a iodine atom bonded to carbon interacts with the iodide anion. The Br Br interactions lead to formation of rings (**II**), chains (**III**), and dimeric units (**IV**).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 96
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SYNTHESIS, STRUCTURE AND PROPERTIES OF C(X)NHP(Y) FRAGMENT CONTAINING COMPOUNDS

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Abstract N-(thio)carbonyl(thio)amidophosphate, their open-chain and crown-containing analogues with a C(X)NHP(Y) fragments are associated with intermolecular hydrogen bonds as C=X...H-N and P=Y...H-N or intramolecular hydrogen bonds of N-H...O(macrocycle).These compounds easily enter into alkylation reaction,are added according to C=N bonds of activated imines, take part in O→S and S→O exchanging reactions.

The object of the present work is to give exhaustive information on synthesis, structure and properties of N-(thio)-carbonyl(thio)amidophosphates (1), their open-chain (2) and crown-containing analogues (3) with a C(X)NHP(Y) fragments:

$$RC(X)NHP(Y)(OR^1)_2 \quad (1)$$

$$(R^1O)_2P(Y)NHC(X)NH\text{-}R^2\text{-}NHC(X)NHP(Y)(OR^1)_2 \quad (2,3)$$

where R=Alk,Ar; R^1=Alk ; R^2=$(CH_2)_7$, $(CH_2)_2O(CH_2)_2O(CH_2)_2$, $(CH_2)_2O(CH_2)_2$, DA-15-CR-5, DA-18-CR-6; X,Y=O,S.

The reactions of phosphorylation of (thio)amides and acylation of (thio)amidophosphates in the "superbasic medium" are the most effective factors for synthesis the compounds (1). The compounds (2,3) were obtained by means of an addition reaction of diaminopodands and diazacrown-ethers to phosphoryliso(thio)cyanates. The compounds (1) are associated with intermolecular hydrogen bonds as C=X...H-N and P=Y...H-N, while the compounds (3) form intramolecular hydrogen bonds of N-H...O(macrocycle). The compounds (1) easily enter into alkylation reaction. They are added according to C=N bonds of activated imines. They are oxidated and take part in O→S and S→O exchanging reactions. Prototropic transformations as C(S)NH ⇄ C(SH)=N and P(Y)NH ⇄ P(YH)=N have been detected in compounds (1,3).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 97
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ACID-BASIC AND COMPLEXING PROPERTIES OF COMPOUNDS WITH A C(X)NHP(Y) FRAGMENTS

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Abstract N-(thio)carbonyl(thio)amidophosphates, their open-chain and crown-containing analogues with a C(X)NHP(Y) fragments are NH acids with pKa 8-11 and the effective complexing agents for "soft" ion metals.

We have investigated acid-basic and complexing properties of N-(thio)carbonyl(thio)amidophosphates (1), their open-chain (2) and crown-containing analogues (3) with a C(X)NHP(Y) fragments:

$$RC(X)NHP(Y)(OR^1)_2 \quad (1)$$

$$(R^1O)_2P(Y)NHC(X)NH\text{-}R^2\text{-}NHC(X)NHP(Y)(OR^1)_2 \quad (2,3)$$

where R=Alk,Ar; R^1=Alk; $R^2=(CH_2)_2O(CH_2)_2$, $(CH_2)_7$, $(CH_2)_2O(CH_2)_2O(CH_2)_2$, DA-15-CR-5, DA-18-CR-6, X,Y=O,S.

The compounds (1-3) are NH acids with pKa 8-11. The compounds (1-3) are effective complexing agents and they bond "soft" ions of Hg(II),Co(II),Pd(II),Ag(I),Cu(II),Pb(II) etc metals according to a chelating type. The investigation carried out have defined the constants of stability of some metal ions with ligands (I) and it has been established that the stability of the complexes falls in a series: $RC(S)NHP(S)(OR^1)_2 > RC(S)NHP(O)(OR^1)_2 > RC(O)NHP(S)(OR^1)_2 > RC(O)NHP(O)(OR^1)_2$. The crown-containing compounds (3) are able to form complexes with "soft" ions of Hg(II), Pd(II), Cu(II) by means of the P(Y)NHC(X) exocyclic fragment as "claws" but when there are "hard" ions of Li(I),Na(I),K(I), the complexes are formed by a macrocycle as "guest-host". The compounds (3) mark the beginning of a new type of complexing agents which have been called "crown-chelating agents" or "hard-soft ligands".

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 98
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INFLUENCE OF AN ORGANOPHOSPHORUS SUBSTITUENT ON THE NEIGHBORING REACTION CENTER

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α-Functionalized organophosphorus substances containing P(O)-C-X fragment (where X is a functional group) are not only extremely promising syntones for the synthesis of various types of organophosphorus structures, but present a very convenient objects for the quantitative studies of electronic and steric influence of a complex organophosphorus group on the reactivity of various reaction centers.

In the presented work on the example of our own and literature kinetic investigations with the use of specially elaborated steric and inductive models it is shown, that this influence may be very considerable, realizing in the frame of electronic, steric and stereo-electronic effects each of whom may be dominating depending on the reaction series type and reaction conditions. It is established, that organophosphorus substituent may noticeably alter not only the reaction rate, but also the mechanism of the reaction, as it takes place for instance in the case of α-hydroxyphosphonates which, unlike the non-phosphorylated alkohols and amines, add to phenyl isocyanate by Ad_E (and not by Ad_N) mechanism.

Polar organophosphorus group at the reaction center may show also such specific effects as "the electrostatic umbrella effect", found and studied in the reaction of nucleophilic substitution in the chloromethylphosphine oxides series.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 99
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KINETIC AND SYNTHETICAL MANIFESTATIONS OF IMPORTANT REACTIONS OF HYDROPHOSPHORYL COMPOUNDS

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IRINA V.GALKINA, ELVIRA R.ZVEREVA,
AND GULCHIRA M.SAAKYAN

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Hydrophosphoryl compounds (HPC) is one of the most important and interesting types of organophosphorus substances. That is why a lot of their reactions are the authorized reactions in organic chemistry (Michaelis-Becker, Pudovik, Abramov and Kabachnic-Fields Reactions).In the presented work we have carried out systematic kinetic and synthetical investigation of mechanisms of the Pudovik, Abramov and Kabachnic-Fields reactions and also the reactivity of HPC in these reactions.

The main features of reaction mechanisms and their dependence on the reagent structure, solvent and catalyst nature have been established. By the method of regression analysis it is shown that the HPC reactivity is determined by electronic, steric and stereoelectronic substituent effects and also is significantly depended on catalyst basicity and protolitic properties of the media.

Quantitative correlations obtained are in a good agreement with qualitative manifestations of the reactions studied, and permit to carry out not only interesting theoretical conclusions but also some important principles of optimal and effective organohosphorus synthesis with the participation of hydrophosphoryl compounds.

The work is realized with financial support of the S.- Petersburg Competition Center.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 100
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NEW SYNTHETIC ROUTE TO PHOSPHONIC ACID ANHYDRIDES

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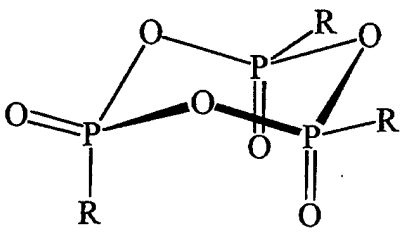
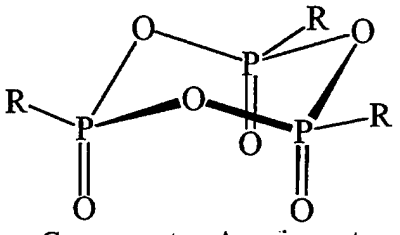
Phosphonic acid anhydrides are useful condensation reagents in the peptide and polyamide synthesis [1,2]. A new method for the preparation of well defined anhydrides is now described and intermediates of the peptide synthesis are elucidated. Cryoscopic and mass spectrometric data confirm the suggested cyclic trimeric molecular structure and the $^{31}P\{^{1}H\}$- as well as ^{1}H-NMR spectra can be explained with the structures:



C_s symmetry, AB_2 spin system;
R = 1,1 Dimethylethyl,
2-Methylphenyl



C_{3v} symmetry, A_3 spin system;
R = 2,4,6 -Trimethylphenyl

Reaction of t-BuP(O)$(SiMe_3)_2$ and $PhBCl_2$ yields the mixed anhydride of t-butylphosphonic and phenylboronic acid $C_{40}H_{57}B_4O_{12}P_4$. The compound forms colourless crystals and the obtained data are in agreement with a 16 membered P-O-B- ring.
By adding H_2O to a solution of the anhydride $[t\text{-}BuPO_2]_3$ [3] the hitherto unknown acid $H_2[t\text{-}Bu_3P_3O_7]$ can be obtained. This acid proved to be a strong acid and rather stable against further hydrolysis with H_2O in alcohohol. Neutralisation leads to the salt $[(t\text{-}Bu)_3P_3O_7]Na_2 * 8\ H_2O$, of which an x-ray structure was determined. Colourless, plate-like crystals; monoclinic, (a = 1086.9, b = 3113.9, c = 912.3 pm, b = 114.59°, $P2_1/c$, Z = 4, R1 = 0.040, wR2 = 0.119). The first of the two independent Na^+ cations is six-coordinated by five water molecules and one oxygen atom of the anion in the form of a distorted octahedra. The coordination of the other Na^+ ion by only five water molecules can best be described as largely distorted square pyramid with an Oxygen as apex. Both polyhedra share a common edge. The anions with their polar PO_2 groups and seven of the eight independent water molecules form hydrogen bonded layers perpendicular to b. Two such layers (equivalent across a centre of symmetry) are now connected to double layers by the eighth water molecule and the embedded Na^+ cations. This polar layer is „sandwich"-like enclosed in two nonpolar layers of t-butyl groups of the triphosphonate anions. Between those „sandwiches" only van der Waals interactions are observed.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 101
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PHOSPHOROTROPIC ISOMERIZATION OF DIPHOSPHORYL CALIX[4]ARENES IN SYNTHESIS OF THEIR CHIRAL DERIVATIVES

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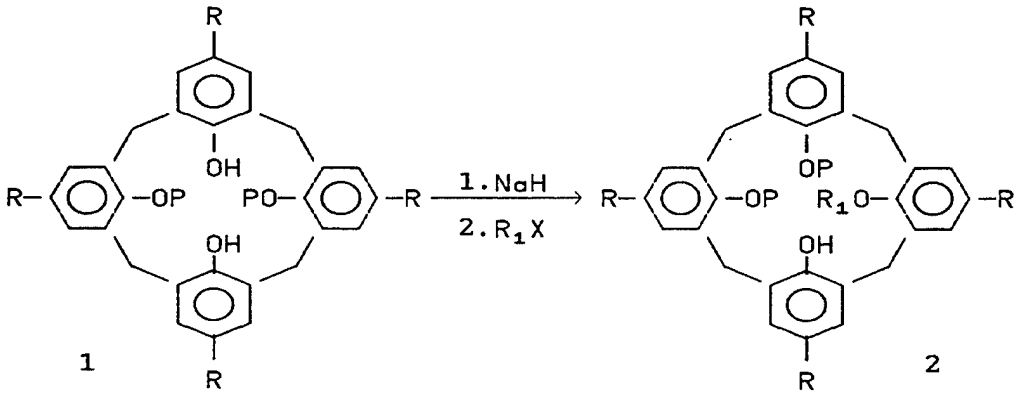
Calixarenes are synthetic macrocycles obtainable by joining phenolic units through methylene bridges. Since they have original molecular architecture, they are considered to be important starting materials in design novel host-molecules for molecular recognition and separation. Introduction of chirality into calixarenes seems to be of great value for development of new class of artificial enzymes.Chiral lower rim trisubstituted calix[4]arenes **2** possessing no plane of symmetry were synthesized with good yields by one-pot procedure consisted in successive treatment of 1,3-diphosphorylcalix[4]arenes **1** in cone conformation with 1 eq. NaH and benzoyl chloride or methyl monobromoacetate.



R = H, t-Bu

P = P(O)(OEt)$_2$

R_1 = PhC(O), $CH_2C(O)OCH_3$

The key step of the reaction is the phosphorotropic rearrangement of the 1,3-diphosphorylcalix[4]arene monoanion into the 1,2-diphosphorylcalix[4]arene monoanion.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 102
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SYNTESIS AND REARRANGEMENT OF N-P^{III}-PHOSPHORYLATED CARBOXYLIC ACID AMIDES.

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Reactions of carboxylic acid lactams with tervalent phosphorus chlorides, leading to N- and/or O- derivatives have been investigated. Synthetic methods for imidoylphosphites and phosphonates, mono- and bisphosphorylated azadienes have been developed. Prototropic migrations in azaallylic triad, phosphorus atom migrations in N-C-O triad and imidoylphosphite-imidoylphosphonate rearrangement were found.
It was encountered, that chlorination of amidophosphites containing one to three trihalogen acetamide groups is accompanied by chlorine or N-acylamide group shift and leads to cyclic and spirocyclic phosphoranes with 1,3,2-^{5}-oxazaphosphetanic cycle.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 103
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FROZEN FRIEDEL-KRAFTS TYPE REACTION OF PHOSPHORUS HALIDES WITH TETRAPHENYLBORATE ANION

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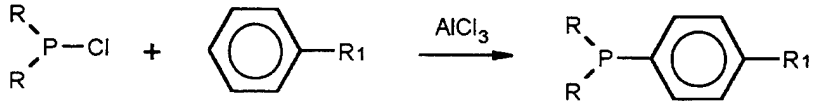
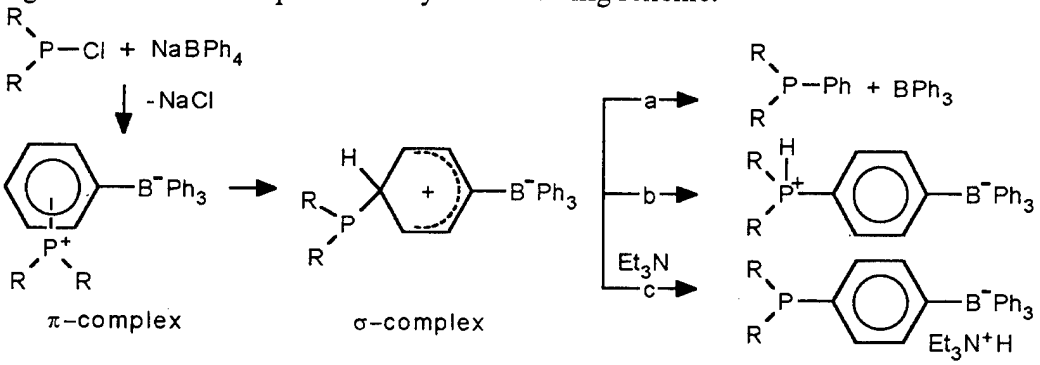
The Friedel-Krafts type reaction of phosphorus halides are well known and widely used in organic synthesis. Usually it requires catalyst and elevated temperature and spreads on the most electrophilic phosphorus halides.



We have shown that tetraphenylborate anion reacts at very mild conditions - at room temperature and without catalyst - and so is a viable substrate for the detailed investigation of this reaction. It provides an opportunity to freeze reaction, observe or even isolate intermediate products and reveal some new reaction pathways.

The reaction proceeds through the formation of π- and σ-complexes and in general case can be presented by the following scheme:



Transformations of σ-complexes showed a clear dependence of substituents R and reaction medium. The proton transfer can induce cleavage of B-C bond (path a) or protonation of phosphorus or other basic centers of molecule (path b). In the presence of outer base products of phosphorylation of tetraphenylborate anion are formed (path c).

The investigation of possibility of polyphosphorylation of BPh_4^- and examination of ligating properties of phosphorus-substituted BPh_4^- towards transition metals are in progress.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 104
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SYNTHESIS AND REACTION PECULIARITIES OF PHOSPHORYLATED TRIFLUOROETHANE IMINES.

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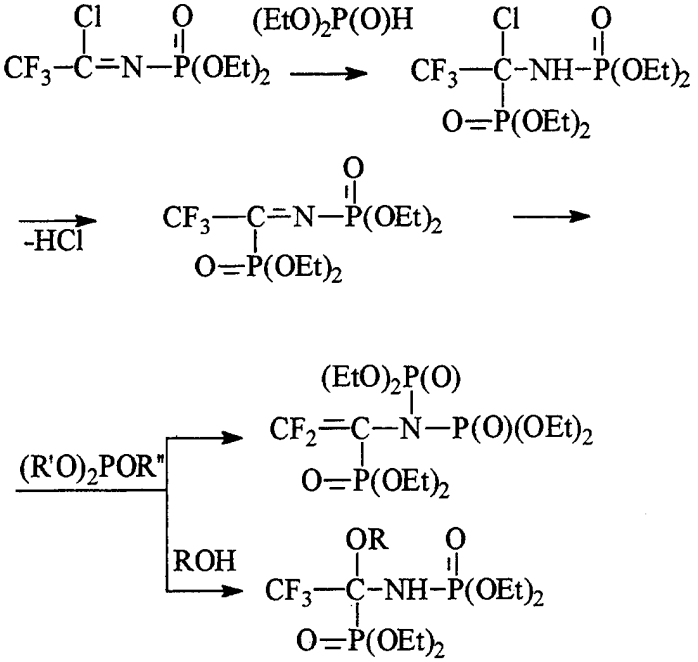
Convenient methods for C,N - mono- and biphosphorylated trifluoroethane imines have been developed. These are reactive synthons allowing important derivatives of aminophosphonic acids, fluorine- and phosphorus-containing heterocycles, vinylamides, etc. A rare example of a Perkov-type reaction involving trifluoromethyl group has been discovered.

The property differences of imines obtained and imines of hexafluoroacetone are discussed.



The rearrangement, $-C(Cl)=NP(O)Ph_2 \rightarrow -C(O)-N=P(Cl)Ph_2$, new for phosphorus chemistry, has been found for N-phosphorylatyed imidoyl chlorides.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 105
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SYNTHESIS AND REACTIVITY OF HYDROLYSIS PRODUCTS OF CYCLIC PHOSPHITES WITH AMINO SUBSTITUENTS

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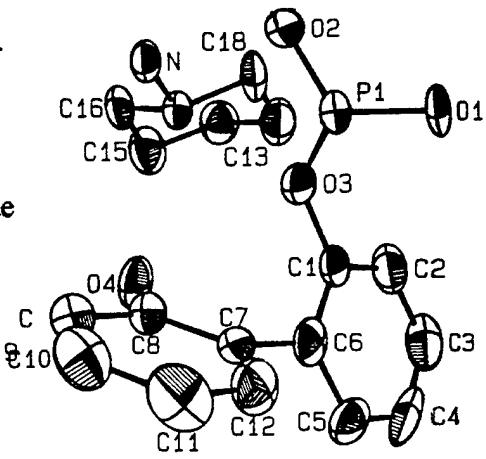
Abstract. **Hydrolysis of several cyclic aminophosphites are discussed and compared with that of cyclic chloro/ phenoxy phosphites. An X-ray structure of a hydrolysis product, $(C_6H_{11}NH_3)^+O^-P(O)(H)(2,2'\text{-}OC_6H_4\text{-}C_6H_4OH)$ has been determined.**

The cyclic phosphite $(C_6H_{11}NH)P\{2,2'\text{-}O_2(C_6H_4)_2\}$(1) undergoes hydrolysis in aqueous medium to afford the acyclic salt $(C_6H_{11}NH_3)^+O^-P(O)(H)(2,2'\text{-}OC_6H_4\text{-}C_6H_4OH)$ (2) which is characterized by ^1H and ^{31}P NMR, elemental analysis as well as a single crystal X-ray structural analysis. Compound 2 [m.p. 180°C; ^{31}P NMR : 2.98 ppm] upon thermal treatment loses the cyclohexyl amino group to lead to a phosphite with a P-H group [^1J (P-H) = 732 Hz]. A similar feature is observed for the amine salt $(C_6H_{11}NH_3)^+O^-P(O)(H)(OCH_2CMe_2\text{-}CH_2OH)$; in this case, however,one of the products is identified as the cyclic phosphite (H) (O) $P(OCH_2CMe_2CH_2O)$ which is characterized by its Pudovik product with p-chlorobenzaldehyde.[1]

Although the phenoxy compound $(PhO)P(OCH_2CMe_2CH_2O)$ hydrolyses to the ring (phosphorinane) preserved product $H(O)P(OCH_2CMe_2CH_2O)$,[2] the oxinate $(NC_9H_6O)P(OCH_2CMe_2\text{-}CH_2O)$ leads to the ring opened product $(C_9H_6ONH^+)O^-P(O)(H)(OCH_2CMe_2\text{-}CH_2OH)$.



Molecular structure of 2; H atoms not shown. Selected distances (Å) and bond angles (°): P1-O1 1.482; P1-O2 1.471 ; P1-O3 1.589; P-H 1.33; O1...O4 2.71; O1-P1-O2 119.8; O1-P1-O3 110.6; O2-P1-O3 104.3.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 106
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A NEW ROUTE TO ARYL-PHOSPHONITES AND ARYLEN-BIS-PHOSPHONITES - STABILIZERS FOR PLASTICS

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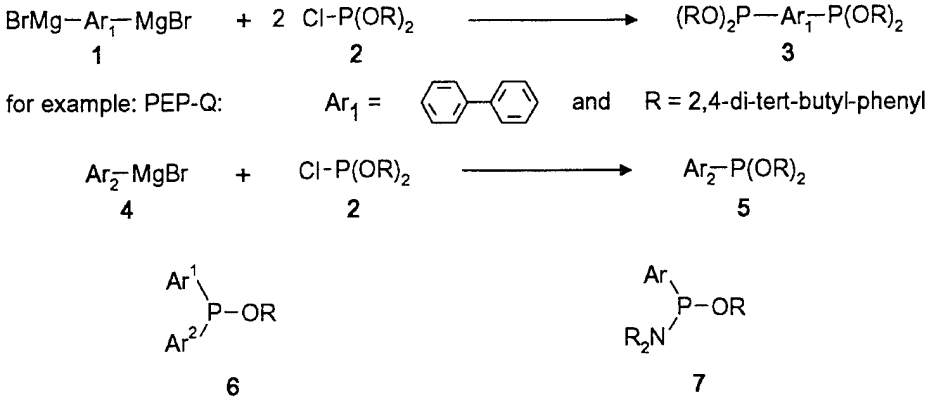
Abstract Aryl-phosphonites and arylen-bis-phosphonites are synthesized by a new grignard route. These compounds are useful as stabilizers for plastics.

Arylen-bis-phosphonites are used as stabilizers for polymeres. The most known is compound **3** with Ar_1 = 4,4'-biphenyl, called PEP-Q. It is produced by a Friedel-Crafts-phosphorylation of biphenyl with PCl_3 and reaction with 2,4-di-tert-butyl-phenol according to a process claimed by the Sandoz AG.[1]

A new grignard route gives access to PEP-Q in high yield. The grignard compound of 4,4'-dibromo biphenyl (**1**) is reacted with bis-(2,4-di-tert-butylphenyl) chloro-phosphite **2** to afford PEP-Q (**3** with Ar_1 = 4,4'-biphenyl). The grignard reaction is strongly influenced by ultrasound. Without using ultrasound the yield is about 35%, while using ultrasound the yield is as high as 85%.



Reacting a grignard reagent Ar_2-MgBr **4** with **2** gives the new phosphonites **5**, with e. g. Ar_1 = 1-naphthyl, 4-tert-butylphenyl, 2,4-dimethylphenyl, in high yields. These compounds are also efficient stabilizers for plastics. In a similar way diaryl-phosphinites **6** and aryl-phosphonamidites **7** are synthesized by the reaction of the corresponding halo-phosphorus-compound and an aryl-grignard reagent.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 107
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STUDIES OF THE REACTIONS OF 2-SUBSTITUTED DIMETHYL BENZOYLPHOSPHONATES WITH TRIMETHYL PHOSPHITE

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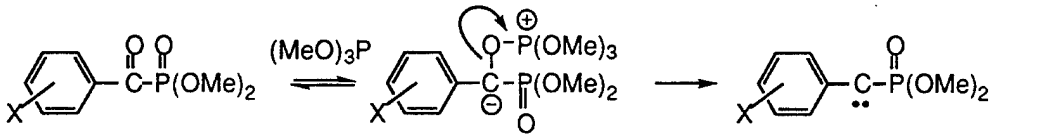
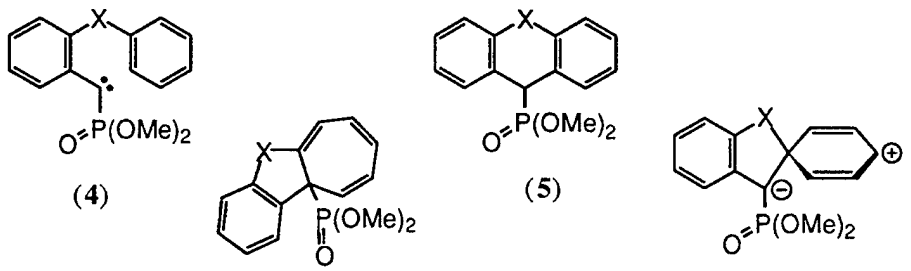
Dimethyl benzoylphosphonates (**1**) react with trimethyl phosphite to give anionic intermediates (**2**) which decompose to give carbenes (**3**) and trimethyl phosphate [1]. When suitable *ortho*-substituents are present on the benzoylphosphonate, intramolecular carbene insertion reactions can occur to give cyclic systems. With alkyl substitutents, where the length of the chain provides a choice of cyclisation pathways, insertion into an appropriate C—H bond to give a 5-membered ring has been found to be the preferred option. We have therefore been investigating the behaviour of systems, such as (**4**), where insertion into a C—H bond to give a 5-membered ring is prevented.



(**1**) (**2**) (**3**)



(**4**) (**5**) (**6**) (**7**)

These studies have led to the formation of some novel products. For the case of (**4**; X=S) subsequent reaction leads to the formation of products including the thioxanthenyl-phosphonate (**5**; X=S) and the ring expanded product (**6**; X=S). Although the formation of (**5**; X=S) appears to involve carbene insertion into the 2'C—H bond of the phenylthio substituent in (**4**; X=S), further work with methyl-substituted derivatives has shown that the formation of (**5**; X=S) occurs via the spiro-diene system (**7**; X=S).

[1] D. V. Griffiths, P. A. Griffiths, B. J. Whitehead, and J. C. Tebby, *J. Chem. Soc. Perkin Trans. 1*, 479, (1992).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 108
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SYNTHESIS OF 2-MERCAPTO- AND 2-HYDROXY-SUBSTITUTED DIPHENYLPHOSPHINES FOR USE AS DIANIONIC BIDENTATE LIGANDS AND POLYDENTATE LIGAND PRECURSORS

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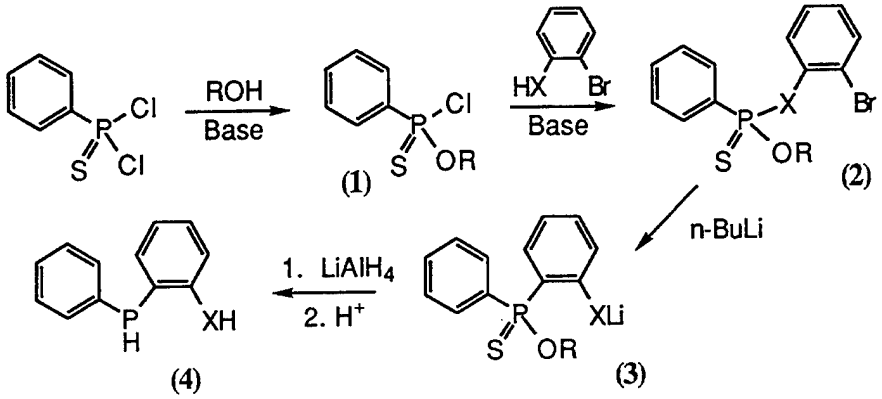
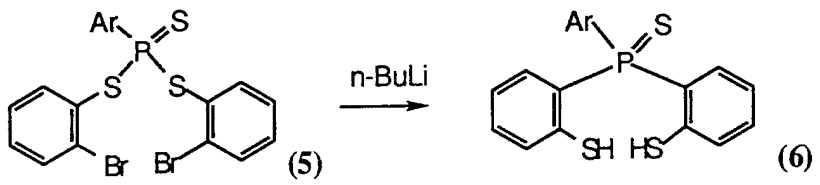
As part of our studies into the synthesis of polydentate phosphine-containing ligands, we have investigated the preparation of the phosphines (**4**; X=O) and (**4**; X=S). These are of interest both as potential dianionic bidentate ligands and as useful precursors of more complex polydentate ligand systems. A synthesis of the thiol system (**4**; X=S) from 1,2-dinitrobenzene has been previously reported [1], but the observation [2], that 2-bromoaryl esters of phosphoric acid rearrange to give esters of arylphosphonic acids in the presence of alkyl lithiums, led us to consider whether a similar type of rearrangement might provide a convenient approach to both (**4**; X=S) and (**4**; X=O).



We have now confirmed this and have also shown that it is possible to extend this approach to bring about the simultaneous rearrangements of two 2-bromoaryl esters groups, such as in the conversion of (**5**; Ar=Ph) to (**6**; Ar=Ph). This offers a potential route to a range of tridentate and phosphine-capped tripodal tetradentate ligand systems.



[1] E.P. Kyba and C.N. Clubb, *Inorg. Chem.*, **23**, 4766, (1984).

[2] J. Heinicke, I. Böhle and A. Tzschach, *J. Organomet. Chem.*, **317**, 11, (1986).

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HALOGENOPHOSPHONIC AND HALOGENOPHOSPHINIC ACIDS

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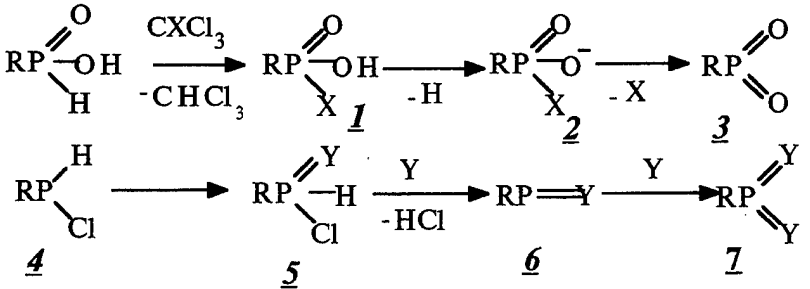
Methods for the synthesis and preparations of first stable halogenophosphonic acids ***1*** (X=Cl, Br) and halogenophosphinic acids ***5*** (Y = O, S) are developed. The chemical properties of the compounds ***1, 4, 5*** are studied



The compounds ***1, 5*** are stable, when they contain sterical hindered substituents R =Mes*, t-Bu. Tert-butylhalogenophosphonic acids ***1*** with triethylamine forms rather stable salts ***2***, which on heating eliminate triethylamine hydrohalogenide to afford trimer of tert-butyldioxaphosphorane. Flesh-vacuum thermolysis (FVT) (600° C, p= 0.01 mm Hg) of trimethylsilyl tert-butylhalogenophosphonates proceeds with elimination of halogenotrimethylsilane to give very unstable tert-butyldioxophosphorane, which readily transforms into trimer. Bis-oxaphosphoranes undergo the reaction of [2+3]-cycloaddition with epoxides to give 1,3,2-dioxaphosphol-2-oxides.

Monochlorophosphines ***4*** oxidizes or add sulfur with formation of chlorophosphinic acids ***5*** (Y=O, S), which may be dehydrochlorinated with formation unstable ***6***. The latter adds sulfur to give ***7*** isolable in high yield.

Acknowledgements: Financial support for this work from International Science Foundation and National Committee on Science and Technology of Ukraine is gratefully acknowledged.

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[2] O.I. Kolodiazhnyi E.V. Grishkun, *Zh. Obshch. Khim.* **64**, 1740 (1994)

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 110
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NEW METHOD OF HALOGENATION OF ORGANOPHOSPHORUS COMPOUNDS

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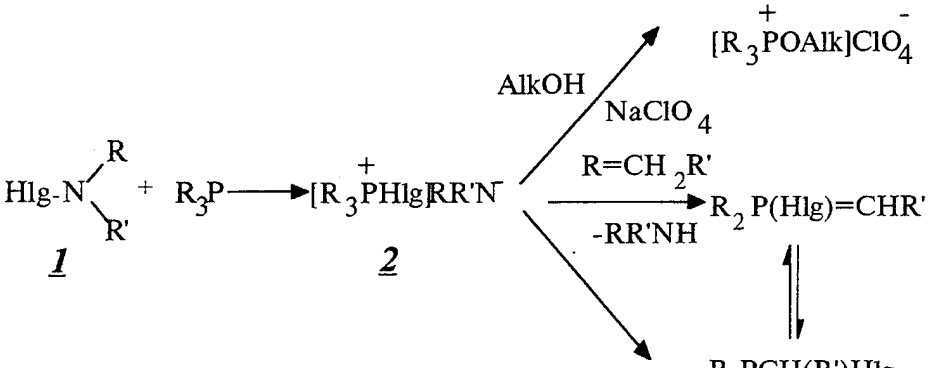
N-Chloroalkylamines react usually with tervalent phosphorus compounds to afford products, containing the phosphorus-nitrogen bond. We found that the sterical hindrances favour to the nucleophilic attack of the tervalent phosphorus atom on the "positive" halogen atom with the formation of phosphorus halogenated products. Sterical hindered N-halogenoalkylamines ***1*** (Hlg=Cl,Br) possess active halogenating properties to react with tervalent phosphorus compounds similarly to methane tetrahalides. Reaction proceeds via the formation of halogenophosphonium intermediates ***2***, containing an anion R_2N, which reacts with alcohols to afford alkoxyphosphonium salts, transforms into halogenophosphonium salts or P-halogenoylids. Advantages of N-halogenoalkylamines ***1*** over methane tetrahalides are more high chemical selectivity. Moreover the inclusion of chiral substituents R into N-halogenoalkylamines gives enantioselective halogenating reagents.



1 ***2***

R(R') = i-Pr$_2$, t-Bu(Me$_3$Si), (Me$_3$ Si)[CH(Me)Ph]
(Me$_3$Si)[CH(R)COOMe]

Acknowledgements: Financial support for this work from International Science Foundation and National Committee on Science and Technology of Ukraine is gratefully acknowledged.

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[2] Kolodiazhnyi O.I, Golovatyi, O. R. *Zh.Obshch.Khim.*,**64**, 1742 (1994)

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 111
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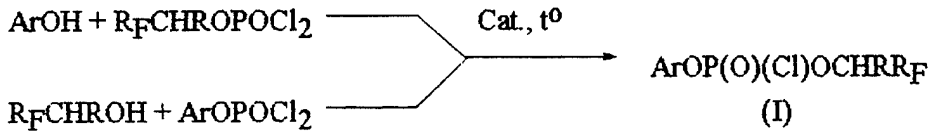
CATALYTIC METHODS FOR SYNTHESIS OF (POLYFLUOROALKYL)-ARYLCHLOROPHOSPHATES AND UNSYMMETRICAL BIS(POLY-FLUOROALKYL)ARYLPHOSPHATES AND THEIR STEREOCHEMISTRY

MARTIN I. KABACHNIK, LEONID S. ZAKHAROV, EVGENII I. GORYUNOV, MIKHAIL A. KURYKIN, GALINA N. MOLCHANOVA, SVETLANA A. KAL'FA, PAVEL V. PETROVSKII, TATYANA M. SHCHERBINA, AND ANNA P. LARETINA

Nesmeyanov Institute of Organoelement Compounds, the Russian Academy of Sciences, ul. Vavilova 28, Moscow, 117334 Russia

Catalytic methods for the synthesis of (polyfluoroalkyl)arylchlorophosphates (I) have been developed



Ar = C_6H_5, 2,6-$(CH_3)_2C_6H_3$, 4-ClC_6H_4, napht-1-yl; $R_F = CF_3$, n-C_6F_{13}, cyclo-C_6F_{11}; R = H, CH_3

The chloridates (I) were found to react with 1,1-dihydropolyfluoroalkanols to give unsymmetrical bis(polyfluoroalkyl)arylphosphates (II) under catalytic phosphorylation conditions.

$$\underset{\text{(I)}}{ArOP(O)(Cl)OCHRR_F} + R'_FCH_2OH \xrightarrow{Cat.,t^o} \underset{\text{(II)}}{ArO(R'_FCH_2O)P(O)OCHRR_F}$$

$R'_F = CF_3$, n-C_4F_9

It has been shown that in the case of chlorophosphates (I, R = CH_3) (which are the statistical mixtures of two diastereomers), the nucleophilic substitution of chlorine atoms by primary polyfluoroalkyl groups proceeds stereoselectively, and in the phosphates (II) the diastereomers ratio differs essentially from statistical one.

This research was made possible in part by Grant No. MSF 000 from the International Science Foundation.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 112
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CATALYTIC PHOSPHORYLATION OF SILAPOLYFLUOROALKANOLS

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O-Aryl-O-(α-perfluoroalkyl-ω-trialkylsilyl)methylphosphonates (II) have been prepared by catalytic phosphorylation of silapolyfluoroalkanols (I) with O-arylmethylphosphonochloridates.

$$R_3Si(CH_2)_nCH(R_F)OH + Cl\text{-}P(O)(Me)OAr \xrightarrow{Mg,\ t^o} R_3Si(CH_2)_nCH(R_F)OP(O)(Me)OAr$$

(I) (II)

n = 1,3; R = Me, Pr, $CF_3CH_2CH_2$; $R_F = CF_3$, C_4F_9; Ar = Ph, 4-t-BuC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$.

According to NMR and GC, the esters II are the mixtures of two diastereomers. A diastereomer ratio differs substantially from statistic one in some cases. We have examined the influence of the distance between silicon atom and reaction site, the nature of R and R_F groups, and a type of phosphorylating agent upon the diastereoselectivity. The maximum stereoselectivity was found for II (n = 1, $R_F = CF_3CH_2CH_2$), with diastereomer ratio being 91:9. The observed diastereoselectivity is unusually high and seems to be due to the tendency of silicon to form coordination bonds. The possible mechanism of the phosphorylation is discussed.

This research was made possible in part by Grant No. MSF 000 from the International Science Foundation.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 113
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N-PHOSPHORYLATED LACTAMS

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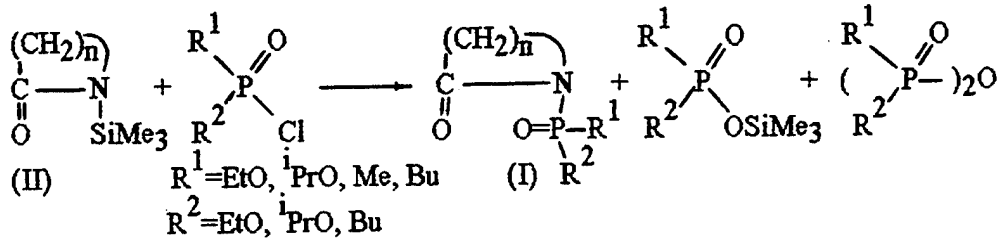
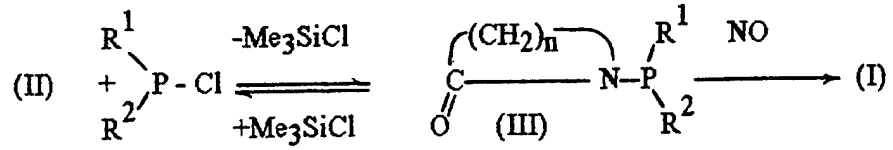
PAVEL V. PETROVSKII, TATYANA A. MASTRYUKOVA,
MARTIN I. KABACHNIK
A.N.Nesmeyanov Institute of Organo-Element compounds, Russian Academy of sciences, 117813, Moscow, Vavilova 28

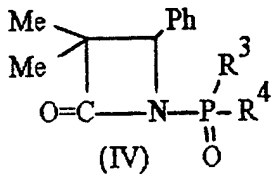
The synthesis of N-phosphorylated lactams (I) has been developed utilizing reaction of corresponding silyllactams (II; n= 3,4,5) with phosphorus acids chlorides. When phosphorylated, silyllactams behave like ambident systems, the substitution at O or N atoms being assumed.



P^{III} acids chlorides are reacted with (II) regioselectively, so that the products of N-phosphorylation - P^{III} amides (III) - could be obtained in good yields. Their oxidation affords phosphoryllactams (I). The reaction of (III) formation was shown to be reversible.



The same approach was applied to obtain thiophosphoryl analogs of (I) as well as N-phosphorylated β-lactams (IV).



$R^3 = R^4 = EtO$; $R^3, R^4 = -O(CH_2)_3O-$

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NON-RACEMIC MIXTURES OF 1,3,2-OXAZAPHOSPHACYCLANES - ENANTIOMERIC COMPOSITION DETERMINATION BY NMR

MARTIN I. KABACHNIK, TATYANA A.MASTRYUKOVA, ANDREI B.OURYUPIN, MIKHAIL I.KADYKO, PAVEL V. PETROVSKII, ERLEN I. FEDIN
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MICHEL SANCHEZ, ROBERT WOLF
Universite Paul Sabatier, Toulouse, France

The enantiomeric ratio in non-racemic mixtures of 2-anilino-2-oxo-1,3,2-oxazaphosphorinane (I) and 3-(α-methylbenzyl)-(I) [1] enantiomers was determined by measurement of the integral intensity ratio of two ^{31}P-NMR signals, assigned to enantiomers and differentiated due to the effect of statistically controlled associate-diastereoisomerism (SCADA), [2] when association occurs under conditions of fast exchange.

To prove the possible application of this analytical approach in the case of other oxazaphosphacyclanes we have synthesized the individual isomers of 2-anilino-3,4-dimethyl-5-phenyl-2-oxo-1,3,2-oxazaphospholane (II):

$$\underset{\text{(I): 1R,2S or 1S,2R}}{PhCH(OH)CH(CH_3)NHCH_3.HCl} + PhNHPOCl_2 \xrightarrow{1.POCl_3,\ 2.PhNH_2} \underset{\text{1S,2R-(I)}}{\text{2R,4R,5S- and 2S,4R,5S-(II)}}$$

$$\text{(II) mixtures: 2R,4S,5R and 2S,4S,5R or 2R,4R,5S and 2S,4R,5S}$$

Individual diastereomers of(II) have been separated from mixtures by column chromatography.Among the purified diastereomers, pairs of isomers,each of them being enantiomeric to other one, have been selected(2R,4R,5S and 2S,4S,5R, or 2S,4R,5S and 2R,4S,5R).NMR-Analysis of non-racemic mixtures of these pair isomers(II) has shown the absence of SCADA in phosphorus spectra and,in controversy,essential diastereomeric anisochronity of NHprotones, their integral intensity ratio being equal to proportion of enantiomers (II) in mixture.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 115
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B-SUBSTITUTED CARBORANYL THIO- AND SELENOPHOSPHITES. SYNTHESIS AND CHEMICAL PROPERTIES

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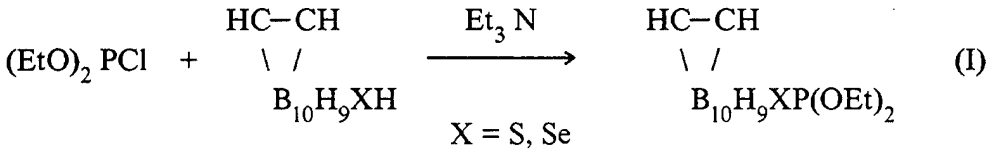
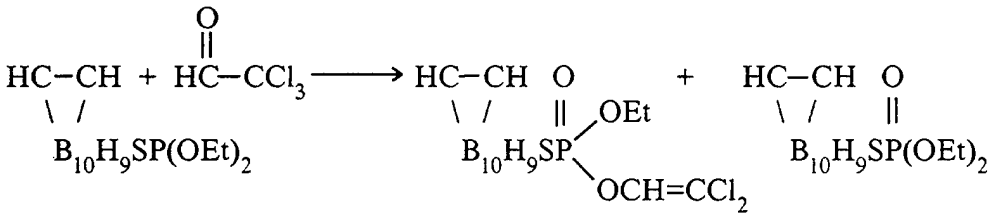
A.N.Nesmeynov Institute of Organoelement Compounds RAS, Moscow, Russia

The first examples of B-substituted carboranyl thio- and selenoesters of trivalent phosphorus acids were synthesized. On the basis of these samples, a series of new corresponding pentavalent phosphorus acids derivatives, potentialy bioactive compounds, was obtained. S- and Se-carborane-9-yl-diethylthiophosphites (I) were obtained by the interaction of diethylchlorphosphites with 9-mercapto- or 9-selenocarboranes in the presence of triethylamine.



Compounds (I) add easily oxygen, sulphur, and selen despite of the presence of the bulk carboranyl substituent. The interaction of (I) with alkyliodides leads to the usual Arbuzov reaction products. The interaction of thiophosphites (I) with chloral give the mixture of the product of the starting compound (I) oxydation along with vinylthiophosphate.



These compounds participate in the reactions mentioned above easier than corresponding C-phosphorilated carboranes due to electron donor ability of the B-carborane-9-yl group.

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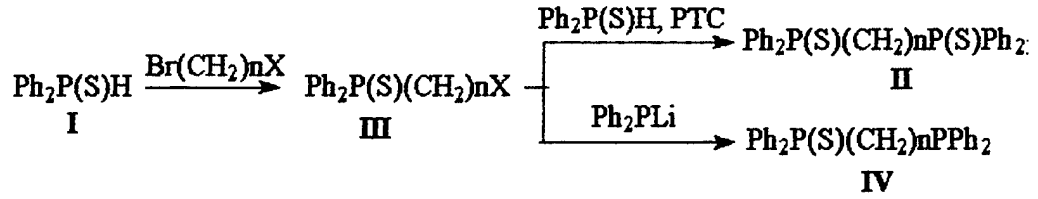
ALKYLATION OF HYDROTHIOPHOSPHORYL COMPOUNDS BY DIGALOGENOALKANES UNDER PHASE TRANSFER CARALYSIS CONDITIONS

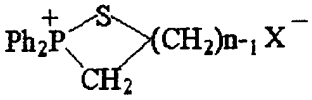
INGA M. ALADZHEVA, OLGA V. BYKHOVSKAYA,
DMITRII I. LOBANOV, PAVEL V. PETROVSKII, MICHAEL Yu. ANTIPIN,
KONSTANTIN A. LYSENKO, TATYANA A. MASTRYUKOVA,
MARTIN I. KABACHNIK
Nesmeyanov Institute of Organo-Element Compounds Russian Academy of Sciences, Vavilova str. 28, Moscow 117813, Russia

The course of reactions of hydrothiophosphoryl compounds with dihalogenoalkanes under PTC conditions depends both on the nature of halogen atom and the length of the alkylene chain.I reacts with CH_2Br_2 to yield $Ph_2P(S)CH_3$; with ICH_2Cl $Ph_2P(S)CH_2Cl$ is formed.



X = Cl, Br; n=3,4

In the case of $BrCH_2CH_2Br$ only $[Ph_2P(S)]_2$ was isolated. Alkylation of I by ω -dibromoalkanes (n = 3,4; 2:1 ratio) produces disulfides II, whereas the reaction of I with ω -bromochloroalkanes yields ω-chloroalkylphosphine sulfides III. Unsymmetrical bisphosphorus ligands were prepared from III (X = Cl) and Ph_2PLi. Compounds III (X = Br, I) produce stable cyclic thiaphosphonium salts V. The structures of V were confirmed by X-ray analysis. This work was partially supported by Russian Fundamental Research Foundation (grant no 93-03-04351)



(V; n=3,4; X = Br, I);

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CHIRAL α-AMINOPHOSPHONATES: SYNTHESIS AND TRANSPORT PROPERTIES.

I.S.ANTIPIN, I.I.STOIKOV, A.R.GARIFZYANOV, A.I.KONOVALOV
Kazan State University, Kazan, 42008, Russia

Abstract Synthesis of chiral α-aminophosphonates and their transport properties (rates, enantioselectivity) as membrane carriers for oxy and amino acids are discussed.

Transport in biological systems of amino acids through lipophilic membrane and their enantioselectivity is well known. To design a new type of the amino and oxy acids membrane carriers some α-aminophosphonates were obtained by Kabachnik-Fields reaction of amine with dialkylphosphite and carbonyl compounds in 70-90% yield.

R^1-NH-C(R^2,R^3)-P(=O)(OR^4)$_2$

(I): R^1 - $PhCH_2$- ; R^4 - amyl; R^2, R^3 - -$(CH_2)_4$-;

(IIa), (IIb): R^1 - d- or l-$PhCH(CH_3)$- ; R^4 - amyl; R^2, R^3 - -$(CH_2)_4$-;

(III): R^1 - l-bornyl; R^4 - amyl; R^2, R^3 - CH_3-;

In the present communication we reports some of our results concerning the transport amino, oxy acids and β-aminoalkohols along their concentration gradient through a liquid membrane supported by a microporous polymer film (Table 1). It was found that the flux follow the order of the distribution coefficients of studied compounds between aqueous and organic phases.

TABLE I Flux of some molecules through supported liquid membrane containing 1 M compound (I) in o-nitrophenyloctyl ether

Substrate c=0.1 mol/l	d,l-Valine	d,l-Tartaric acid	Glicolic acid	d,l-Mandelic acid	$NH_2(CH2)_2OH$ *HCl
Flux, mol/hr cm^2	$7.3\ 10^{-5}$	10^{-7}	$1.4\ 10^{-6}$	$7.6\ 10^{-5}$	$2.2\ 10^{-6}$

Chiral α-aminophosphonates (IIa), (IIb), (III) as enantioselective carriers have demonstrated a high enantiomer discrimination for oxy and amino acids.

This work was supported by RFFI grant.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 118
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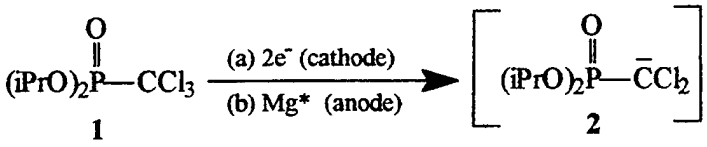
ELECTROCHEMICAL GENERATION OFDIISOPROPYL 1,1-DICHLOROMETHYLPHOSPHONATE ANION. APPLICATION TO AN EFFICIENT SYNTHESIS OF VARIOUS CYCLOALKYLPHOSPHONATES

PHILIPPE JUBAULT, CHRISTIAN FEASSON* AND NOEL COLLIGNON
INSA Rouen- IRCOF, BP 08, F-76131 Mont-Saint-Aignan, France

Key Words: Cycloalkylphosphonates, Electrosynthesis, Electrochemical activation of magnesium.

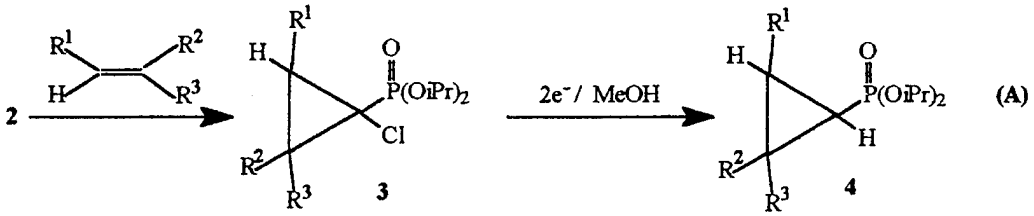
The electrochemical reduction of phosphonate **1**, in DMF, in a one-compartment electrolysis cell equipped with a felt carbon cathode and a sacrificial anode of magnesium gave the carbanion **2** according to an unusual mechanism, involving two simultaneous phenomena: (a) a bielectronic process at the cathode, (b) a direct reduction of phosphonate **1** by the magnesium rod, activated on its surface by the anodic process:



1 **2**

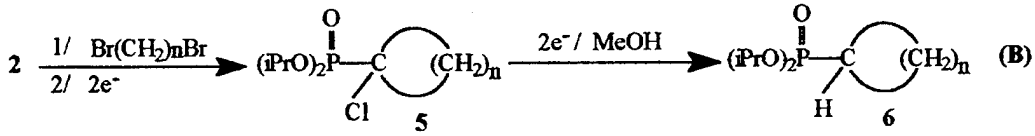
The electrogenerated carbanion **2** was reacted:

(**A**) with Michael acceptors giving α-chloro cyclopropylphosphonates **3** (64-85 % yield):



3 **4** **(A)**

(**B**) with ω,ω-dibromoalcanes leading to monoalkylated intermediates, which after electrochemical reduction, followed by cyclisation gave α-chloro cycloalkylphosphonates **5** (64 - 72 % yield):



5 **6** **(B)**

Moreover, the further electrochemical reduction of **3** or **5** in the presence of a protic agent, led to cycloalkylphosphonates **4** or **6** respectively, in a one-pot operation starting from **1** (50 - 58 % overall yield).

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HYDROXYALKYLATION OF α-PHOSPHONYLATED α-SILYLATED ALLYLIC CARBANIONS. AN UNEXPECTED CYCLIZATION REACTION

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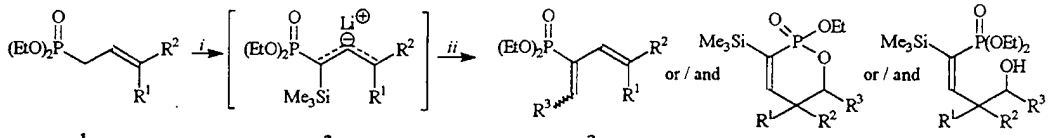
Abstract When reacted with aldehydes, *in situ* generated title carbanions **2** can give phosphonodienes (**4** or **6**), phosphonolactones (**5** or **8**) or phosphonoalcohols **7**, depending on structure of reagents and on reaction conditions.

INTRODUCTION

Carbanions derived from γ-substituted allylic-type phosphonates **1** show high α-regioselectivity in their reactions with electrophiles [1-3]. We have recently proved that the nucleophilic reactivity of such anions is dramatically modified by the presence of trimethylsilyl group in the α position [4]. We hereby present results concerning the reactivity of these *in situ* generated carbanions **2** towards aldehydes (Scheme).

RESULTS

In the cinnamyl series (R^1=H, R^2=Φ), usual Peterson reaction occurs giving phosphonodienes **3**, in excellent yield. In the prenyl series (R^1=R^2=Me), γ-regioselective reaction is observed, leading to phosphonolactones **4**, as the sole product with aromatic aldehydes, or as the major product with aliphatic aldehydes (minor product is diene **3**). In the crotyl series (R^1=H, R^2=Me), strict γ-regioselectivity is observed with aromatic or aliphatic aldehydes : phosphonoalcohols **5** can be isolated after acidic hydrolysis at -70°C. By raising the reaction temperature or by warming **5** near 50°C, phosphonolactones **4** are obtained, in very good yield and with good diastereoselectivity.



1 2 3 4 5

i : 1/ LDA, THF, -70°C; 2/ Me_3SiCl, -70°C. *ii* : 1/ R^3CHO; H_3O^+

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 120
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UNUSUAL AND EFFICIENT (*Z*)-STEREOSELECTIVE PETERSON SYNTHESIS OF 2-DIETHOXYPHOSPHONYL-1-ALKOXY-3-METHYLPENTA-1,3-DIENES. THEIR USE IN THE DIELS-ALDER REACTION.

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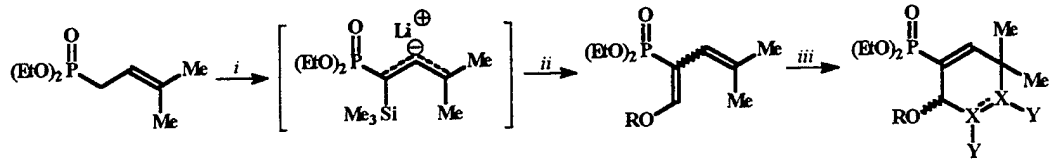
Abstract *In situ* generated from diethyl prenylphosphonate **1**, carbanion **2** reacts with alkyl formates leading to phosphonodienes **3**, which are used in Diels-Alder reactions to give phosphonoadducts **4**.

INTRODUCTION

Peterson olefination reaction with carboxylic acid derivatives are rare [1,2]. We have recently found that lithiated diethyl α-trimethylsilylcrotylphosphonate reacts γ-regio-selectively with ethyl formate [3]. We describe here the behavior of similar anion derived from diethyl prenylphosphonate towards some alkyl formates.

RESULTS

When reacted at -70°C with various alkyl formates, carbanion **2**, quantitatively *in situ* generated from diethyl prenylphosphonate **1**, behaves as a Peterson reagent and gives, in very good yield, 1-alkoxy-2-phosphonodienes **3**, of exclusive 1-(*Z*)-geometry. Dienes **3** react with dienophiles, leading to new variously substituted Diels-Alder phosphono-adducts **4**, obtained with excellent diastereoselectivity and isolated in very good yield (Scheme).



1 2 3 4

i : 1/ LDA, THF, -70°C; 2/ Me_3SiCl, -70°C.
ii : 1/ HCO_2R, -70°C; 2/ H_3O^+
iii : Dienophile / solvent, reflux.

R = Me, Et, iPr, tBu

X=X = a/ C=C; b/ N—N; c/ C—C
Y = a/ CO_2Me; b/ CO_2Et; c/ C(O)—N—C(O) (Φ)

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THE 2,2'-COUPLED PYRROLIDINE-PHOSPHOLANE RING SYSTEM: A HIGHLY ENANTIOSELECTIVE SYNTHESIS AND KINETIC RESOLUTION OF THE PHOSPHORUS CENTRE.

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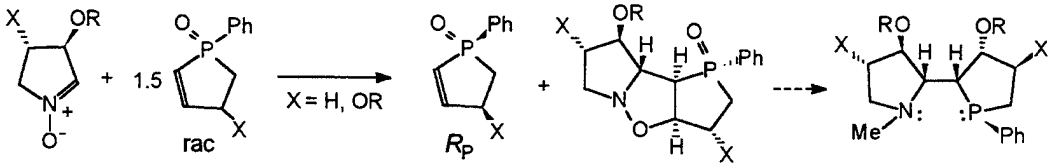
Enantiopure five-membered ring nitrones derived from *L*-tartaric acid and from *L*-malic acid undergo highly regio- and stereoselective cycloaddition reactions with an excess of racemic 2,3-dihydro-1-phenyl-1*H*-phospholes producing two readily separable tricyclic cycloadducts and concomitantly effecting kinetic resolution of the dihydrophosphole derivative (diastereomeric ratio up to 10:1; stereoselectivity factor $s = k_S/k_R = 14$). The tricyclic cycloadducts feature 2,2'-connection of pyrrolidine and phospholane rings and five to seven contiguous stereogenic centers of which three are induced and one or two are kinetically resolved during the cycloaddition process.



The kinetic resolution process can be adjusted to produce dihydrophosphole derivatives in virtually 100% e.e. Also, single cycloadducts of 100% e.e. can be directly obtained by means of the corresponding doubly asymmetric processes utilizing enantiopure nitrones and enantiopure 1-phenyl dihydrophosphole oxide in matched configurational pairings. In these cycloadditions processes 1-phenyl dihydrophosphole oxide approaches the nitrones exclusively from the P=O side and in the exo mode. The tricyclic cycloadducts serve as precursors to novel C,P-chiral pyrrolidine-phospholane ligands.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 122
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PHOSPHORYLATED BROMONITROETHENE IN THE REACTIONS WITH NH- AND CH- ACIDS

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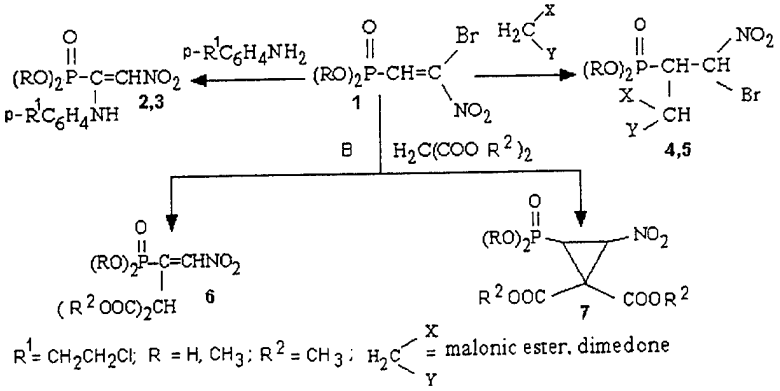
Abstract The interaction between *O,O*-di(2-dichloroethyl)-2- bromo-2-nitroethenephosphonate and some NH- and CH-acids is discussed.

The highly reactive halonitroethenes attract the attention of scientists so as they are active synthons in the synthesis of various classes of organic compounds. Phosphorylated halonitroethenes can represent particular interest, because of phosphoryl group introduction "a priori" makes the reactivity of such compounds to be higher and allows to synthesize a big number of biologically active compounds.
The very first study of interaction between *O,O*-di(2-chloroethyl)-2-nitroethenephosphonate **(1)**[1] with some representatives of NH-and CH-acids such as anyline, p-toluydine, dimedone, and malonic ester was conducted by our research group.



In contrast with well-known halonitroethenes[2] reactions, interactions of compound **(1)** even with low basic aromatic amines were found to proceed in ether at room temperature according to addition-elimination mechanism and result in recently unknown phosporylated nitroenamines **(2,3)**.

The interaction between bromonitroethenephosphonate **(1)** with dimedone and malonic ester proceeds along the more complicated pathways. Condensation in the presence of equimole amounts of sodium methylate results in the mixture of products isolated by column chromatography. Individual Michael's adducts **(4,5)** with total yield 20% and mixture of products of their dehydrobromination were isolated. Analysis of the spectral data shows the products of compound **(4)** dehydrobromination to be the mixture of the structural isomers - substituted nitroethenephosphonate **(6)** and nitrocyclopropanephosphonate **(7)**. The structure of synthesized compounds is proved by methods of mass-spectrometry, IR, UV and ^{1}H, ^{13}C, ^{31}P NMR spectroscopy.

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SYNTHETIC APPLICATIONS OF PHOSPHONIUM DIYLIDES

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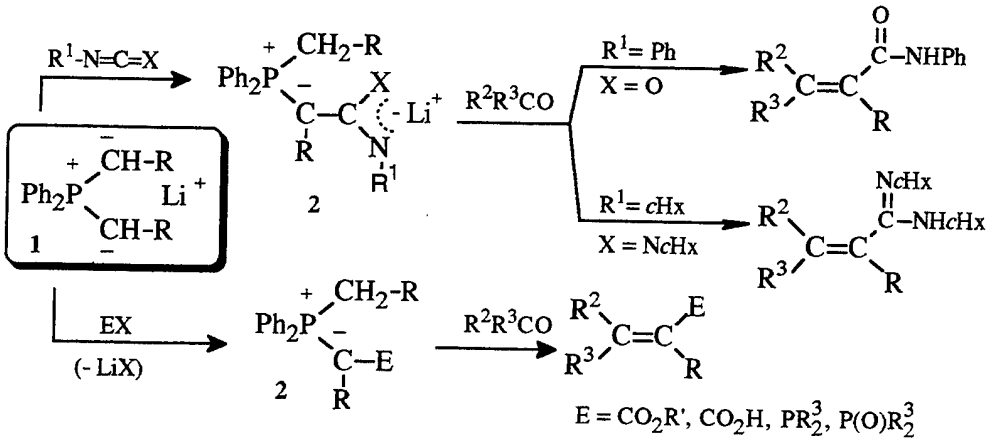
34053 Montpellier, France.

Abstract Phosphonium diylides **1** react with electrophiles leading to new monoylides which permit, by a Wittig reaction, the *E* stereoselective synthesis of various di- or tri-substituted α,β-unsaturated functionalized compounds.

Recently we have shown that phosphonium diylides **1**, allowing the formation of various α,β-unsaturated functions, can be consider as very good tools in organic synthesis [1].

We report here a generalization of the method which permit, *via* the *in situ* formation of a new intermediate monoylide **2**, the synthesis of α,β-unsaturated amides, amidines, esters, acids, phosphines, phosphonates and phosphine oxides.



In the case or R = H, alkyl, and when R^2R^3CO is an aldehyde, the products are isolated in good yields (60-90%) and excellent *E* stereoselectivity. When R = Ph, COPh or in presence of ketones, the yields are often lower or the reaction leads to the direct formation of the *E* alkene $R^2R^3C{=}CHR$.

REFERENCE

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 124
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A FACILE AND GENERAL SYNTHESIS OF PHOSPHINYLGUANIDINES

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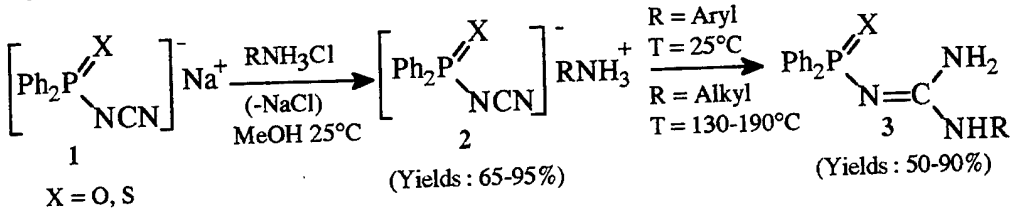
[b] Laboratoire de Chimie Organique, ENSCM, URA 458, 8 rue de l'Ecole Normale, 34053 Montpellier, France.

Abstract : In order to synthesize new phosphorus guanidines **3**, **5** as potential agrochemicals the reactivity of phosphorus cyanamides **1**, **4**, was investigated towards aliphatic and aromatic amines.

Sodium diphenylphosphinyl cyanamides **1** reacts with alkyl-, aryl-ammonium-chlorides under mild conditions to alkyl-, aryl-diphenylphosphinyl cyanamides **2**, which rearrange, at temperature depending on the amine basicity, to give N-alkyl or (aryl) N'-diphenylphosphinyl guanidines **3**[1].



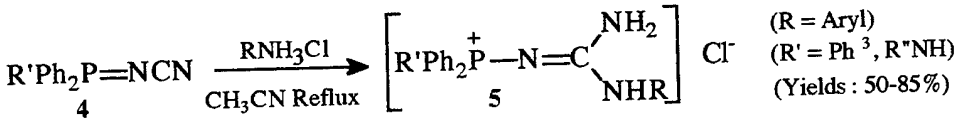
1
X = O, S

2
(Yields : 65-95%)

3
(Yields : 50-90%)

Low temperature ^{1}H-NMR and X-Ray cristallographic investigations show that only one tautomeric form exist, in which the imino substituent is in α position to the phosphorus atom.

This work was extended to the synthesis of phosphonioguanidines **5** [2].



4

5
(R = Aryl)
(R' = Ph [3], R"NH)
(Yields : 50-85%)

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A NEW WAY FOR POTENTIAL AMINOPHOSPHONIC ACIDS PRECURSORS

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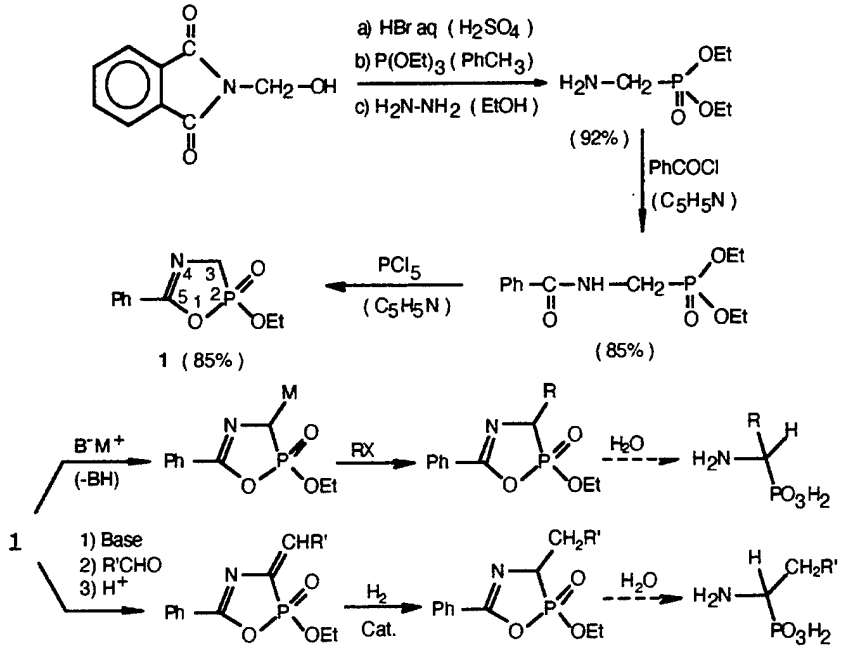
Abstract New five membered-ring 3,3-dihydro-1,4,2-oxazaphospholenes **1**, potential precursors of aminophosphonic acids, have been synthesized and characterized by ^{1}H, ^{13}C and ^{31}P NMR.

The replacement of COOH group by $P(O)(OH)_2$ or related functions exhibit a broad range of interest because several synthetic and natural phosphonic analogs of amino acids have rather interesting biological properties[1]. We directed our research to the synthesis of five membered ring with P-C-N unit **1** which could provide, after mono-, di-alkylation or Knœvenagel reactions on the 3-position and hydrolysis, a convenient procedure to synthesize a wide range of aminophosphonic acids **2**.



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NEW CARBAMOYL ORGANOPHOSPHORUS COMPOUNDS

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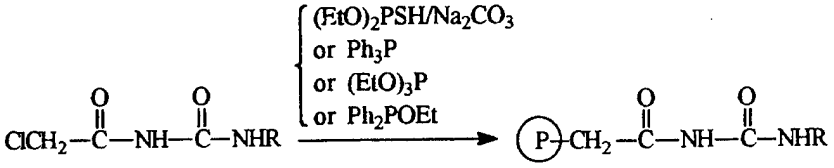
Abstract The syntheses of various organophosphorus compounds, which contain a function with potentially agropharmaceutical properties (acylureas [1], acylsemicarbazides [2] or imidazolidinetriones [3]) are described.

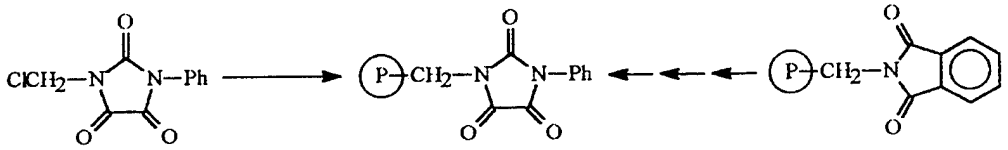
Phosphorus acylureas and acylsemicarbazides were prepared by condensation between various phosphorus starting materials (dithiophosphate, phosphine, phosphite and phosphinite) and two chlorinated precursors (N-chloroacetyl N'-phenylurea and 4-chloroacetyl (2,4-dinitro 1-phenyl)semicarbazide) :



R = C_6H_5 or 2,4-$(NO_2)_2C_6H_3NH$

(P) = $(EtO)_2P(S)S^-$ / $Cl^\ominus$ $Ph_3P^\oplus$ / $(EtO)_2P(O)^-$ / $Ph_2P(O)^-$

Phosphorus 2,4,5-imidazolidinetriones were obtained in two different ways : the syntheses of the dithiophosphate and phosphonium salt derivatives involved the reaction between a common N-chloromethyl heterocycle and corresponding phosphorus partners, while the preparation of phosphonylmethyl and phosphine oxide imidazolidinetriones was realized using a multi-step synthesis strategy starting from different phosphorus phthalimides :



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SYNTHESIS OF NEW PHOSPHOMYCIN ANALOGUES

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XAVIER YANGKOU MBIANDA, ANNABELLE GEZE.
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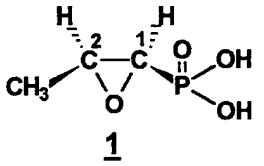
Abstract: In the aim to carry out a quantitative reactivity/structure/biological activity relationship, a general four step synthesis, gives us access to a number of new phosphomycin analogues. A new synthesis of di- and tri-substituted vinylphosphonates *via* cuprate reactions and their epoxidation by dioxirane are described.

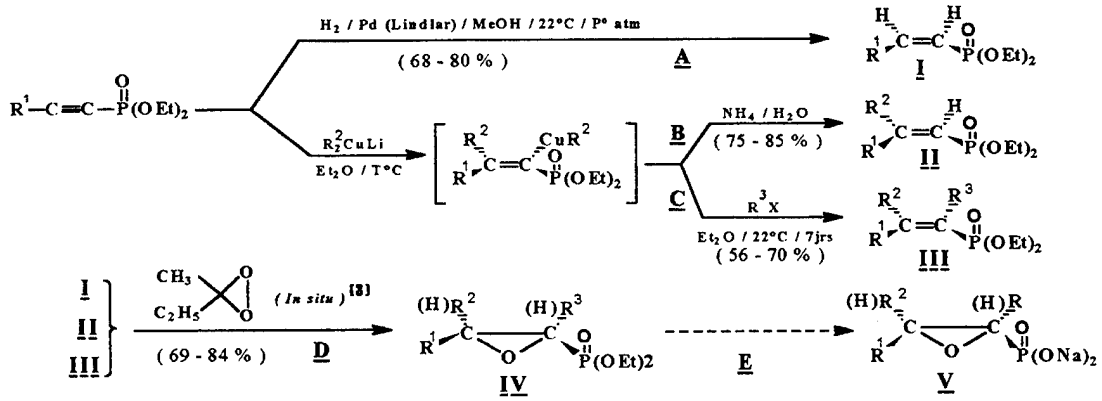
Phosphomycin **1** [(-)(1R,2S) 1,2-epoxypropylphosphonic acid)] has been isolated in 1969 from *streptomyces* and described as a large spectrum antibiotic.[1]



1

The strategic point for the biological activity seems to be the C_2 carbon of the molecule.[2] For this reason we decided to synthesize new phosphorus analogues with differently substituted C_2 and C_1 carbon atoms in the aim to carry out a quantitative reactivity / structure / biological activity relationship.

We present here our first results concerning the preparation of a series of compounds through the following pathway:



R^1 = alkyl, aryl; R^2 = alkyl, aryl; R^3 = alkyl, halogen, functionnal groups.

The **B** and **C** reactions exhibit high stereo and regioselectivity and constitute a new acces to di- and tri-substituted vinylphosphonates[4]. The **D** reaction is stereospecific and constitute the first epoxidation of vinylphosphonates by dioxirane.

1. D. HENDLIN, E.D. STAPLEY, M. JACKSON, H. WALLICK, A.K. MILLER, F.J. WOLF, T.W. MILLER, L. CHAÎET,F.M. KAHAN, E.L.FOLTZ, H.B. WOODRUPP, J.M. MATA, S. HERNANDEZ, S. MOCHALES. *SCIENCES*, **166**, 122.(1969)
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4 -H.J. CRISTAU, M.B. GASC, X.YANGKOU-MBIANDA, *J. ORGANOMETAL. CHEM.*, **474**, C_{14}-C_{15}, (1994)

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CHIRAL δ-HYDROXYALKYL WITTIG REAGENTS :SYNTHESIS AND REACTIVITY

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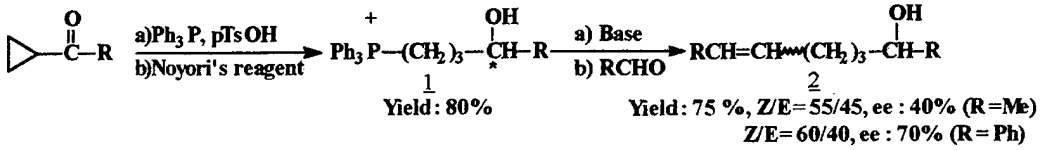
Laboratoire de Chimie Organique,URA 458 ENSCM, 8 Rue Ecole Normale, 34053 - MONTPELLIER Cédex, FRANCE.
JEAN-ROGER DESMURS, HELENE IERNO, ISABELLE LOUSTAU-THEN.
Rhone-Poulenc Recherche (CRC), 85, avenue des Frères Perret - 69192 - SAINT-FONS ,FRANCE.

Abstracts:enantioselective reduction of ketophosphonium salts give chiral synthons used in WITTIG reactions to prepare opticaly active ethylenic alcohols.

Chiral hydroxyalkyl phosphonium salts could be a convenient way to introduce an assymetric center in a given molecule via a Wittig reaction. For such reagents we choosed δ-functionalized phosphonium salts **1** for which we have developped a convenient way of access to the keto precursors [1]:



The enantioselective reduction of the keto phosphonium salts to the corresponding hydroxy chiral products were performed using NOYORI'S reagent, a chiral complex hydride prepared from $AlLiH_4$ and optically active β binaphtol [2] easily recovered after the work-up of the reaction. The salts **1** can be used in Wittig reactions with aliphatic and aromatic aldehydes leading to the corresponding ethylenic alcohols.**2** The enantiomeric excess can be ascertained by chiral HPLC,and/or NMR spectroscopy (^1H and ^{31}P).depending on the compound.

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DESTRUCTION OF TOXIC ORGANOPHOSPHORUS ESTERS BY OXIDATIVE α NUCLEOPHILIC REAGENT

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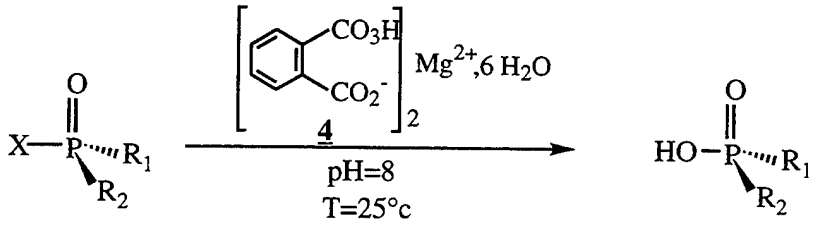
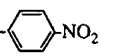
Abstract Despite its self-decomposition, Magnesium MonoPeroxyPhtalate **4** is an excellent reagent to totally detoxify phosphonothiolate **1** and fluoridate **2** in basic aqueous medium.

Decontamination of toxic organophosphorus[1] compounds in mild conditions presents an important challenge, MMPP **4** is an effective oxidative α nucleophilic reagent in basic aqueous medium.At pH=8, with 50 % peroxyanions forms, its self decomposition rate is important ($\tau_{1/2}$=8 min.).

With 10 eq. of MMPP **4**, phosphonothiolate **1** and fluoridate **2** are totally detoxified by spliting the P-S and P-F bonds in a short time (20 min.and 40 min.).P-O bond (phosphate ester **3**) is less reactive than P-S and P-F, so decontamination is incomplete (40 %).



	R_1	R_2	X
1	CH_3	O-Et	S-CH2-CH2-N(iPr)2
2	CH_3	O-CH(CH_3)-tBu	F
3	O-Et	O-Et	O- 

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 130
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SYNTHESIS AND REACTIVITY OF NEW 1,1-DIPHENYL-2,5-DIHYDRO-PHOSPHOLIUM SALTS

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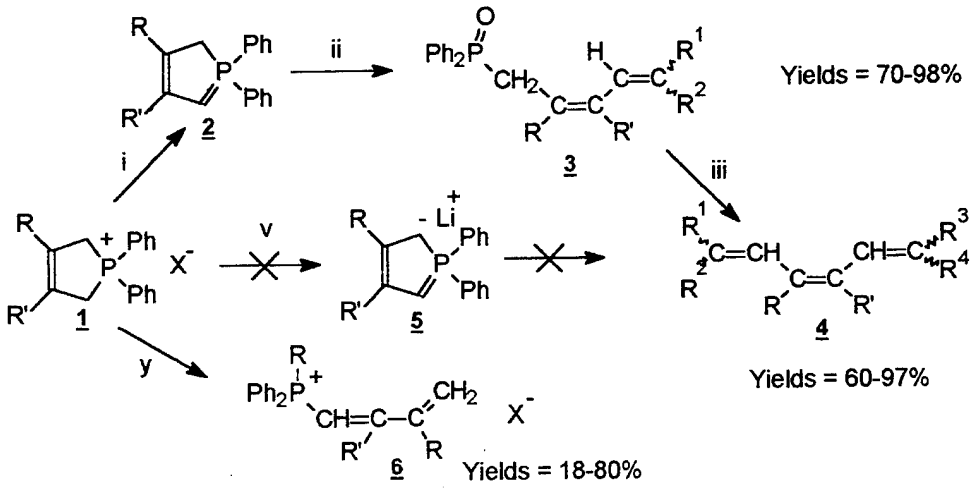
Abstract: We describe the first synthesis of new 1,1-diphenyl-2,5-dihydro-phospholium salts of type **1**. These salts allow the access to interesting alkadienyl phosphine oxides **3** and trienes **4**. Unfortunately we could not obtain the strong nucleophilic diylide **5**.

Key words: *Dihydrophospholium Salts, ylides, Wittig Reaction, Trienes.*

In the course of our investigations on the highly nucleophilic diylides[1], we could not obtain the ***de***stabilized diylide **5**: a nucleophilic attack of the base occurs with ring opening. But the monoylide **1a** (R= R'= Me) is a really interesting synthetic precursor to provide with excellent yields and stereoselectivities phosphine oxides **3** and trienes **4**[2]. The salt **1a** affords an unexpected alkylation on the phosphorus atom with ring opening.



SCHEME 1: Reactivity of salt **1**. R= R'= Me; R= Me, R'= H; R= R'= H. i) 1.0 eq. nBuLi (THF) or 1.0 eq *t*BuOK (THF); ii) 1,1 eq. R^1R^2CO; iii) 1,0 eq. nBuLi (THF); 1,1 eq. R^3R^4CO; v) 2.0 eq nBuLi (THF) or 2.0 eq CH_3SOCH_2Li (DMSO); y) 1,0 eq RX (THF).

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 131
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HYDRIDE TRANSFER REACTIONS OF AMINOMETHYLPHOSPHINES AND BIS(AMINO)METHANES WITH DIPHENYLBORIC ACID ESTER IN THE PRESENCE OF CARBONYL COMPOUNDS.

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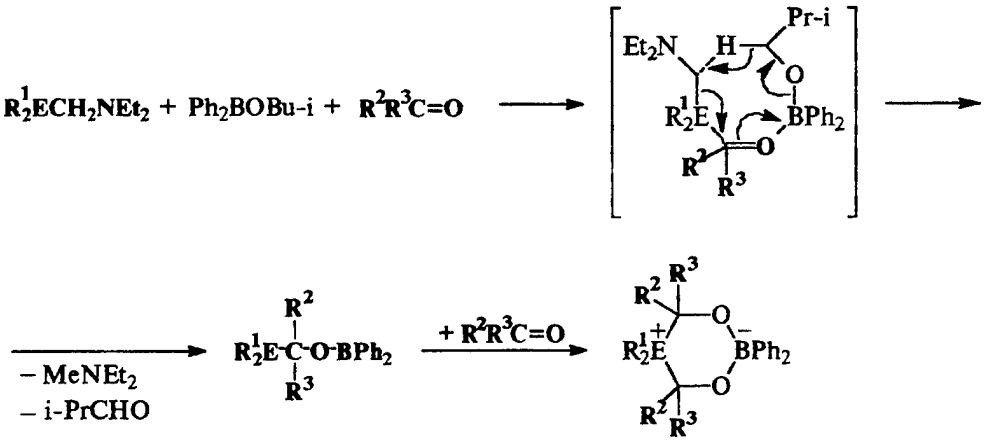
A.E. Arbuzov Institute of Organic and Physical Chemistry,
Russian Academy of Sciences, Kazan Scientific Center, Kazan, Russia

The interaction of diethylaminomethylphosphines and diphenylboric acid isobutyl ester proceeds only in the presence of active carbonyl compounds, namely alkyl aldehydes, followed by the formation of 1,3,2,5-dioxaborataphosphoniarinanes with the second molecule of the carbonyl compound. Reactions don't take place in the presence of ketones and aromatic aldehydes. Bis(N,N-diethylamino)methane reacts analogously to give corresponding N,B-containing zwitter-iones.



E=P; R¹=Me, Ph; R²=H; R³=H, n-Pr, i-Pr.
E=N; R¹=Et; R²=H; R³=H, i-Pr.

These reactions are aldehyde-initiated reduction of aminals or analogous compounds by borinic acid esters and lead to unusual replacement of the aminometyl group by the boroxymethyl group. Reactions proceed presumably by hydride transfer via cyclic transition state.

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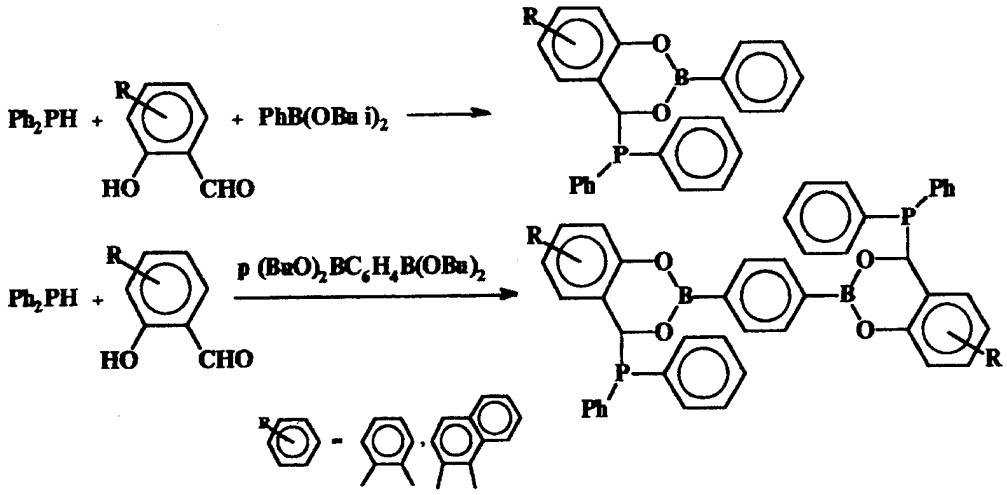
SYNTHESIS AND INTRAMOLECULAR INTERACTIONS OF 1,3,2-DIOXABORINANES CONTAINING EXOCYCLIC PHOSPHINOGROUPS.

E.I. AYUPOVA, A.S. BALUEVA, G.N. NIKONOV
A.E. Arbuzov Institute of Organic and Physical Chemistry,
Russian Academy of Sciences, Kazan Scientific Center, Kazan, Russia

Abstract The intramolecular dispersion interaction between the aryl group at phosphorus and the oxyboryl fragment is observed for 4-phosphino-1,3,2-dioxaborinanes.

The X-ray analysis and NMR spectra of 4-phosphino-1,3,2-dioxaborinanes prepared from primary or secondary arylphosphines, aromatic aldehydes containing an ortho-hydroxygroup and phenylboronic or benzene-1,4-diboronic acid esters indicate the unusual intramolecular dispersion interaction between the π-systems of the boronic ester fragment and the phenyl group at phosphorus.



The absence of such interactions in conformationally labile 4-diphenylphosphino-6-methyl-2-phenyl-1,3,2-dioxaborinane indicates that the planarity of the dioxaborinane ring due to the presence of the condensed rigid aromatic fragment is essential to the realization of the intramolecular stacking-interaction.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 133
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BIS(O-CARBOXYPHENYLAMINOMETHYL)PHENYLPHOSPHINE - A NOVEL HYBRIDE LIGAND IN COORDINATION CHEMISTRY OF TRANSITION METALS.

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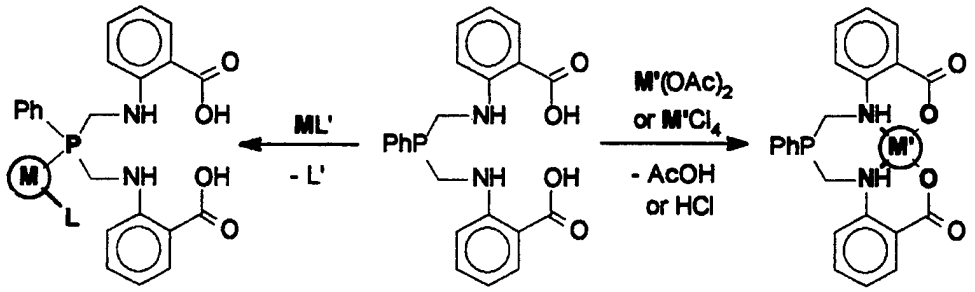
Russian Academy of Sciences, Kazan Scientific Center, Kazan, RUSSIA

Functional hybride phosphines with hard (O, N) and soft (P) donor sites are a base for synthesis of heterobinuclear complexes, in particular of early-late d-block elements, which are perspective high effective and selective homogenous catalysts.

At has been shown that bis(o-carboxyphenylaminomethyl)phenylphosphine in the course of complex formation gave two types of compounds: P-complexes with polydentate ligand (A) and O,N-chelate metalocyclic phosphines (B).



(A) L = $PhP(CH_2NHC_6H_4COOH\text{-}o)_2$ (B)

M = $PtCl_2$, $PdCl_2$, CuCl, CuJ(Py), $Ni(CO)_2$

M' = Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, $TiCl_2^{2+}$, $ZrCl_2^{2+}$

The chlorides and carbonyls of the late d-block transition metals gave complexes of the type (A), but the acetates of late and chlorides of early d-block transition metals formed the metalcontaining phosphines of the type (B). The obtained mononuclear complexes are the suitable synthons for heterobinuclear compounds.

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THE STUDY OF ELECTRONIC AND SPATIAL STRUCTURE OF SOME DERIVATIVES OF 5-PHOSPHORANYLIDENBARBITURIC ACID AND 5-PHOSPHORANYLIDENTHIOBARBITURIC ACID

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INTRODUCTION

Barbituric acid derivatives are known to participate in formation of ordered supramolecular structures with other pyrimidine derivatives.The properties of such species are determined by the structure and specific features of molecules which are the building blocks of such arrangements. Here, the results of MNDO study of spatial and electronic structure of a number of derivatives of 5-phosphoranylidenbarbituric acid (I) and 5-phosphoranylidenthiobarbituric acid (II) are presented (the substituents at P are: H, Me, Et, Ph; the substituents at N are: H, t-Bu, OH).

RESULTS AND CONCLUSIONS

All molecules under consideration are shown to have nearly planar configuration of heterocycle, the deviation from planarity being essentially dependent on the size and nature of substituents at phosphorus and nitrogen[1].The ability of molecules of type I to self-association with vertical π-bonding is considered. The formation of weak van der Waals complex is shown to be possible, the energy of formation being estimated as ≅ 4 kcal/mole. In this structure heterocycles retain their planarity, the distance between the planes being 4.3A. The attempt to stabilize this structure by means of $(CH_2)_n$-bridges, so that the formed structure may have parallel-plane arrangement of heterocycles, is undertaken. The structures with various length of bridges (n=2,3) are studied. The heterocycles in the resulting structures are shifted relative to each other; therefore, the overlap between π-orbitals of donor cen-ters of one molecule with acceptor centers of the other is impossible.

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PREPARATION, REACTIONS, AND STEREOCHEMISTRY OF 4-*TERT*-BUTYL-1-CHLOROPHOSPHORINANE 1-SULFIDE AND DERIVATIVES

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Nucleophilic substitution at tetracoordinated phosphorus centers has been extensively investigated.[1] Transesterification of acyclic phosphinates proceeds with inversion of configuration,[2] whereas four-membered phosphinates react with retention.[3] In previous work[4] we suggested that transesterification in six-membered phosphinates occurs via an S_N2 mechanism. The title compound was synthesized as a model structure to study the stereochemical and mechanistic aspects of nucleophilic substitution at phosphorus in a six-membered ring. A mixture of diastereomers was produced and separated by column chromatography. Both the mixture and separate isomers were used for an investigation of substitution with methanol, methoxide ions, and phenoxide ions; the reactions proceeded with inversion. Transesterification reactions of the resulting thiophosphinates were studied and found to proceed with inversion. Reactions of these with phenyllithium, benzyllithium, lithium phenylacetylide, and the corresponding organomagnesium halides were also carried out. The stereochemical assignments for the title compound (*cis* and *trans*) and two derivatives have been firmly anchored by X-ray studies;[5] assignments for others are tentative and based on spectroscopic measurements, including ^{1}H, ^{13}C, and ^{31}P NMR data.

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CONFORMATIONAL STUDIES OF A SIX-MEMBERED PHOSTONE

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Although 1,3,2-dioxaphosphorinanes generally assume chair conformations,[1] there are examples in which the ring adopts the boat or twist-boat form.[1] Recent studies on the synthesis, stereochemistry, and reactivity of 2-alkoxy-2-oxo-1,2-oxaphosphorinanes (phostones) have revealed both *cis* and *trans* isomers of 3-(diphenylhydroxymethyl)-2-ethoxy-2-oxo-1,2-oxaphosphorinane[2] to assume a chair conformation in the solid state. In the present work, the conformational properties of *cis* and *trans*-3-methoxycarbonyl-2-methoxy-2-oxo-1,2-oxaphosphorinanes were investigated by X-ray analysis, variable temperature ^{31}P, ^{1}H and $^{1}H\{^{31}P\}$ NMR spectroscopy, molecular mechanics, and semiempirical calculations. The X-ray crystal structure of the *trans* isomer revealed a chair conformation with equatorial phosphoryl and carbomethoxy groups. No changes were observed in the ^{31}P NMR spectra of either isomer in the temperature range of 183-333 K. A complete set of vicinal J_{HH} coupling constants was extracted from the $^{1}H\{^{31}P\}$ spectra of each isomer taken at five temperatures over the range of 213-293 K and refined by simulation of the spectra. The best-fit analysis of this data using a generalized Karplus equation[3] revealed that the conformation of the *trans* isomer in solution was close to that found in the solid state. This conformation corresponded to the global energy minimum calculated by both molecular mechanics and PM3 semiempirical method. A substantial contribution from an inverted chair conformation of the *cis* isomer had to be assumed to achieve a reasonable fit of the coupling constants calculated from the generalized Karplus equation.

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SYNTHESIS AND UNEXPECTED REARRANGEMENT OF A HYDROXYPHOSTONE (1)

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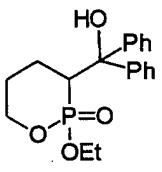
During our investigations on the wide range of stereoselective alkylations of 6-membered ring phostones,[1] we uncovered a novel rearrangement of 3-(diphenylhydroxymethyl)-2-ethoxy-2-oxo-1,2-oxaphosphorinane (**1**). The *cis/trans* diastereomers of **1** were prepared by the reaction of benzophenone with the appropriate ylide of the parent phostone (**3**).[2] When *trans*-**1** was left unattended at rt in CH_2Cl_2 a new compound, **2**, was isolated which showed a significant downfield ^{31}P shift and a higher melting point. Upon heating to the melting point **2** decomposed to give **4**, which suggests that **2** may be an intermediate in the conversion of **1** to the Wittig-like product **4**. The IR, ^{1}H, ^{13}C, ^{31}P, and 2-D NMR spectral data along with independent synthesis confirmed the identity of **2**. Subsequently, **2** was also produced in 70% yield when *cis*-**1** was treated with CH_2Cl_2/ether-HCl_{aq} at 50-60°C for 2 weeks, but this product was contaminated with 30% of the exocyclic alkene **5**. No rearrangement was observed when **1** was treated with TsOH/EtOH or HPF_6; only **5** was produced. The stereochemistry and mechanisms of these transformations are presented.



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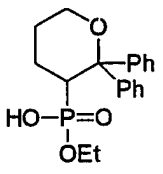

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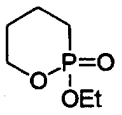

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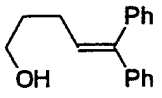

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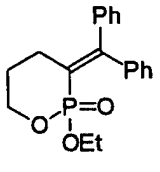

5

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PREPARATION OF BICYCLIC SECONDARY AND TERTIARY PHOSPHINES FROM RADICAL ADDITION OF PHOSPHINE AND PRIMARY PHOSPHINES TO LIMONENE

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CYTEC Canada Inc., Niagara Falls, Ont., Canada L2E 6T4

In the presence of a free radical initiator, limonene combines with a primary phosphine to yield a 1:1 adduct (I). Initially the addition takes place at the isopropenyl moiety. The resulting secondary phosphine subsequently undergoes an intramolecular addition to produce two isomeric 2-alkyl-4,8-dimethyl-3-phosphabicyclo [3.3.1]nonanes (II, III) in >85% yield. Analogous bicyclic secondary phosphines are formed by free radical addition of phosphine to limonene. Yields are slightly lower due to the addition of the reactive secondary phosphines to a second mole of limonene.

A proton coupled ^{31}P NMR spectrum of II/III where R=isobutyl, contained two singlets (-50.34 and -56.62 ppm) and verified that II and III are tertiary phosphines. The relative areas are 1:1.17. The ^{31}P NMR spectrum of II/III derived from limonene and phosphine contained two doublets centered at -73.31 and -97.69 ppm. The H/P coupling constants are 2.419 and 2.367 ppm. The relative areas are 1.:0.84. The corresponding ^{13}C NMR spectrum for the secondary phosphine mixture contained twenty signals (8 CH_2 and 12 CH_3/CH) which are consistent with the twenty distinct carbons expected from a mixture of II and III.

The tertiary phosphines derived from optically pure limonene may have potential utility as chiral catalyst ligands. The bridgehead carbon configuration at position 5 will be fixed at R and S respectively when starting with R(+) and S(-) limonene. Fixing the configuration at position 5 will predetermine the configurations at 2 and 8.

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Imides of 2-Trifluoroacetylphenol and other Trifluoracetic acid Esters: Novel Reactions with Phosphorus(III) Derivates

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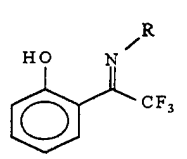
The imido derivates of 2-trifluoroacetylphenol, **1** (R^1=H, Me, iPr) react with the isocyanatophosphites $(R^2O)_2PNCO$, **2** (R^2=Et, R^2-R^2=CMe_2-CMe_2) to yield the bicyclic compounds **3**, wheras in case of **1** (R^1=$(CH_2)_2NMe_2$) the $\lambda^3\sigma^3$P compounds **4** are found. The phosphorus(III) chlorides R^3PCl_2 (R^3=Ph, OEt) and **1** (R^1=H, Me) give rise to furnish the tricyclic phosphoranes **5.** However with **1** (R^1=iPr) phosphite **6** is obtained, which adds hexafluoracetone to give the 1,3,2$\lambda^5\sigma^5$-dioxaphospholane **7**. 2-(Trifluoracetoxy)pyridine **8** reacts with Tris(trimethylsilyl)phosphite to yield the bis(phosphonate) **10**. Some molecular structures are discussed on the basis of x-ray diffraction results.



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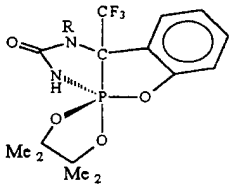

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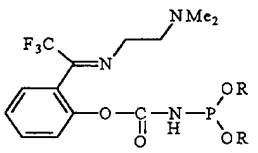

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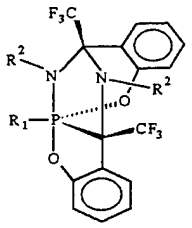

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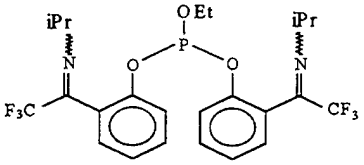

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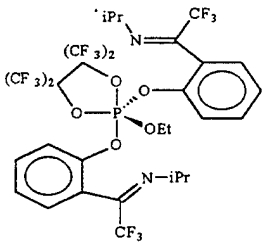

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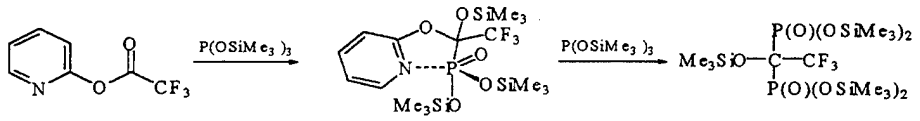

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 140
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SELECTIVE PHOSPHORYLATION OF α,β-UNSATURATED CARBONYL COMPOUNDS

VLADIMIR I.GALKIN, GULCHIRA M.SAAKYAN,
IRINA V.GALKINA, AND RAFAEL A.CHERKASOV

Kazan State University, Kazan, Russia

Elaboration of effective methods of selective phosphorylation of α,β-unsaturated carbonyl compounds containing simultaneously C=C and C=O bonds, which may compete with each other or react consistently one after another, is one of the most complex problems in the modern organophosphorus synthesis. On the basis of our previous systematic investigations of kinetics and mechanism of the Pudovik and Abramov reactions in the series of α,β-unsaturated carbonyl compounds we have suggested three possible ways to solve this problem: a) soft reaction conditions, regulated by solvent, catalyst and temperature; b) interface catalysis; c) metallocomlex catalysis (reaction in the coordination sphere of transition metal).

Experimental verification show, that all three approaches give enough satisfactory results and permit to obtain corresponding α-hydroxyphosphonates (products of the Abramov reaction) with a good yield even for a such "unsuitable" subsrate as benzylideneacetophenone (chalcone) which in common conditions always gives the adducts on the C=C bond (product of the Pudovik reaction).

Thus suitable methods of selective phosphorilation of α-enones C=O bond have been elaborated. α-Hydroxyphosphonates obtained may be easily isomerized into corresponding γ-ketophosphonates by heating or alkoholate action.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 141
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A NEW MODEL OF INDUCTIVE EFFECT IN THE ANALYSIS OF ORGANOPHOSPHORUS REACTIVITY

ARTEM R.CHERKASOV, VLADIMIR I.GALKIN,
IGOR M.SIBGATULLIN, AND RAFAEL A.CHERKASOV

Kazan State University, Kazan, Russia

Structure and reactivity correlation is one of the most important problems of modern organic and organoelement chemistry.

We have suggested a new model of inductive effect, which allows to calculate the inductive constant of any substituent at any reaction center on the basis of fundamental physical laws and enough simple mathematical apparatus. Experimental and calculated constants in Taft`s inductive scale for a wide series organic,organoelement and charged substituents form with each other a correlation of high quality :

$$\sigma^{*}\ (\text{theor.}) = (0.031 \pm 0.012) + (0.993 \pm 0.006)\ \sigma^{*}\ (\text{exper.})$$

$N = 427$, $S = 0.190$, $R = 0.9910$

The model suggested allows to calculate easily the inductive constants of any substituents at phosphorus and any other heteroatom and may be very useful in analysis of organoelement (and organophosphorus in particular) reactivity. Besides theoretical results obtained , show that in common case the inductive effect in organoelement chemistry is non-linear with that in organic chemistry - that is why carbon inductive constants may be used in organoelement reactivity correlations with a great caution.

The work is realized with financial support of the S.- Petersburg Competition Center.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 142
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KINETICS AND MECHANISM OF THE KABACHNIC-FIELDS REACTION

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ALEXANDER A.SOBANOV, IRINA V.GALKINA,
AND RAFAEL A.CHERKASOV

Kazan State University, Kazan, Russia

The Kabachnic-Fields reaction is one of the most important methods of synthesis of functionally substituted derivatives of tetracoordinated phosphorus with P-C bond. At the same time mechanism of this important and interesting reaction practically has not been investigated.

This issue is devoted to results of systematic preparative and kinetic investigations of the Kabachnic-Fields reaction mechanism in different three components systems dialkylphosphite-carbonyl compound-amine and also the kinetic laws of all the possible in these systems concurrent bimolecular reactions.

It has been established that the mechanism of the Kabachnic-Fields reaction is significantly depended on amine basicity. If this basicity is high enough, as for instance in the case of cyclohexylamine, amine activates the dialkyl hydrogen phosphite (DAHP) molecule and reaction is carrying out through the primary addition of DAHP on the carbonyl group with the subsequent substitution of hydroxyl in α-hydroxy-derivative on the amino group. In the case of amines with low basicity (for instance, aniline) the obtained results digitally proves the formation of the imine on the first stage of the Kabachnic-Fields reaction with the following addition of DAHP on C=N bond with the same α-aminophosphonate formation.

The work is realized with financial support of International Science Foundation (Grant RH 2300).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 143
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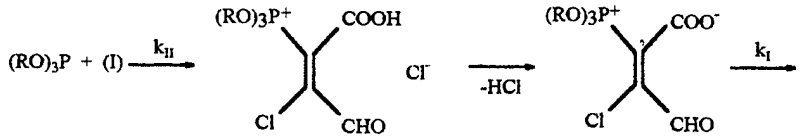
KINETIC INVESTIGATION OF UNUSUAL ARBUZOV REACTION

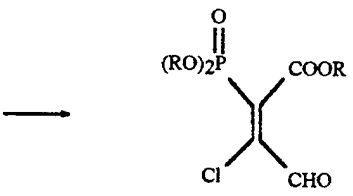
NINA A.POLEZHAEVA, IRINA V.LOGINOVA,
ELENA V.OVECHKINA, VLADIMIR I.GALKIN,
AND RAFAEL A.CHERKASOV

Kazan State University, Kazan, Russia

3,4-Dichloro-5-hydroxy-2(5H)furanone (mucochloric acid) (I), which may exist in two (cyclic and acyclic) forms, reacts with trialkylphosphites under mild conditions to form two products, one and the most interesting of which is (II). Kinetic study if this process has shown the following reaction mechanism which is an unusual Arbuzov reaction with the elimination of HCl (but not RCl) from the intermediate (A):



(A) (B)



(II)

Kinetic and activation parameters of two limiting stages have been estimated. The mechanism suggested has been proved also by fixation of HCl with the help of triethylamine and by preparation of intermediates in the case of triphenylphosphine.

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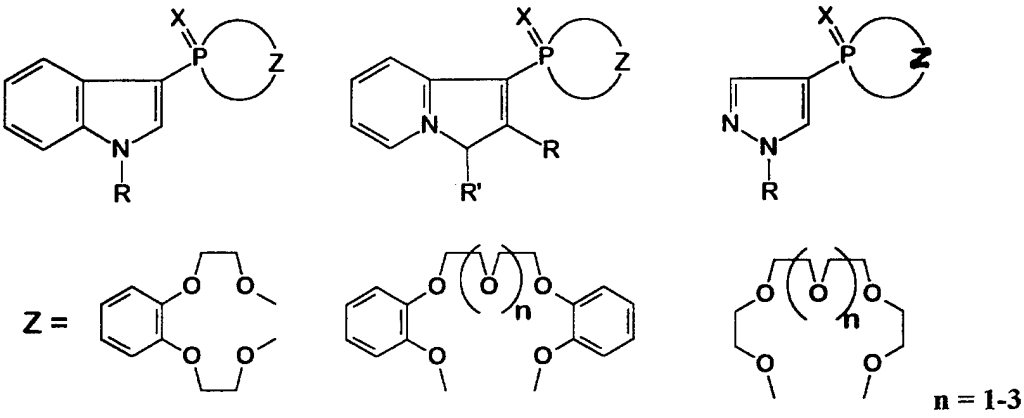
PHOSPHORUS CROWN-ETHERS WITH NITROGEN-CONTAINING HETEROCYCLES

ALEXANDRA A. CHAIKOVSKAYA, TAMARA N. KUDRYA, TAT'JANA E. TEREKOVSKAYA, ANDREW A. TOLMACHEV, ALEXANDER M. PINCHUK
Institute of Organic Chemistry of the Ukrainian National Academy of Sciences; Murmanskaya Str., 5, KIEV-94, 253660, UKRAINE.

Phosphorus-containing crown-ethers functionalized by heterocycle fragments have essential advantages over the usual ones. The introduction of structural units of indoles, pyrroles and indolizines to phosphorus atom of the macrocyclic chain is capable to change lipophilic, complexing, biological and other properties of the initial crown-ethers. For synthesis of such compounds we have used dihalidophosphines obtained by direct substitution of the electron-rich aromatic compounds with phosphorus (III) halides. As a result, series of highly efficient macrocyclic compounds of a nowel type have been obtained.



Details of the synthesis and the relation between a structure of the compounds obtained and their physiological activity are discussed.

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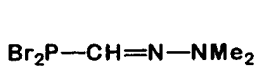
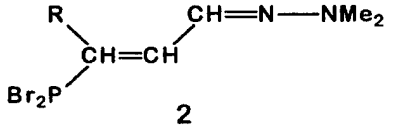
C-PHOSPHORYLATION OF COMPOUNDS WITH THE ELECTRON-RICH DOUBLE CARBON-NITROGEN BOND

ANDREW A. TOLMACHEV, ANATOLY S. MERKULOV, SERGEI I. DOVGOPLY, GENNADY V. OSHOVSKIY, ALEXANDER M. PINCHUK
Institute of Organic Chemistry of the Ukrainian National Academy of Sciences;
Murmanskaya Str., 5, KIEV-94, 253660, UKRAINE.

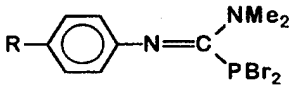
C-phosphorylation of N,N-dimethylhydrazones and N,N-dimethyl- N'-arylamidines by phosphorus tribromide was first accomplished. It directs to the formation of novel types of functional P(III) derivatives (**1-3**).



1

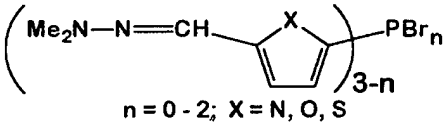


2



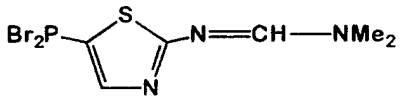
3

The N,N-dimethylhydrazono- or N,N-dimethylamidino groups can be used as the electrodonating substituents for the activation of heteroaromatic compounds in their reactions of electrophilic phosphorylation, what let to synthesize such phosphines as **4** and **5**, benzazophosphole derivatives (**6**), heteroaromatic aldehydes(**7**) and other types of phosphorus compounds.

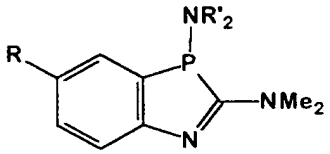


n = 0 - 2; X = N, O, S

4

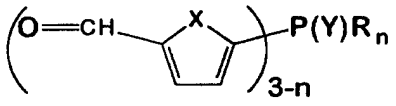


5



R = Alk, Hal, Me $_2$N
R' = Me, Et, i-Pr

6



n = 0 - 2; X = N, O, S;
Y = O, S; R =Ph, Et $_2$N

7

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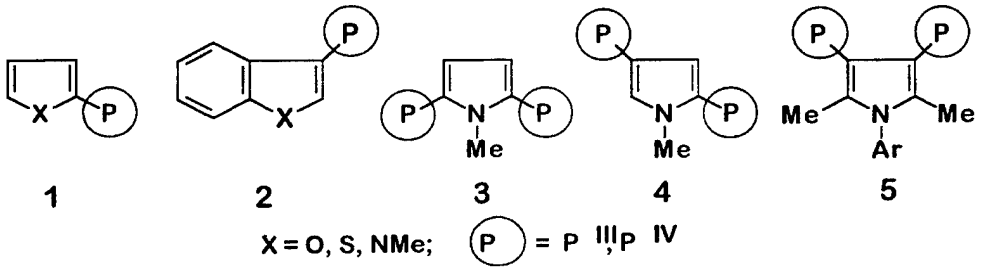
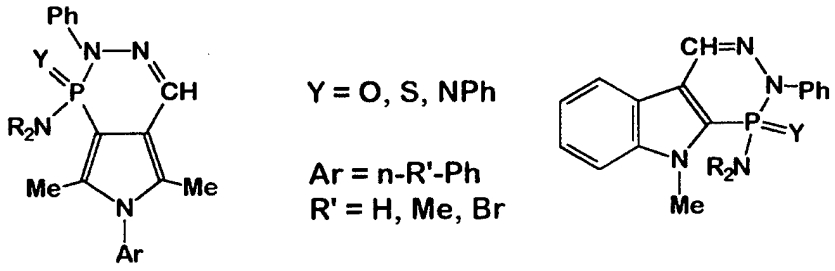
C-PHOSPHORYLATION OF ELECTRON-RICH HETEROCYCLES

ANDREW A. TOLMACHEV, SERGEI P. IVONIN, ALEXANDRA A. CHAIKOVSKAYA, TAMARA N. KUDRYA, TAT' JANA E. TEREKOVSKAYA
Institute of Organic Chemistry of the Ukrainian National Academy of Sciences; Murmanskaya Str., 5, KIEV-94, 253660, UKRAINE.

C-phosphorylation of pyrrole, furan, thiophene derivatives and their benzanalogs by phosphorus tribromide has been studied. Perspective methods for involving trivalent phosphorus residues at a different position of the rings have been developed. Unknown early the heterocycle's derivatives with tri- and tetracoordinated phosphorus substituents (**1-5**) and novel types of phosphoruscontaining heterocycles (**6,7**) have been obtained.



1 2 3 4 5



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THE REACTIONS OF PHOSPHORYL - STABILIZED CARBANIONS WITH α,β-UNSATURATED CYCLOALKENONES DERIVATIVES

MALOSE J. MPHAHLELE and TOMASZ A. MODRO
Centre for Heteroatom Chemistry, Department of Chemistry,
University of Pretoria, Pretoria 0002, South Africa

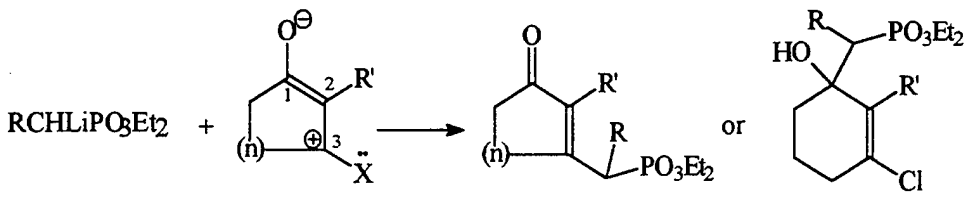
Abstract The effects of the β-leaving group of the cycloalkenone on the regioselectivity of nucleophilic addition by $RCHLiP(O)(OEt)_2$ are discussed.

INTRODUCTION

The reactions of diethyl (lithiomethyl)phosphonate with cycloalkenones afford carbonyl - addition products.[1] In this work, using cycloalkenones bearing Cl or MeO substituent in the β-position, we found that the course of the reaction depends on the β-substituent.

RESULTS AND DISCUSSION

The diethyl lithioalkylphosphonates **1** were found to add regioselectively across the C-C double bond of the β-methoxycycloalkenones **2** (X = OMe) with the elimination of CH_3O^- to form the vinylketophosphonates **3**. On the other hand, the same nucleophiles undergo carbonyl addition to the β-chlorocyclohexenones **2** (X = Cl) to afford the β-hydroxyalkylphosphonates **4** . The observed regioselectivity can be explained in terms of the stabilizing effect of MeO *vs.* Cl on the electrophilicity of C-3 relative to C-1.



1 (R = H, CH_3) **2** (n = 1,2) **3** (if X = OMe) **4** (if X = Cl)

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SYNTHESIS AND CHEMISTRY OF PHOSPHONIC DERIVATIVES

A PIENAAR and T A MODRO
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Abstract The reaction of thionyl chloride with mixed diesters of the type $RP(O)(OCH_2CH_2NR'_2)OR''$ are discussed.

INTRODUCTION

Compounds of the type $R\text{-}P(O)(OCH_2CH_2NR'_2)Y$ were required for kinetic studies to elucidate the mechanism of decomposition of these compounds [1].

RESULTS AND DISCUSSION

It was found that phosphonic monochlorides, prepared according to a literature procedure [2] provided a reliable method for the synthesis of mixed diesters [3]. The nature of the groups R' and Y in these mixed diesters however influenced the course of the reaction with thionyl chloride. The nitrogen atom in the substrate is available to participate in the reaction in the cases where R' = Me. In these cases dealkylation occurs when Y = OMe whereas only the free acid is formed when OR" = OEt or OiPr. Steric factors protect this nitrogen atom when R' = Et and the normal Maier's reaction [2] takes place affording the monochloride.

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SPECTROSCOPIC STUDIES OF MIXED PHOSPHORIC-CARBOXYLIC IMIDES

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Centre for Heteroatom Chemistry, Department of Chemistry, University of Pretoria, 0002 Pretoria, South Africa

Abstract IR spectroscopic studies of hydrogen bonding (intra- *vs* intermolecular) in selected mixed phosphoric-carboxylic imides $(RO)_2P(O)NR'C(O)R''$ **1**, R = Et, R' = H, alkyl, R" = OEt, Ph, are presented.

INTRODUCTION

IR spectroscopy proved ideal to determine the position of the double bonds and possible intramolecular hydrogen bond formation[1] in the title compounds. Compounds **1** and their salts show antiviral activity[2] and also some interesting complexing properties.[3] These systems exhibit ambident properties both in electrophilic and nucleophilic reactions.[4]

RESULTS AND DISCUSSION

While β-dicarbonyl compounds exist as an intramolecularly hydrogen bonded keto-enol system, no intramolecular hydrogen bond formation was observed for β-diphosphonates.[1] For mixed methylene derivatives, the C=O group exists in its enolic form, while the P=O group forms intermolecular hydrogen bonds with external donors. Methanol proved to be a too weak hydrogen donor towards substrates **1**, while phenol caused a strong to modest $\nu_{C=O}$ shift indicating that the C=O group is a better hydrogen bonding acceptor than the P=O group. The large P=O frequency shift difference for the *N*-unsubstituted and *N*-substituted ethoxycarbonyl phosphoramidate substrates in the absence of an external donor, indicates the existence of tautomerism towards the P=O group and not the C=O group.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 150
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FLUORINATED DERIVATIVES OF 4-PHOSPHINO- AND 4-IMINOPHOSPHORANO-2,5-DIMETHYL-2*H*-1,2,3-DIAZAPHOSPHOLES AND THEIR METAL COMPLEXES

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Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

Although there has been considerable interest in the chemistry and metal complexation of low coordinate phosphines, there are very few examples of bisphosphine systems where both phosphorus atoms are trivalent and only one of the centers is two-coordinate[1,2]. An example of such a system is the 4-phosphino-2,5-dimethyl-1,2,3-diazaphosphole obtained from acetone methylhydrazone and phosphorus trichloride[3]. This bisphosphine contains a two-coordinate endocyclic phosphorus and a three-coordinate exo phosphorus center. The exo phosphorus preferentially coordinates to metals but under certain conditions the two-coordinate phosphorus will also coordinate[4].

The reaction of 4-dichlorophosphino-2,5-dimethyl-1,2,3-diazaphosphole in acetonitrile with sodium fluoride in the presence of 15-crown-5 ether gave the 4-difluoro-phosphino derivative. The analogous fluoroalcohol derivatives, dimethyldiazaphosphole-PE_2 (E = OCH_2CF_3, OC_6F_5, and $OCH_2C_6F_5$) were obtained from the reaction of the fluorinated alcohol in diethyl ether in the presence of triethylamine acting as base. The oxidation of the exo phosphorus to iminophosphorano derivatives of these phospholes was achieved with the usual Staudinger azide reaction. These oxidized phosphorus centers showed large upfield ^{31}P NMR shifts with a shift of over 200 ppm in the case of the 4-{difluoro(*p*-cyanotetrafluoro-phenyl)iminophosphorano}diazaphosphole. These iminophosphorano-phospholes may act as bidentate as well as monodentate ligands with metal complexes. The 4-phosphinophospholes however typically act as mono-dentate ligands toward $Mo(CO)_4$, Cp*Rh, $PtCl_2$, and $PdCl_2$with the 4-phosphino group coordinated to the metal.

We thank the Natural Sciences and Engineering Research Council of Canada for support.

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NEUTRAL HEXACOORDINATE PHOSPHORUS(V) COMPOUNDS CONTAINING TRIDENTATE DIANIONIC LIGANDS OBTAINED FROM SALICYLIDENEAMINES, 2,2'-AZODIPHENOL AND A THIO(DIPHENOL).

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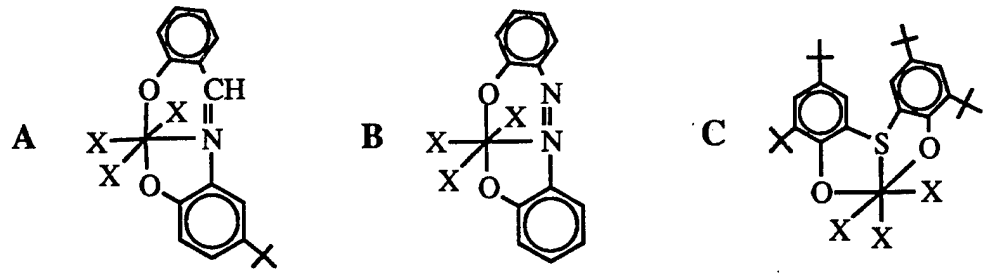
Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

Neutral hexacoordinate phosphorus(V) compounds of a number of univalent bidentate ligands are known.[1,2] The silylated forms of tridentate, dianionic Schiff base ligands: *N*-(2-hydroxyphenyl)salicylideneamine H_2L^I, *N*-(4-*tert*-butyl-2-hydroxyphenyl)-salicylideneamine H_2L^{II}, *N*-(2-hydroxy-4-nitrophenyl)salicylidene-amine H_2L^{III}, and 2,2'-azodiphenol H_2L^{IV} gave, with halogeno- and (trifluoromethyl)halogenophosph-oranes, neutral hexa-coordinate derivatives with bis-chelate structures. The ligands form bicyclic five- and six-membered chelate rings in a meridional conformation, with two P-O bonds and one N→P donor bond. Hexacoordinate structures were evidenced by high-field ^{31}P NMR chemical shifts (-136 to -148 ppm), characteristic J_{PF} coupling patterns and was further substantiated by crystal structures of Cl_3PL^{II} (**A**) and F_3PL^{IV} (**B**).



NMR spectra of $(CF_3)F_2PL^I$ show exclusive *cis* conformation in solution but $(CF_3)F_2PL^{IV}$ formed an approximate 1:1 ratio of *cis*:*trans* isomers. The sulfur ligand, 2,2'-thiobis(4,6-ditertbutylphenol), H_2L^V, formed a *fac* bis-chelate, Cl_3PL^V (structure **C**), with a relatively short P-S bond (2.331(1) Å). A similar structure, reported by Holmes *et al.*[3] for a derivative of the same ligand, has a longer P-S bond.

We thank the Natural Sciences and Engineering Research Council of Canada for support.

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THE FIRST EXAMPLE OF 1,1-σ-COMPLEXES OF PHOSPHORUS NUCLEOPHILES.

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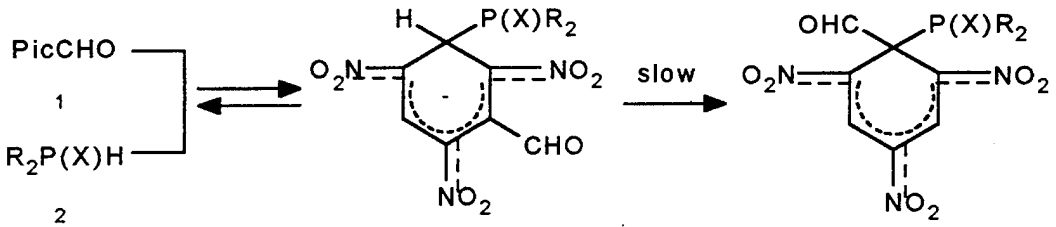
Kiev 252660, 5 Murmanskaya St., Ukraine

We report on the first phosphorus 1,1-σ-complexes, relatively stable in DMSO. Adducts of this type are important as possible intermediates in nucleophilic aromatic substitution reactions but for phosphorus nucleophiles 1,1-σ-complexes were never detected [1]. We have found that interaction of 1 with 2 in DMSO leads initially to 1,3-σ-complexes 3 which slowly rearrange to 1,1-σ-complexes 4.



R = Alk, Ph; X = O, S

The effect of R and X on the σ-complexation and mechanism of 1,3-phosphorotropic rearrangement 3→4 will be discussed. The results obtained show that nucleophilic phosphorylation of electron-deficient aromatics can, in principle, proceed by addition-elimination S_NAr mechanism. The capability of phosphorus atom to change its coordination number provides new pathways (in particular, those involving five-coordinated intermediates) of aromatic substitution for phosphorus nucleophiles.

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ISOTHIOCYANATOCHLOROMETHYLPHOSPHONATES AND PHOSPHINATES - VERSATILE SYNTHONES FOR OBTAINING OF S (Se), N, P-CONTAINING HETEROCYCLES

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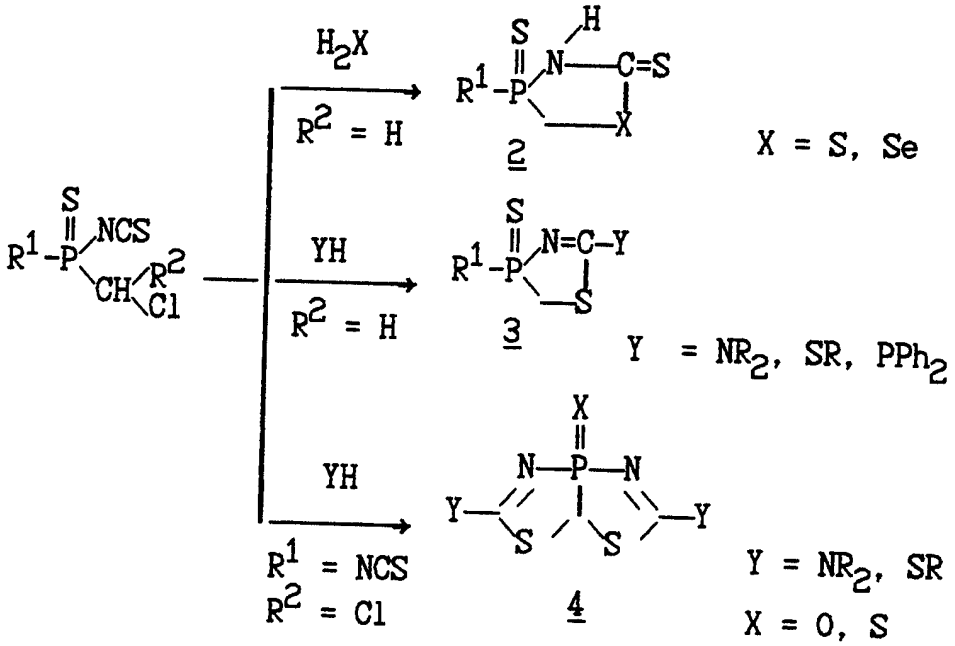
Isothiocyanatochloromethyl(thio)phosphonates and (thio)-phosphinates 1 (X=O, S; R^1 = OPh, CH_2Cl, NCS; R^2 = H, Cl) have been found to be convenient starting material for synthesis of a variety of S (Se), N, P-containing cyclic compounds. They react with different proton containing nucleophiles in the presence of a base with formation of saturated 2 and unsaturated 3 five membered phosphacyclanes. Diisothiocyanatodichloromethylphospho-nates 1 (R^1 = NCS, R^2 = Cl) produce with amines and thiols appropriate bicyclic compounds 4.



Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 154
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REACTION OF HALIDEMETHYLDITHIO- AND SELENO-THIOPHOSPHONIC ACIDS WITH ALKYLTHIOCYANATES - A NOVEL METHOD OF SYNTHESIZING P, N, S (Se)-CONTAINING HETEROCYCLES

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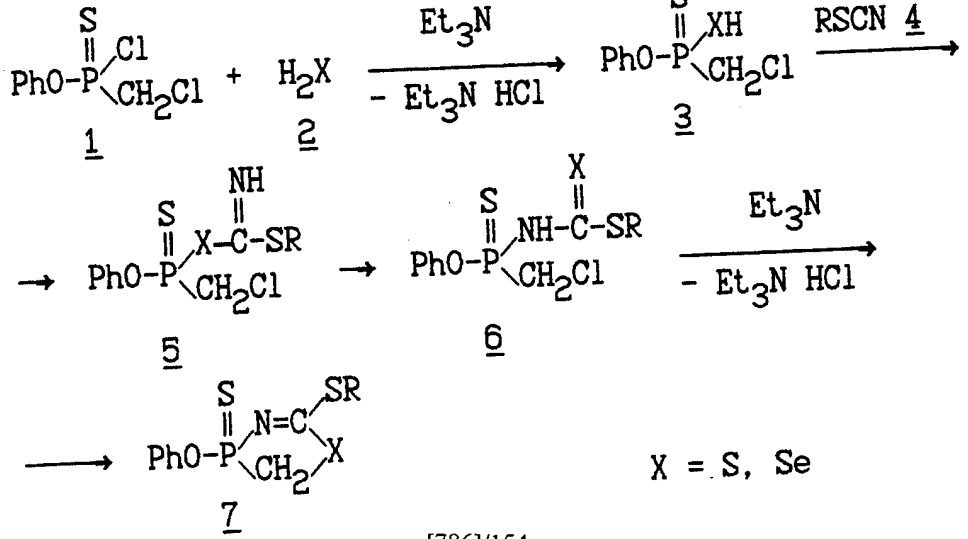
Novel heterocyclic derivatives - 1,3,4-thiazaphospholines and 1,3,4-selenoazaphospolines 7 were obtained passing hydrogen sulfide or hydrogen selenide 2 through the solution of O-phenylchloromethyl (chloro)thiophosphonate 1 and alkylthiocyanate followed by addition of triethyl-amine. It is assumed that O-phenylchloromethylthio-phosphonic and -selenophosphonic acids 3 are formed at the first stage, which further add to CN triple bond of alkylthiocyanates 4 to produce S- or Se-thiophosphonyl-dithio- or selenothioiminocarbonates 5. The latter undergo phosphorotropic rearrangement into appropriate S-thiophosphonyl dithio- or selenothiocarbamates 6.



1 2 3 5 6 7

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 155
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PHOSHA-MEERWEIN REACTION OF DIAZO ESTERS

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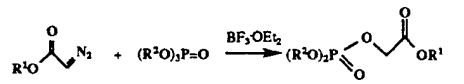
Abstract.

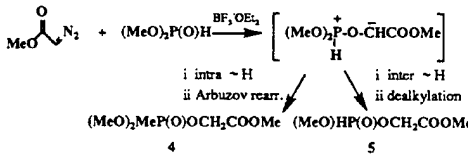
Diazo esters (**1a,b**) react with trialkyl phosphates (**2a-c**) in the presence of $BF_3{\cdot}OEt_2$ to give the corresponding phosphates (**3a-c**) in 42-58 % yields. The competed intra/intermolecular protonation in the reaction of **1a** with dimethyl hydrogen phosphite leads to phosphonate **4** and phosphite **5**.

Key Words: Diazo ester; dimethyl hydrogen phosphite; Lewis acid catalysis; phoshate; zwitterionic phosphonium intermediate.

We have found that diazo esters (**1a,b**) react with trialkyl phosphates (**2a-c**)) in the presence of $BF_3{\cdot}OEt_2$ (10 Mol %) to give the corresponding phosphates (**3a-c**) in 42-58 % yields.



The catalytic capability of a set of catalysts indicates a Lewis acid promoted process: $BF_3{\cdot}OEt_2$ (52 %) > (p-Br-$C_6H_4)_3N^{+}{\cdot}SbCl_6^{-}$ (35 %) > $SnCl_2$ (17 %) > $Rh_2(OAc)_4$ (14 %) > $Cu(OTf)_2$ (5 %) (**3a**). Using CD_2Cl_2, D_2O, $(CD_3O)_3PO$ and $N_2CDCOOCH_3$, the reaction is explained by a step mechanism *via* zwitterionic phosphonium intermediate, followed by protonation at C atom by H_2O impurities and dealkylation at P atoms.



The competed intra/intermolecular protonation in the reaction of **1a** with dimethyl hydrogen phosphite leads to mixtute of phosphonate **4** and phosphite **5**, whereas in the presence of large excess of **1a** a product of complete replacement, $(MeOOCH_2O)_2P(O)Me$ has been isolated, arose from both **4** and **5**.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 156
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C-SPIROOXYPHOSPHORANYL (P^V) α-ANIONS. ALKYLATION AND OLEFINATION CHEMISTRY

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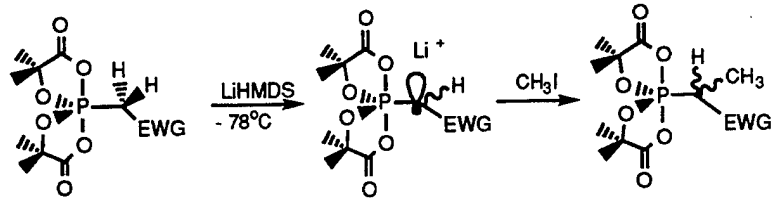
Abstract The chemical features of C-spirooxyphosphoranyl α-anions are investigated toward alkylation and olefination reactions. Proposed mechanistic pathways are based on low temperature ^{31}P-NMR data.

Key Words : spirooxyphosphorane, α-phosphoranyl carbanion, alkylation, olefination.

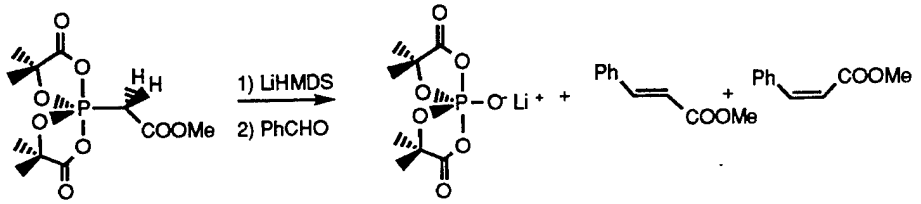
The C-spirooxyphosphorane **1** is selectively deprotonated by LiHMDS at -78°C to obtain one diastereomeric lithiated α-anion **2**.



1 **2** **3**

To examine the reactivity of **2**, the alkylation of these species (EWG = phenyl, α-naphthyl) was performed by addition of CH_3I at -78°C. A diastereomeric alkylated product (**3**) was obtained with low selectivity (9% d.e.). NMR studies suggest that this low selectivity is the result of the epimerization of anion **2** *via* an "ylide-like" form.

Alternatively, the deprotonation of methylester phosphorane **4** (EWG = COOMe) followed by the addition of benzaldehyde showed that the titled species could undergo olefination reaction. In fact, besides phosphorane **5**, a mixture of *E*-**6** and *Z*-**6** is observed with a ratio *E*/*Z* =60/40 (GC-MS). A mechanistic rationale is proposed based on an evaluation of the ^{31}P-NMR data which indicate the presence of a diastereomeric mixture of hexacoordinated organophosporus intermediates. These intermediates equilibrate to a mixture of pentacoordinated organophosphorus species, and they subsequently decompose to the *E*, *Z*-alkenes.



4 **5** ***E*-6** ***Z*-6**

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ASYMMETRIC SYNTHESIS OF α-AMINO PHOSPHONIC ACIDS EMPLOYING THE CONDENSATION OF NITRONES WITH PHOSPHITE DERIVATIVES

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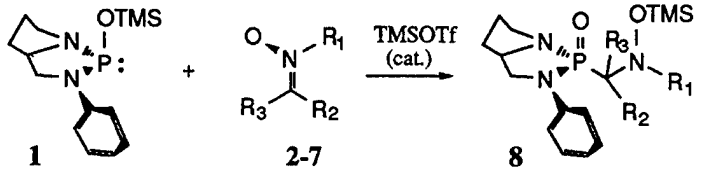
Abstract Chiral α-amino phosphonic acid derivatives were synthesized by condensing an enantiomerically homogeneous diazasilyl phosphite with a series of prochiral nitrones. The reactions proceed under mild conditions with moderate to high enantioselectivities and good yields.

Key Words : α-amino phosphonic acid, asymmetric synthesis, silyl phosphite, nitrone.

Increased interest in the synthesis of α-amino phosphonic acids as synthetic and structural analogs of α-amino carboxylic acids [1] have promoted considerable research activity in developing novel chirality transfer methods. In this light, we have examined the reactions of an enantiomerically-homogeneous silyl phosphite **1**, derived from L-glutamic acid [2], with nitrones as a synthetic approach to α-amino phosphonic acids. Our preliminary results show that the reactions between phosphite **1** and imines are slow even in the presence of trimethylsilyltriflate (TMSOTf) and the selectivities are poor. By contrast, nitrones (*e.g.* **2-7**) were more reactive and afforded higher selectivities.



1 **2-7** **8**

Nitrone	R_1	R_2	R_3	de% [a]	**8** (^{31}P-NMR δ, ppm) major	minor
2	Me	H	Ph	>98	17.16	-
3	t-Bu	H	Ph	>98	14.13	-
4	CH_2Ph	H	Ph	47	19.34	18.87
5	Me	H	iPr	43.6	22.55	24.05
6	$-CH_2-CH_2-CH_2-$		H	71.9	22.25	21.36
7	$-C(CH_3)_2-CH_2-CH_2-$		H	37.9	25.66	22.36

[a]- Determined from ^{31}P-NMR data.

Based on our mechanistic investigations and the resulting diastereoselectivities, we propose a stepwise mechanism where the active C=N moiety-containing species is the silylated nitrone (oxoiminium salt).

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 158
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(HYDROXYIMINO)PHOSPHONOACETIC ACIDS: SYNTHESIS, STEREOCHEMISTRY AND REACTIVITY

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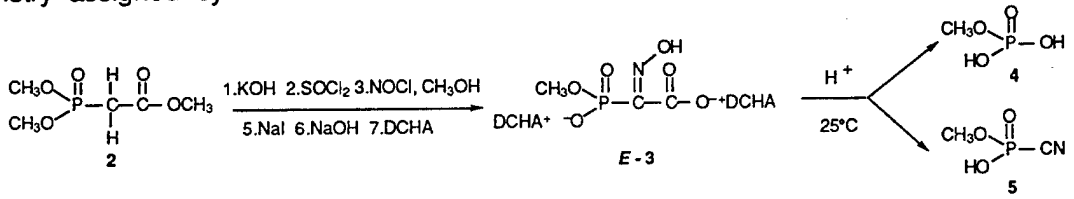
Individual *E*/*Z* isomers of the C-methyl ester **1** of α-(hydroxyimino)phosphonoacetic acid ("troika acid") were recently prepared as dicyclohexylammonium salts and found to be stable at neutral pH.[1] On alkaline demethylation followed by pH adjustment to 6–7, *E*-**1** and *Z*-**1** stereospecifically undergo P-C_α and C_α-C_β cleavage, respectively.[1] Herein we report synthesis of the corresponding P-methyl ester from trimethyl phosphonoacetate **2**. The product was isolated as its bis-DCHA$^+$ salt *E*-**3**, with stereochemistry assigned by NMR.[2]



Like **1**, *E*-**3** was stable at pH 7 for 24 h (25°C). However, in contrast to **1**, which is also stable at low pH, *E*-**3** decomposed over 2.5 h at pH 1.5 to a mixture of methyl phosphate **4** (15%; ^{31}P NMR δ 2.1 ppm) and methyl phosphorocyanidate **5** (85 %; ^{31}P NMR δ –17.4 ppm). Formation of these products suggests that two fragmentation pathways are available to *E*-**3**: 1) P-C_α cleavage to **4**; 2) *E* ➡ *Z* isomerization followed by C_α-C_β cleavage to **5**. Process (2) overall is more rapid than process (1). Further evidence of dual fragmentation pathways was observed (^{31}P NMR) when *E*-**3** was heated in ethanol or acetonitrile: **5** (81-84%) was obtained in both solvents in addition to the expected phosphorylation products ethyl methyl phosphate (ethanol; 19%) and P,P'-dimethyl pyrophosphate (acetonitrile; 16%).

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FLUORINATED N-ARYLAMINOARYLMETHANEPHOSPHONIC ACIDS AND BISFUNCTIONAL DERIVATIVES

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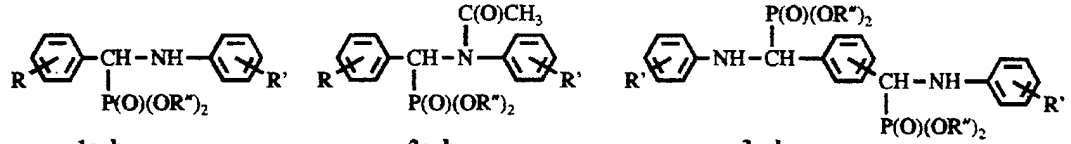
INTRODUCTION

Aminophosphonic acids and corresponding derivatives are of widespread biological and biochemical interest. Especially fluorinated and aromatically substituted compounds acting as antibacterial agents and showing fungicidal activities are important for medicine and agriculture.

RESULTS AND DISCUSSION

Specific properties are expected from fluorinated N-arylaminoarylmethanephosphonic acid dialkylesters **1a** (R" = Me) and **1b** (R" = Et) which are accessible in high yields by a two-step-procedure: Primarily imines are obtained by condensation of benzaldehydes with anilines, which, after isolation, add stoichiometric amounts of dialkyl phosphites at 100°C. N-atoms are acylated by acetyl chloride in the presence of a tert. amine in chloroform leading to **2**. The phosphonate ester groups are cleaved by silylation with an excess of $BrSiMe_3$ in chloroform at 20°C, followed by hydrolysis with water yielding **1c** (R" = H). Bisfunctional aminophosphonates **3** are available by the reaction of bisimines (derived from 1,4- or 1,3-phthaldialdehydes and anilines) with an excess of dialkyl phosphites in THF solution and basic catalysts. Due to the chiral α-C atoms two diastereomeric products are formed. The nature of the catalytic system (NaH or $NaOP(OEt)_2$/THF solution), the reaction temperature and time govern the ratio of those diastereomers. Under simiar conditions the addition of dialkyl phosphites to bisimines (derived from 1,4-phenylenediamine and benzaldehydes) leads specifically to one diastereomeric form only.
The aminophosphonates give rise to interesting $^{31}P\{^1H\}$, ^1H, ^{19}F and $^{13}C\{^1H\}$ NMR studies with respect to chirality and the complex spin systems. Biological investigations show insecticidal properties of some aminophosphonates towards harmful and parasitic insects, they exert slight inhibitoral activity on NADH-ubiquinone reductase (complex I) in the mitochondrial respiratory chain and behaves like an uncoupler there.



1a, b, c **2a, b** **3a, b**

R, R' = H; 4-, 3-, 2-F; 4-, 3-, 2-CF_3; 4-, 2-CF_3O; 2,4-F_2; 3,4-F_2; 2,3,4-F_3

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 160
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SYNTHESIS AND NMR-SPECTROSCOPICAL STUDIES OF FLUORINATED ARYLMETHYL-PHOSPHINIC ACID DERIVATIVES

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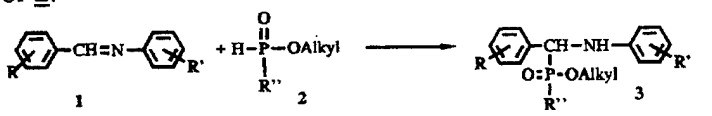
INTRODUCTION

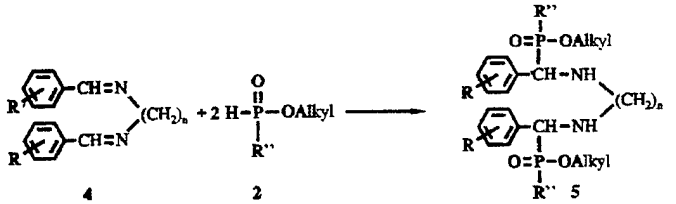
Since Horiguchi in 1959 isolated CILIATIN from rumen protozoa the class of amino phosphonic and phosphinic acids has generated widespread interests directed towards synthetical problems and biological applications such as insecticides, fungicides, virostatica and enzyme inhibitors. Recent efforts have been devoted to more convenient preparations and stereospecific aspects. Here we wish to report on a facile method for the synthesis of C-fluorinated aminoalkane-mono- and bis-phosphinic acids and corresponding derivatives.

RESULTS AND DISCUSSIONS:

C-fluorinated imines react readily with aryl- or alkyl phosphonous acid esters without any catalyst at temperatures between 90 and 110°C to yield phosphinic acid esters of type 1 or 2.



3: R = H, 3,4-F_2, 2-F, 3-F, 4- F, 4-CF_3; R' =H, 2-F, 3-F, 4-F, 4-CF_3; R" = CH_3, C_2H_5, C_5H_6; Alkyl = CH_3, C_2H_5, n-C_4H_9;



5: R = 3,4-F_2, 2-F, 3-F, 4-F; n = 2, 3; R" = CH_3, C_2H_5; Alkyl = C_2H_5, n-C_4H_9

Ortho substituents on the aromatic residues give rise to extended reaction times and a decrease of the yields. The crude products are crystallised from unpolar solvents. Compounds **3** exist as pairs of diastereomers, which in fortunate cases are separated by crystallisation. Cleavage of 1 by the Bromosilane method lead to the free acids. NMR deduced the existence of 2-4 stereoisomers of esters **5**. Extensive ^{1}H-, ^{13}C-, ^{19}F- and ^{31}P-NMR in 1D- and 2D-techniques deduced purity and structures of **3** and **5**.

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SYNTHESIS OF (2-FURYL)AMINOMETHANEPHOSPHONIC ACIDS DERIVATIVES

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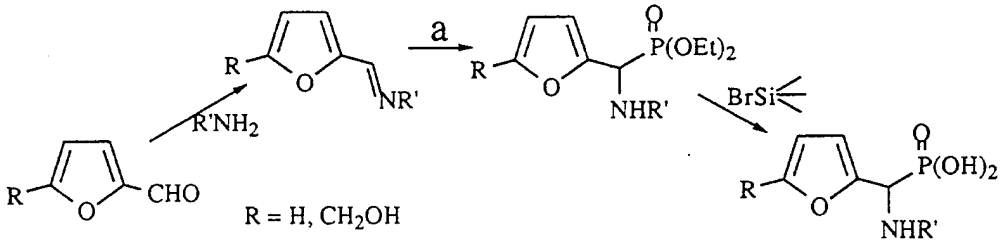
Abstract: Synthetical aspects of furylaminophosphonic acids are discussed here.

Studies on aminophosphonic acids started in late 40's[1], since then various derivatives containing alkyl, aryl or heterocyclic groups[2,3] were synthesized.

To our knowledge, furylaminophosphonic acids derivatives were scarcely studied.Here we want to report some preliminary results of their synthesis. The reaction sequence, when based on a published procedures[3], gave poor results (conv. rate = 75% after 72 hrs). But operating on such factors as temperature, a catalyst and an amount of a reagent, we improved conversion rates and consequently yields.



R' = $C(CH_3)_3$; CH_2Ph; CH_2Fur; (+) and (-) $CH(CH_3)Ph$

a: 80°, MeCN, $HP(O)(OEt)_{2(xs)}$,CF_3COOH, 6 hrs, conv. rate - 98%, Y ≈ 65 - 90%

We also performed stereochemical studies. Chiral (+) and (-) -α-methylbenzylimines when applied, yielded two diastereoisomers in 1 : 4 ratio.These results show a certain stereoselectivity of the addition of a phosphonate.But this topic is still under study.

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ISOSTERES OF NATURAL PHOSPHATES. METHYLENE AND HYDROXYMETHYLENE ANALOGUES OF TYROSINE *O*-PHOSPHATE

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The ability of phosphonic acid analogues isosteric with natural phosphate esters to serve as inhibitors of enzymatic phosphate hydrolysis has been documented in a wide variety of systems.[1] The use of such an analogue in place of the natural phosphate ester provides a functionality which the enzyme may not be able to distinguish from the natural ester, but which is incapable of being hydrolyzed. In some instances the use of hydroxymethylene analogues has resulted in a greater degree of recognition, and resultant inhibition of hydrolytic activity, than the simple methylene analogues.[2] On this basis, the methylene and hydroxymethylene analogues of tyrosine *O*-phosphate appear to be reasonable candidates to serve as inhibitors for phosphoprotein phosphatases and alkaline phosphatase, and as probes for biological mechanisms.

The isosteric methylene analogue of tyrosine *O*-phosphate has been synthesized beginning with an Arbuzov reaction performed on *p*-bis(bromomethyl)benzene using triethyl phosphite. The isolated yield of the desired monosubstitution product was optimized at 48.5% by the use of a two-fold amount of the dibromide and controlling the heating at 120 for 3 hours. (Under these conditions the yield of the disubstitution diphosphonate by-product was limited to 11.8%.) The remaining bromide was then displaced using diethyl acetamidomalonate anion by a standard procedure,[3] and the target isosteric analogue of tyrosine *O*-phosphate was isolated by acidic hydrolysis and the accompanying decarboxylation.

Initial attempts to generate the hydroxymethylene analogue *via* a standard Abramov reaction of diethyl phosphite with *p*-(bromomethyl)benzaldehyde failed under all conditions attempted.[4] An alternative approach involved the direct introduction of a hydroxyl group at the site adjacent to the phosphonic ester function of the material previously described, the phosphonic ester upon which displacement of the remaining bromide using diethyl acetamidomalonate anion had been performed. This was accomplished using a modification of a procedure commonly used for allylic oxidation,[5] the benzylic site adjacent to the phosphonic ester functionality exhibiting behavior analogous to that of an allylic site. Treatment of this phosphonic ester with a catalytic portion of selenium dioxide and an excess of the regenerating agent, *t*-butylhydroperoxide, standard conditions for allylic oxidation, introduced with reasonable efficiency the hydroxyl group on carbon adjacent to phosphorus. Unmasking and subsequent decarboxylation of this material to generate the desired hydroxymethylenephosphonate analogue of tyrosine *O*-phosphate was again accomplished under acidic conditions.

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THE REACTION OF PHOSPHORYL CHLORIDES WITH ENAMINES - A NEW APPROACH TO ß-KETOPHOSPHONATES

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Several approaches are available for the preparation of ß-ketophosphonate esters. A Michaelis-Arbuzov approach using the reaction of an α-halo ketone with a trialkyl phosphite may in certain instances be controlled to favor the preparation of the target materials. However, an alternative pathway leading to the formation of vinyl phosphate esters often predominates. (This reaction system has recently been reviewed by Borowitz and Borowitz.[1]) An alternative approach is that developed in recent years by Wiemer, *et al.*[2] involving the rearrangement of vinyl phosphate esters to the ß-ketophosphonates.

Our laboratory has been interested in exploring additional approaches to this interesting class of compounds. Of particular interest is the reaction involving phosphonylation of enamines, an approach completely analogous to the acylation of enamines for the preparation of ß-diketones[3] and one which does not involve as a reactant the α-haloketone. The current report is an initial presentation of our efforts in the application of this general approach toward the preparation of ß-ketophosphonates.

Enamines derived from the condensation reaction of piperidine with the corresponding ketones were taken in reaction with diethyl phosphorochloridate or diphenyl phosphorochloridate. A three-fold excess of enamine was used in each instance for the formation of the corresponding ß-ketophosphonates.

Reactions were performed using the piperidine enamine derived from four symmetrical ketones: (a) 3-pentanone; (b) cyclopentanone; (c) cyclohexanone; and (d) cycloheptanone. Yields of ß-ketophosphonate products after work-up with aqueous acid were in the range 50-70%. All ß-ketophosphonate products exhibited spectra in accord with their proposed structrues, and single spots on TLC visualized using phosphomolybdate spray reagent. Of particular interest are the IR spectra of these materials which indicate the presence of significant enol content in solution, the amount varying with the structure.

The IR spectra of all products exhibit, in addition to the broadened hydroxyl stretch indicative of hydrogen bonding, a pair of phosphoryl bands resulting from "keto" and "enol" forms of the compounds. The IR bands for the "keto" forms occur at frequencies in accord with that predicted using the correlations of Thomas and Chittenden.[4] At higher frequencies, albeit lower than those predicted[4] for vinylicphosphonate esters, are found the phosphoryl stretching bands corresponding to the intramolecularly hydrogen bonded "enol" forms. Based on intensities of these IR bands, the "enol" forms are more important for the cyclic systems than the open-chain systems, and for the phenyl esters as compared to the ethyl esters.

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ALDOL-TYPE CYCLIZATION OF BISACYLPHOSPHONATES. A UNIQUE CONCERTED CATALYTIC EFFECT OF DIAMINES

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Some bisacylphosphonates are biologically active in calcium related disorders, such as bone resorption and ectopic calcification.[1] In the course of our studies directed towards the preparation of stable, pharmaceutically acceptable salts of bisacylphosphonates, we found that in the presence of N,N'-dibenzylethylenediamine (benzathine), adipoylbisphosphonate (AdBP) underwent cyclization to 2-hydroxy-2-phosphonocyclopentanecarbonylphosphonic acid. Similarly, pimeloylbisphosphonate (PiBP) cyclized to 2-hydroxy-2-phosphonocyclohexanecarbonylphosphonic acid, although at a rate about 30 times slower than AdBP. Study of the catalytic effect of amines on the cyclization of PiBP revealed a striking dependence on the pH, the chain length of the diamine, and the amine used. Thus the following relative efficacy was observed for the different amines at pH 5: $Me_2N(CH_2)_2NH_2$ (120), $H_2N(CH_2)_2NH_2$ (100), $H_2N(CH_2)_3NH_2$ (4), $H_2N(CH_2)_4NH_2$ (1), $PhCH_2NHCH_2CH_2NHCH_2Ph$ (0.1), $Me_2NCH_2CH_2NMe_2$ (0.02), $MeNH_2$ (0.02). These data show that depending on the chain length, 1,2-diamines are far more efficient catalysts than longer chain diamines and monoamines in these cyclizations. The mechanism which accommodates these results involves attack of a primary amine group on one of the keto groups, followed be removal of an alpha proton by the second amine group and the formation of an enamine. The latter then cyclizes by attacking the second keto group.

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Acknowledgement This research was supported by a grant from the G.I.F., The German Israeli Foundation for Scientific Research and Development.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 165
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INTRAMOLECULAR INTERACTIONS IN PHOSPHONOHYDROXAMIC ACIDS.

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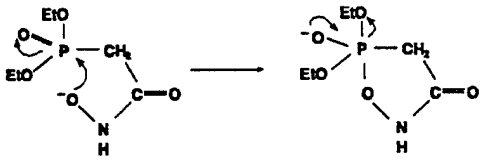
In recent years the hydroxamic function appears with increasing frequency in biologically active compounds (such as antimalarials, inhibitors of various enzymes, and anticancer agents). However, only few cases are reported in which the hydroxamic and the phosphonic functions are combined in one molecule.

In a program directed towards the synthesis and the study of new types of multifunctional phosphonates, one of our target compounds to synthesize was $(EtO)_2P(O)CH_2CONHOH$. In an attempted synthesis of this compound, using the standard approach to hydroxamic acids based on esters, we found that the reaction of $(EtO)_2P(O)CH_2COOMe$ with NH_2OH involved dealkylation, and gave $(EtO)(O^-)P(O)CH_2CONHOH$ and $(EtO)_2P(O)CH_2COO^-$ as byproduct. Monitoring the reaction of $(EtO)_2P(O)CH_2COOMe$ (δ_P= 23.1 ppm) with NH_2OH by ^{31}P nmr spectroscopy we found that it led first to the transient formation of $(EtO)_2P(O)CH_2CONHOH$ (δ_P= 26.2 ppm), which was subsequently transformed to $(EtO)(O^-)P(O)CH_2CONHOH$ (δ_P= 17.1 ppm). In contrast, reaction of $(EtO)_2P(O)CH_2COOMe$ with NH_2OMe gave $(EtO)_2P(O)CH_2CONHOMe$ (δ_P= 25.7 ppm) and $(EtO)_2P(O)CH_2COO^-$ (δ_P= 27.3 ppm) as byproduct. Upon extended standing in $NaHCO_3$ solution, the methyl hydroxamate hydrolyzed to $(EtO)_2P(O)CH_2COO^-$. No P-monoethyl ester was observed at all in the latter reaction. In control experiments we found that neither $(EtO)_2P(O)CH_2COOMe$ nor $(EtO)_2P(O)CH_2COO^-$ underwent deethylation under the reaction conditions. These results indicate that the OH group of the hydroxamic function has a role in the deethylation during the attempted synthesis of diethylphosphinylacethydroxamic acid. The mechanism suggested (see scheme) involves intramolecular attack of the hydroxamate anion on the phosphorus, leading to a pentacoordinated intermediate which loses an ethoxy group and then opens to the final product. (Only the first step of the mechanism is shown.)



Acknowledgement This research was supported by a grant from the G.I.F., The German Israeli Foundation for Scientific Research and Development.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 166
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STUDIES ON THE CONDENSATION OF HIGHLY HINDERED α-AMINO METHYLPHOSPHONATES WITH β-TRIPHENYLGERMANYL PROPIONIC ACID

LI-JUAN MAO* AND RU-YU CHEN
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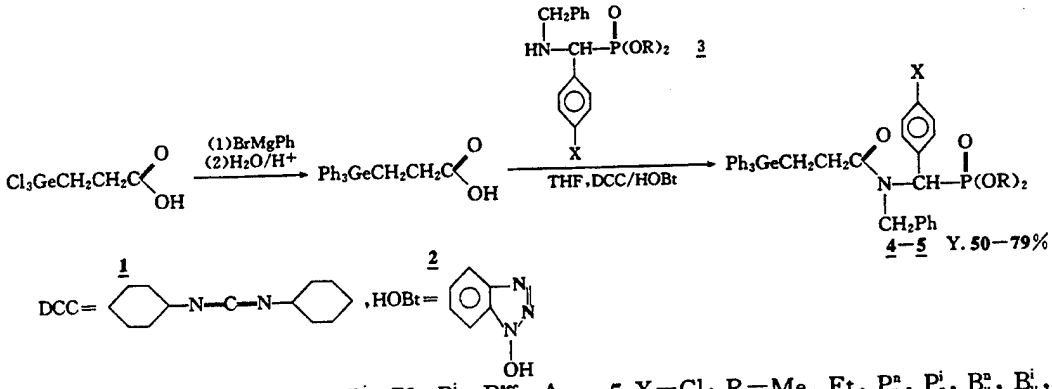
Abstract The condensation reaction of highly hindered α-amino methylphosphonates with β-triphenylgermanyl propionic acid was studied. The two novel series 4—5 were designed and synthesized in good yields. Preliminary bioassays showed that the compounds 4—5 exhibited significant antitumor activities both in vivo and in vitro.

Key Words Condensation reaction, α-Amino methylphosphonate, β-Triphenylgermanyl propionic acid, Antitumor activity

It has been previously reported that α-Amino phosphonic acids and their derivatives show anticancer properties[1]. In order to look for novel antitumor drugs with high activities and low toxicities, two novel series 4 and 5 were designed and synthesized by the direct condensation of highly sterically hindered α-aminophosphonates 3 with triphenylgermanyl propionic acid 2 in good yields (see scheme I).



4: X=OMe; R=Me, Et, P^n_r, P^i_r, B^n_u, B^i_u, B^{sec}_u, Am 5: X=Cl; R=Me, Et, P^n_r, P^i_r, B^n_u, B^i_u,

Scheme I

For synthesizing the compounds 4 and 5, different routes were attempted. Firstly, the conventional ways were tried, but they all failed. Only did the way shown in scheme I be quite successful for the hindered condensation due to both the effective catalysis of HOBt and the irreversible dehydration of DCC. The reaction rate of the condensation has much to do with R groups. The bulkier the R group, the slower the reaction rate was. When R group varied from Me to Am, the condensation would last from 6 to 15 days at room temperature. The preliminary bioassays indicated that most of 4 and 5 exhibited significant antitumor activities both in vivo and in vitro. One of them was indeed effective against sarcoma—180 in rats even compared to 5—fluorouracil (5—FU). It has been also found that the series 4 and 5 showed much higher antitumor activities than the corresponding aminophosphonates 3.

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HIGHLY SELECTIVE ARBUZOV REACTION OF α-CHLOROCARBONYL COMPOUNDS WITH $P(OEt)_3$ AND SUBSTITUTED AMINO UREA

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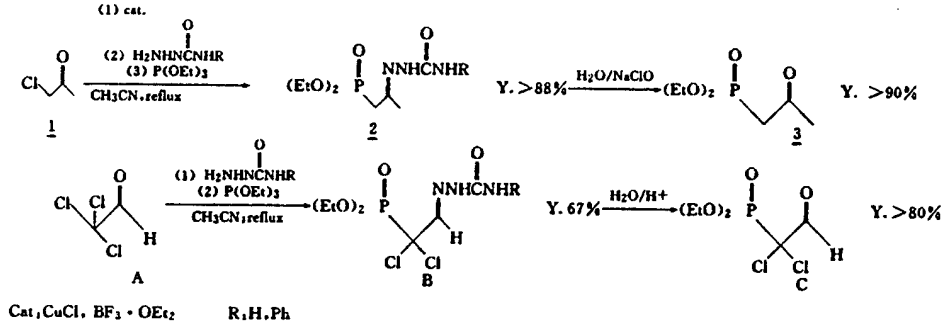
Institute of Elemento—Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

Abstract A facile one—pot Arbuzov reaction of α-chlorocarbonyl compounds with $P(OEt)_3$ and substituted amino urea is described. The highly selective Arbuzov reaction of α-chlorocarbonyl compounds could take place under relatively mild conditions, giving products in high yields.

Key Words Arbuzov reaction, α-Chlorocarbonyl compound, $P(OEt)_3$, Selective reaction

As it has been known, Arbuzov reaction of RX can be easily carried out. Whereas the reaction of α-chlorocarbonyl compounds with $P(OR)_3$ usually takes an alternative course of Perkow reaction[1]. Herein, we report a facile one—pot method in which the Arbuzov reaction of α-chloroacetone and trichloroacetaldehyde could selectively be carried out and provide products in relatively high yields(see scheme I).



Scheme I

Both the compounds 2 and B, and products 3 and C are important blocks for building complex molecules. The compounds 2 and B are all new compounds, and confirmed by ^1H NMR, IR, and Elemental Analysis.

The ^{31}P NMR data of 2 and B showed that there were two isomers ($\delta = 23.42$ and 24.90ppm, when R=H in the compound 2), which probably resulted from cis and trans isomers of the imine double bonds.

By the determination of ^{31}P NMR, it has been found that the rate of above Arbuzov reaction is directly proportional to both reaction temperatwre and solvent polarity. An acidic catalyst is also necessary to accelerate the above reaction.

In addition, the order adding the starting materials into reaction system is another key factor for raising reaction selectivity. Only after α-chlorocarbonyl compound reacted with substituted amino urea for 1—2hr, could $P(OEt)_3$ be added dropwise, especially when the α-chlorocarbonyl compound is trichloroacetaldehyde.

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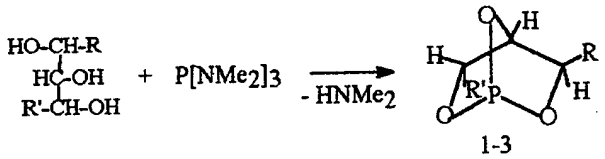
BICYCLOPHOSPHITES OF TERMINAL-SUBSTITUTED GLYCEROLS

ALEKSANDR M. KOROTEEV, MIKHAIL P. KOROTEEV, ANNA R.BEKKER, VITALII K. BELSKII, and EDUARD E. NIFANTYEV

Moscow Pedagogical State University, 1 M.Pirogovskaya, Moscow 119882, Russia

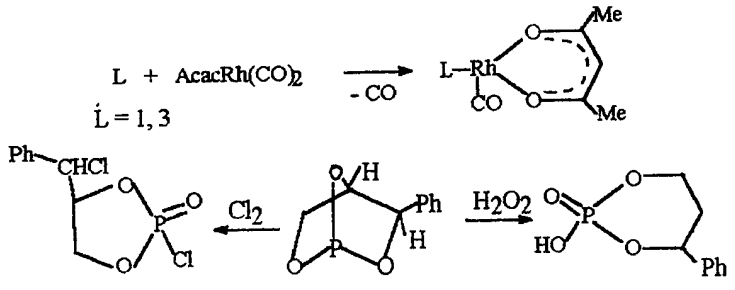
For the first time a systematic study was performed for the phosphorylation of 1,2,3-triols with total amides of phosphorous acid. The initial-matrix-structure dependence of phospholane-phospholane bicyclophosphites was found and investigated. The introducing of terminal substituents into a triol molecule was shown to essentially increase their stability.



1-3

1 R = R' = CH_2OCPh_3; 2 R = Ph, R' = H; 3 R = Et, R' = H

The reactions of the obtained phosphites were studied that operated with retention of phosphobicyclic moiety or disruption of a ring. Rhodium(I) bicyclic complexes were synthesized. It was shown that the bicyclic esters reacted vigorously and regioselectively with chlorine and hydrogen peroxide to form monocyclophosphates of various cyclicity.



A correlation was made between structural parameters and chemical features of obtained phospholane-phospholane systems and previously known analogues. The structure of the compounds was proved by means of H, C, and P NMR spectroscopy, for isolated derivatives by means of X-ray analysis.

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CATALYTIC ACTIVITY OF AMINES HYDROCHLORIDES, INTRAMOLECULAR CATALYSIS AND STEREOSELECTIVITY OF PHOSPHORYLATION OF HYDROXYLCONTAINING NUCLEOPHILES WITH P(III)-N-ETHYLANILINES

SERGEI YU.BURMISTROV, MIKHAIL K.GRATCHEV, GALINA I. KUROCHKINA, LARISA K. VASYANINA AND EDWARD E. NIFANTYEV

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Key words: Phosphorylation; aminophosphines; alcoholysis; acid catalysis.

The effect of acid-base properties of amines hydrochlorides (AH) on their catalytic activity in methanolysis of P(III)-N-ethylaniline has been studied. The analysis of Brönsted correlation equation was indicative of *general acid catalysis* and it was thus confirmed, that general regularities had place during alcoholysis of P(III)-amines under catalysis with AH. In addition, the increasing of alcohol polarity leads to the increasing of proton transfer degree (α) from acid catalysts to phospho(III)amine substrate and to the increasing of the positive charge at the phosphorus in the transition state.Besides, the comparison of α values indicates that in more polar methanol (in comparison with t-butanol) the catalysis is more sensitive to the acidity change of used catalysts.

$$>P\text{-}NEtPh + ROH \xrightarrow{HN^{+}<} >P\text{-}OR + HNEtPh$$

As it was shown earlier[1] the application of optically active catalysts may lead to the stereoselectivity during phosphorylation with P(III)-amines. At present this fact was used to attain a more effective "contact" between P(III)-amine and AH forming part of this molecule, which ensured effective *intramolecular catalysis* resulting in a sharp increase in rates of phosphorylation (in 150-300 times) and in a significant stereoselectivity of the process following the inclusion of a chiral fragment in the molecule of the "catalytic" part of P(III)-amine. The stereoselectivity thus revealed was used for the enrichment of racemic mixtures of protonodonor nucleophiles.

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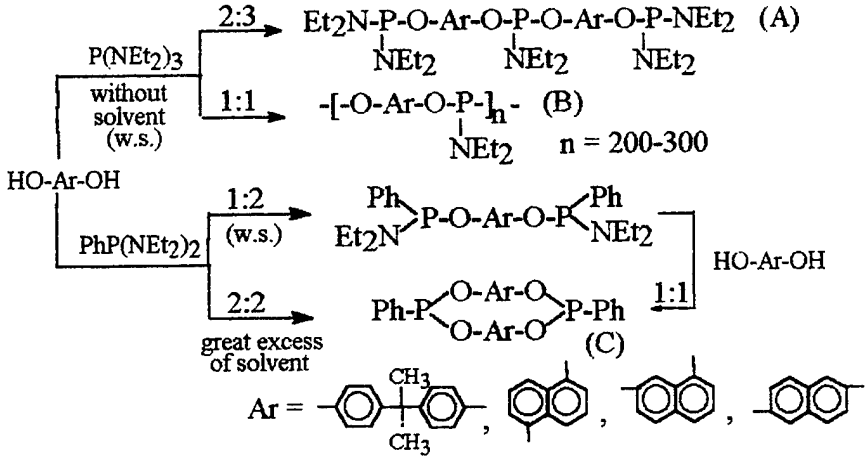
ON PHOSPHORYLATION OF DIHYDRIC PHENOLS WITH AMINES OF PHOSPHORIC AND PHENYLPHOSPHONIC ACIDS

YURII I. BLOKHIN, FLISA M.GALIASKAROVA, DMITRII V.GUSEV, MANSUR YA. ERGASHOV, VITALY K. BELSKY AND EDVARD E. NIFANTYEV
Moscow Pedagogical State University, 1 M.Pirogovskaya, Moscow119882 Russia

With the aim to create macrocyclic phosphorus-containing heterocycles (new phosphorus crown-ethers) and corresponding polyesters the interaction between dihydric phenols and complete anides of phosphoric and phenylphosphonic acids was studied. It was shown that, according to reaction conditions and reagents ratio, the resulting products can have a linear structure, with oligo- (A) or polymeric (B) molecules, and a macrocyclic structure (C) alike : phospho(III)arylene crown-ethers obtained for example by the consecutive assembling of planned macrocyclic systems or by the direct interaction.



The individuality and structure of the products obtained were proved by means of ^{1}H and ^{31}P NMR spectroscopy, mass spectrometry and X-ray analysis. Some peculiarities of phosphorylation of dihydric phenols were revealed when obtaining the polymeric compounds.The first syntheses are performed to create inclusion compounds of the "host-guest" type based on macrocyclic arylenephosphonites with transition metals salts (CuBr, $HgCl_2$). Argumentation in favor of the latter is evidenced by NMR and mass-spectroscopy data.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 171
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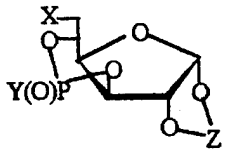
SYNTHESIS AND STRUCTURAL STUDY OF 3,5-CYCLOPHOSPHORUS DERIVATIVES OF 1,2-O-ALKYLIDENE-6-DESOXY-6-HALOGENO-α-D-GLUCOFURANOSES

SVETLANA B. KHREBTOVA, ANNA R. BEKKER, VITALII K. BELSKII, MIKHAIL P. KOROTEEV, and EDUARD E. NIFANTYEV

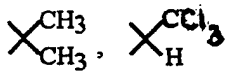
Moscow Pedagogical State University, 1 M. Pirogovskaya, Moscow 119882, Russia

Reactions of 3,5-halogenocyclophosphates of 1,2-*O*-alkylidene-6-desoxy-6-halogeno-α-D-glucofuranoses with water, alcohols, and amines were studied, which permit the obtaining of corresponding 3,5-cyclophosphates, their salts, and amides:



X = Cl, Br

Y = NHR, NR_2, OR, OH, OMet

Z = 

The structure of the obtained cyclophosphates was studied by means of X-ray diffraction analysis and NMR spectroscopy. It was shown that the obtained amidophosphites have predominantly an inverse configuration, and the phosphates conserve the initial conformation.

Cis-amidophosphates can be obtained by the interaction of 3,5,6-bicyclophosphites of 1,2-*O*-alkylideneglucofuranoses with *N*-chloramines.

Phosphorinane cycles of different phosphate can have the chair conformation, as well as the boat or twist one. The furanose cycles have always the twist-envelop conformation with the C3 atom declined to the C5 atom.

The aklylating effect of glucofuranose methylcyclophosphates was revealed.

The study of the regulation of cell fission by the obtained cyclophosphates was launched.

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REGIOSPECIFIC ADDITION OF BIS(TRIMETHYLSILYL)-HYPOPHOSPHITE TO 2-HALOGEN-2-ALKENALS

ALEXANDER RULEV, ALEXANDER MOKOV and MIKHAIL VORONKOV
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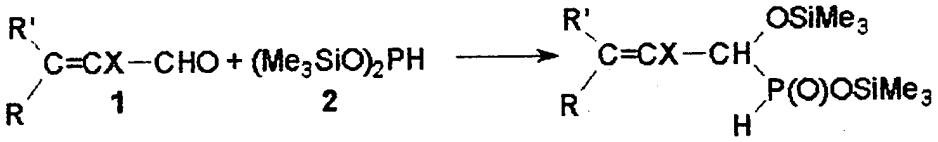
Abstract 2-Halogen-2-alkenals react regiospecifically with one equivalent of bis(trimethylsilyl)hypophosphite in 1,2-addition mode.

2-Halo-2-alkenals **1** are polydental compounds having two sites of possible nucleophilic attack: β-olefin carbon atom and the carbon atom of the aldehyde group. Recently we have shown that alkenals **1** react with trimethylsilyl derivatives of primary or secondary amines in 1,2- and 1,4-addition mode.[1] On the other hand bis(trimethylsilyl)hypophosphite **2** can react on both the P-H and P-O-Si bonds.[2]

We have found that bis(trimethylsilyl)hypophosphite **2** reacts easily with aldehydes **1** in 1,2-addition mode only (on the carbonyl group) with the cleavage of the P-O-Si bond. The reaction proceeds regiospecifically irrespectively of both the nature of the halogen atom and the β-substituent in the molecule of initial substrate. The compounds obtained are a mixture of two diastereomers the structure of which is confirmed by ^{1}H and ^{31}P NMR spectroscopy.



R'= R = H; R'= Me, R = H; R'= Ph, R = H; R'= R = Ph; X = Cl, Br

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REACTION OF PHOSPHORUS RED WITH α,ω-DIHALOALKANES UNDER PHASE-TRANSFER CONDITIONS

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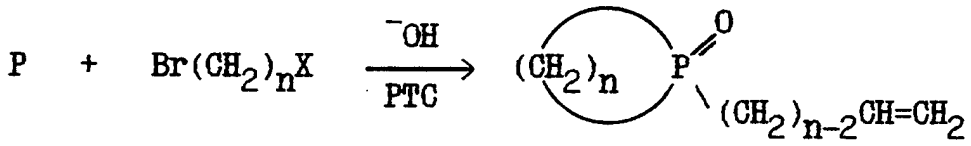
Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 1, Favorsky Street, 664033 Irkutsk, Russia

*Irkutsk State University, 1, K.Marx Street, 664003, Russia

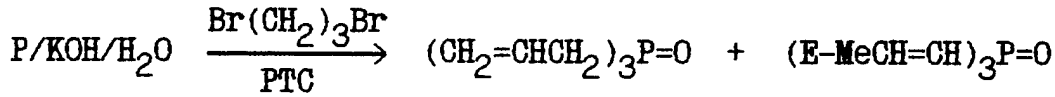
Abstract The regularities and peculiarities of the redox interaction of red phosphorus with α,ω-dihaloalkanes in the presence of strong bases have been studied.

Interaction of 1,4- and 1,5-dihaloalkanes with phosphorus nucleophiles produced from red phosphorus in the KOH/H_2O/dioxane/phase-transfer catalyst system (PTC) at 90°C gives 1-alkenylphospholane- and 1-alkenylphosphorinane-1-oxides in satisfactory yield.



n = 4 or 5, X = Cl or Br

Under similar conditions 1,3-dibromopropane reacts with red phosphorus to form tri(allyl)- and tri(E-propen-1-yl)phosphine oxides.



Acknowledgement: The financial support of the Russian Fund of Fundamental Research is gratefully acknowledged.

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REACTION OF RED PHOSPHORUS AND PHOSPHINE WITH ARYL(HETARYL)ETHENES AND -ETHYNES

NINA GUSAROVA, LAMBERT BRANDSMA*, SVETLANA MALYSHEVA, SVETLANA ARBUZOVA, BORIS TROFIMOV
Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 1, Favorsky Street, 664033 Irkutsk, Russia
*Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Abstract Nucleophilic addition of phosphide anions generated from phosphorus red or phosphine to ethenes and ethynes in the presence of super bases to afford organylphosphines and -oxides has been performed.

Secondary and tertiary phosphines and phosphine oxides have been prepared in good yields by the reaction of phosphorus red or phosphine with ethenes [1] and ethynes [2] in the superbasic suspensions KOH/DMSO (or HMPA).

$$(RCH_2CH_2)_3P{=}O \xleftarrow{RCH{=}CH_2} P/KOH/HMPA \xrightarrow{PhC{\equiv}CH} (Z\text{-}PhCH{=}CH)_3P$$

$$(RCH_2CH_2)_2PH \xleftarrow{RCH{=}CH_2} PH_3/KOH/DMSO \xrightarrow{RC{\equiv}CH} (Z\text{-}RCH{=}CH)_3P$$

R = Ph, 4-F-C_6H_4, 2-furyl, 4-pyridyl, 2-methyl-5-pyridyl, 2-thienyl

Acknowledgement: The financial support of the Shell (Amsterdam) and Russian Fund of Fundamental Research is gratefully acknowledged.

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t-BUTYL ALCOHOL-ASSISTED FISSION OF THE P-P BONDS IN RED PHOSPHORUS WITH LITHIUM IN LIQUID AMMONIA

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Abstract A new method of the selective generation of mono- or diphosphide anions from red phosphorus by the system Li/NH_3 liq in the presence of *t*-BuOH has been developed.

The addition of one or two equivalent of *t*-butyl alcohol which is a mild proton donor to a mixture of red phosphorus, lithium and liquid ammonia drastically assists the fission of P-P bonds in the phosphorus molecule. As a result of subsequent alkylation the primary or secondary phosphines have been prepared in 65-85% yield [1, 2].

$$R_2PH \xleftarrow[2.\ 2RHal]{1.\ t\text{-BuOH}} P\,/\,3Li\,/\,NH_3\ liq \xrightarrow[2.\ RHal]{1.\ 2t\text{-BuOH}} RPH_2$$

R = *n*-alkyl, $PhCH_2$, cycloalkyl; Hal = Cl, Br

Acknowledgement: The financial support of the Shell (Amsterdam) is gratefully acknowledged.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 176
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AROMATIC AND CHIRAL PHOSPHONATE-PHOSPHANES - NEW TYPES OF HEMILABILE LIGANDS

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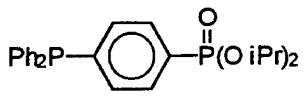
Mixed bidentate ligands gained growing interest in catalytic chemistry. These ligands are able to form hemilabile complexes, in which the phosphane group is strongly bonded to the central atom and the second ligand moiety containing O, N or S is weakly co-ordinated. In view of recent developments in asymmetric carbonylation, introduction of chirality in hemilabile ligands should be a promising approach. Recently, we have published the properties of aliphatic phosphonate-phosphanes and their rhodium complexes as catalysts in carbonylation[1,2]. Now we wish to present new types of phosphonate-phosphanes **1,2,4** and **5** where both phosphorus-containing groups are connected with aromatic rings and/or are part of chiral compounds. For example, when dibromo-binaphthyl was used as starting material, both a chiral mixed bidentate ligand **2** and a monodentate phosphinate **3** were obtained, depending on the synthesis route.



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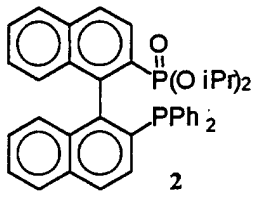

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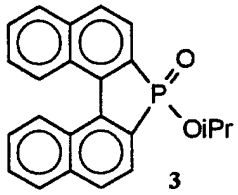

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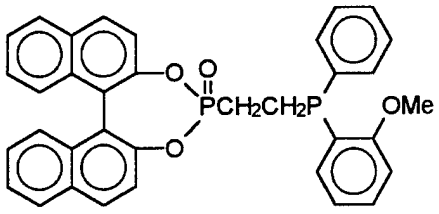

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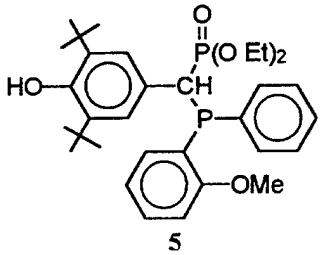

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 177
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SYNTHESIS OF AMINOPHOSPHONIUM SALTS AND THEIR TRANSFORMATION

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Abstract Aminophosponium salts were obtained by two different methods: (1) catalytic phosphorilation of halogen derivatives containing Csp2-Hlg bonds; (2) uncatalytic phosphorilation of bromoacetal.Reactions mechanisms are discussed.

The synthesis of aminophosphonium salts have been achieved by the reaction of amido phosphorus (III) acid with various halogen derivatives (1,2).

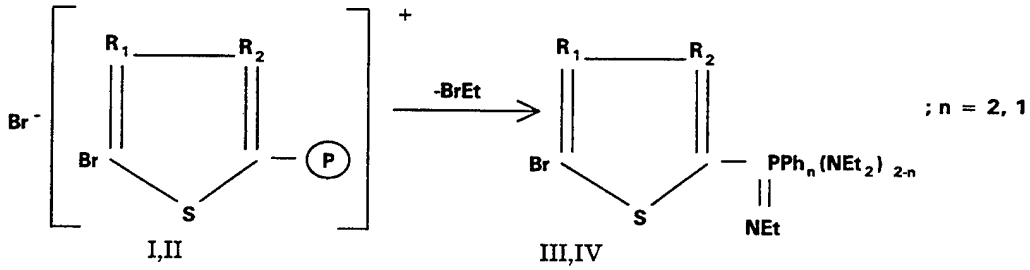
1. Catalytic phosphorylation.

a) $Ph_nP(NEt_2)_{3-n} + ArHlg \xrightarrow{NiX_2} [Ph_nP^+(NEt_2)_{3-n}Ar]Hlg^-$ 1

Ar=C_6H_4Y, $C_{10}H_7$; Y=H, o-, p-CH_3O, m-CH_3, p-C_6H_5O, Br

X=Hlg=Br, Cl; n=0-2

b) It was found that thienylaminophosphonium salts undergo further transformations to the iminophosphin structures:



I,II III,IV

(I,III) R_1=Ph, R_2=Me; (II,IV) R_1=Me, R_2=Ph; Ⓟ= $Ph_nP(NEt_2)_{3-n}$

c) It was found that electronic factors in styrylaminophosphonium salts promote separation of diethylamin forming polimer structure.

2. Uncatalytic phosphorylation.

Ⓟ+ $BrCH_2CH(OEt)_2$ ----> {$Br^-[ⓅCH_2CH(OEt)_2]^+ \overset{EtOH}{\Leftrightarrow} Br^-[ⓅCH=CH(OEt)]^+$} (V)

(V) $\xrightarrow[-EtOH]{H_2O,HCl} Br^-[ⓅCH_2C(O)H]^+ \xrightarrow{H_2O}$ ------> $Br^-[ⓅCH_2\ CH(OH)_2]^+$

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 178
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NEW FREE RADICAL SYNTHESES AND REACTIONS OF FUNCTIONALIZED PHOSPHONATES

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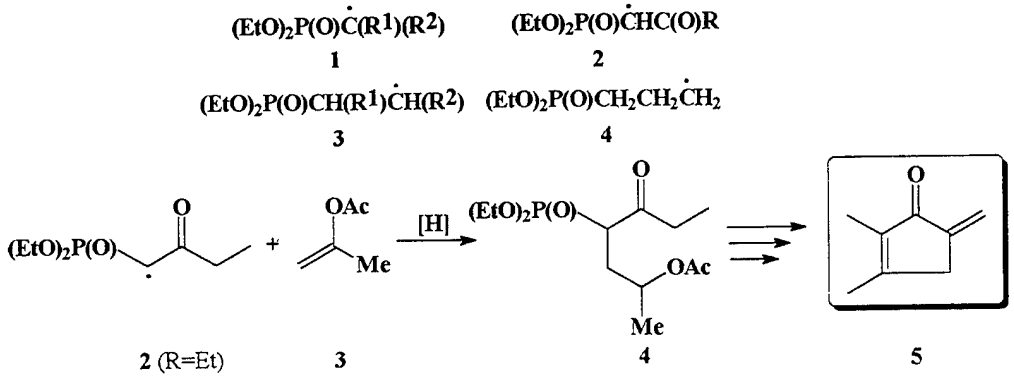
Abstract Reactions of α,β and γ-phosphonyl radicals with alkenes leading to the formation of the $P(C)_n$-C bonds (n=1÷3) and illustrated by a synthesis of Methylenomycin B are described. Desulfenylation and deselenylation reactions of α-heterosubstituted α-phosphoryl sulfides and selenides are also presented.

A new free radical approach to synthesis of functionalized phosphonates is based on the reactions of α,β and γ-phosphonyl radicals of the type **1-4** derived from α-phosphorylalkyl halides, sulfides and selenides with alkenes and alkynes. It leads to the formation of the new $P(C)_n$-C bonds (n=1÷3).



The utility of the elaborated approach is exemplified by the formal synthesis of Methylenomycin B. This synthesis is based on the free radical reaction of **2** (R=Et) with isopropenyl acetate **3**. New free radical desulfenylation and deselenylation reactions of the α-heterosubstituted (OR, $(EtO)_2P(O)$, SR, Cl) α-phosphoryl sulfides and selenides are also presented.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 179
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SYNTHESIS OF PHOSPHONIC ACIDS RELATED TO THE ANTIBIOTIC FOSMIDOMYCIN FROM ALLYLIC α- AND γ-HYDROXYPHOSPHONATES

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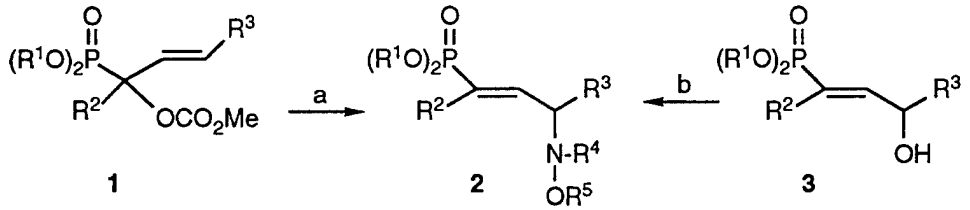
Fosmidomycin is the most active compound of a group of natural phosphonic acid antibiotics bearing a unique hydroxamic acid functionality in the γ-position [1]. We present here two efficient and novel routes to precursors and analogues of these compounds.

Pd(0) catalyzed amination of dialkyl (1-methoxycarbonyloxy-2-alkenyl)phosphonates **1** (R^2 = H) with the hydroxylamine derivatives BocNHOBoc, MocNHOMoc, BocNHOBn, and AcNHOAc proceeds regiospecifically and with high (*E*)-stereoselectivity to give the protected (3-hydroxyamino-1-alkenyl)phosphonates **2** in good to excellent yields.[2] Alternatively compounds **2** (R^2 = H or alkyl) can be prepared with yields of 84-96% by N-alkylation of BocNHOBoc and MocNHOMoc with allylic γ-hydroxyphosphonates **3** under Mitsunobu conditions. Poor results have been obtained using BocNHOBzl or AcNHOAc as nucleophiles.



1 **2** **3**

a: $Pd(PPh_3)_4$ / R^4NHOR^5 / THF; b: PPh_3 / DEAD / R^4NHOR^5 / toluene

Compounds **2** are easily transformed to precursors and analogues of the natural phosphonic acid antibiotics.

1. K. HEMMI, H. TAKENO, M. HASHIMOTO and T. KAMIYA, *Chem. Pharm. Bull.* **30**, 111 (1983), and references therein.
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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 180
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PREPARATION OF NOVEL POLYOXO YLIDES AND DIYLIDES AND THEIR BEHAVIOUR TOWARDS PYROLYSIS AND OXIDATION

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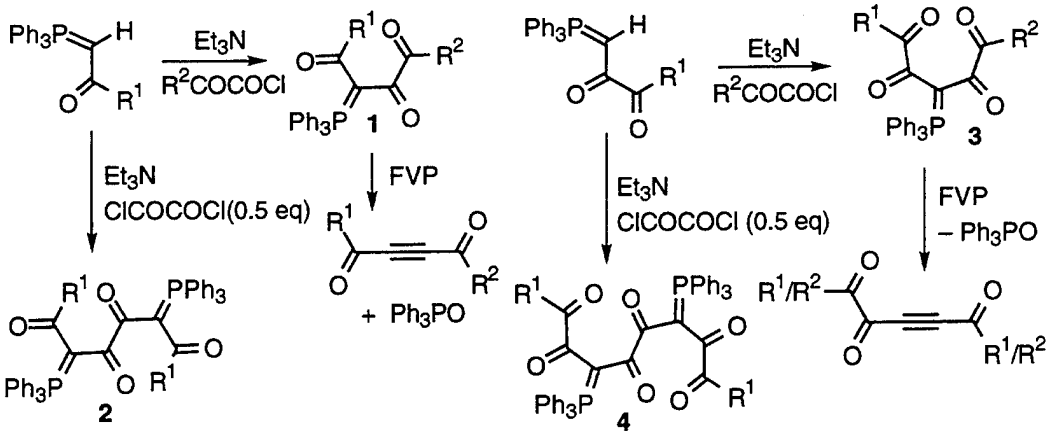
School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, U. K.

We recently reported the preparation of the new trioxoylides **1** and their pyrolysis to give symmetrical diacylalkynes.[1] Reaction of acyl ylides with oxalyl chloride gives the tetraoxo diylides **2** as shown. The corresponding reactions starting from the α-oxoacyl ylides have been used to obtain examples of tetraoxo ylides **3** and hexaoxo diylides **4**.



All the compounds are stable crystalline solids whose structure is fully supported by the interesting ^{13}C NMR spectra. Flash vacuum pyrolysis (FVP) of **3** gives a mixture of isomeric alkynes as shown but the FVP of both **2** and **4** is rather complex. Oxidative cleavage of the ylide functions in all these compound types is of great interest as a route to vicinal polycarbonyl compounds and has already been achieved for **1** to give tetraones. Other aspects of the structure and reactivity of these compounds have been examined.

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 181
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PYROLYSIS OF AMINO ACID DERIVED STABILISED YLIDES AS A ROUTE TO CHIRAL ACETYLENIC AMINES AND AMINO ACIDS AND GABA ANALOGUES

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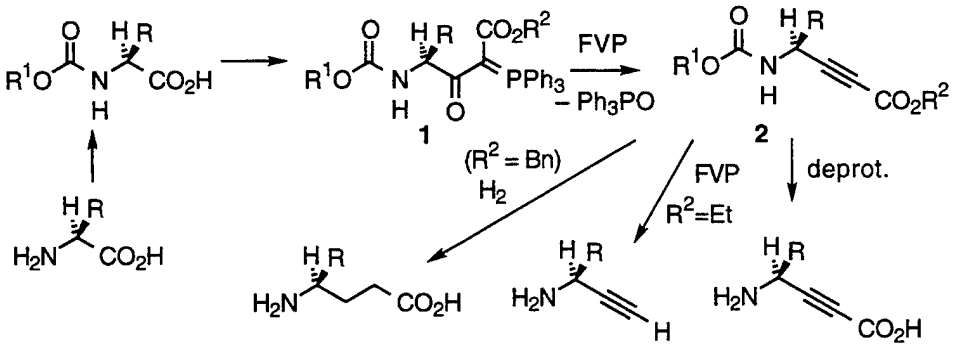
We recently reported the pyrolysis of stabilised ylides as a method for overall conversion of carboxylic acids to homologous acetylenic esters and terminal alkynes.[1,2] This has now been applied successfully to amino acids. A wide range of alkoxycarbonyl protected amino acids have been converted to the stable crystalline ylides **1**. These have been fully characterised, and upon FVP, eliminate Ph_3PO to afford the protected



acetylenic amino acids **2** in good yield and without significant racemisation. Subsequent reactions of these extremely versatile intermediates have been used to gain access to a wide variety of chiral amine and amino acids of great interest as potential selective enzyme inhibitors and components for modified peptide structures.

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GAS-PHASE GENERATED PHOSPHINIDENES AS A ROUTE TO PHOSPHORUS HETEROCYCLES – FORMATION OF THE FIRST 3H-PHOSPHINDOLE

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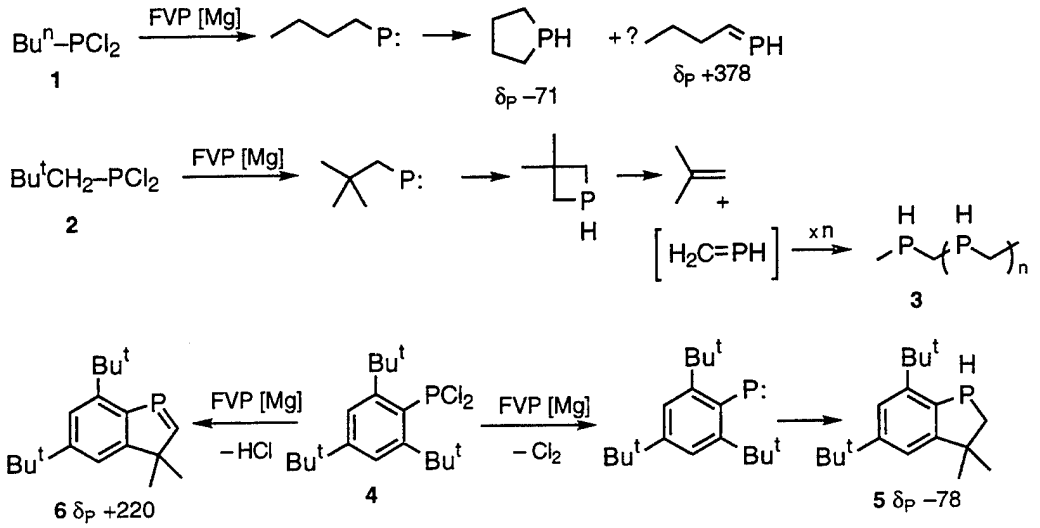
‡ Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, U. S. A.

Flash vacuum pyrolysis (FVP) over freshly resublimed magnesium on glass wool is a convenient and powerful dehalogenating procedure for a wide range of organic halides. We have now applied this system to the generation of phosphinidenes from the corresponding dichlorophosphines. As shown below, the production of phospholane from **1** and the interesting pyrophoric polymer **3** from **2** are readily explained by intramolecular insertion of the phosphinidenes. Under similar conditions **4** gives not



only the expected phosphinidene insertion product, the phosphaindane **5**, but also as a minor product, the 3-*H*-phosphaindene ("phosphindole") **6** – the first example of a new heterocyclic system and the first 3-*H*-phosphole of any type.

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SCOPE AND LIMITATION FOR THE REACTION OF α,β-UNSATURATED CARBONYL COMPOUNDS WITH PHOSPHORUS NUCLEOPHILES BY DETERMINATION OF THE HALF-WAVE POTENTIAL

LÁSZLÓ TŐKE, GYÖRGY CLEMENTIS, IMRE PETNEHÁZY,
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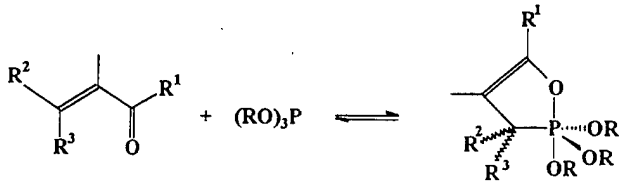
During the formation of oxaphospholenes the phosphorus in the reagent gets oxidised and the double bond in the enones gets reduced.



The polarographic $E_{1/2}$ potential of the enones have been measured in nonprotic solvents and it was found that not only their reducibility but also the production of the oxaphospholene can be predicted from these $E_{1/2}$ values. We found that when the $E_{1/2}$ of enone was lower than -1600 mV the reaction did occur with trimethyl phosphite, while no reaction could be observed with enones having higher $E_{1/2}$ values. In case of using a better nucleophile like triethyl phosphite the border of $E_{1/2}$ value lies at -1710 mV, while the triphenyl phosphite of a weaker nucleophilic character does not react even with the enone having the $E_{1/2}$ at -1294 mV.

reaction occurs with trimethyl phosphite

R1	**R2**	**R3**	**$E_{1/2}$(mV)**
Ph	Ph	H	-1464
Ph	$4NO_2Ph$	H	-1294
Ph	4ClPh	H	-1403
Ph	4MeOPh	H	-1525
$4NO_2Ph$	Ph	H	-1320
4ClPh	Ph	H	-1403
4MeOPh	Ph	H	-1540

no reaction

R1	**R2**	**R3**	**$E_{1/2}$(mV)**
Ph	$4Me_2NPh$	H	-1770
Me	Ph	H	-1692
Me	Ph	Me	-1878
$(CH_2)_3$		H	-2124
$(CH_2)_2$		H	-2184
Me	Me	H	-2300

Moreover, a linear correlation was observed between the $E_{1/2}$ values of the enones and the equilibrium constants of the reaction

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NEW SYNTHESIS OF SUBSTITUTED CYCLOPROPANEPHOSPHONIC ACID ESTERS

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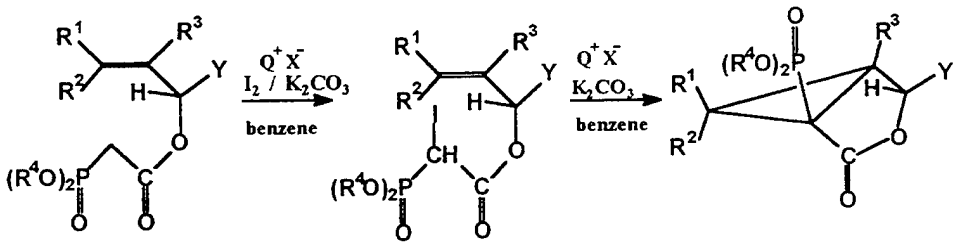
Aminocyclopropane phosphonic acids are considered to be "transition state analogues" of aminocyclopropanecarboxylic acids and they may serve as enzyme inhibitors[1]. We attempted to synthesise aminocyclopropane derivatives by a new route[2]. Phosphonoacetic acid allylic esters were subjected to an intramolecular, radical cyclisation in the presence of iodine, solid potassium carbonate and phase transfer catalyst.



The corresponding iodo phosphonoacetic acid ester is formed first by phase transfer catalytic iodination, which results in a phosphonoacetic acid radical in a SET induced process. Since there is a double bond in a favourable position to the radical centre cyclic radical will be formed, which will be stabilised in a multistep process as cyclopropane fused to a five membered lactone ring. The intermediates were detected and identified by their GC-MS and ESR spectra and a rational mechanism is assumed for the process.

The resulting cyclopropane lactones are very useful in the synthesis of different type of compounds in a stereoselective manner. Subsequent lactone ring opening and further steps can lead to substituted aminocyclopropane phosphonic acids.

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BIS(PENTAMETHYLCYCLOPENTADIENYL)-SUBSTITUTED PHOSPHANES AND PHOSPHORANES

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Abstract The synthesis and crystal structures of a series of phosphanes and phosphoranes will be reported

Only a few representatives of phosphanes of the type Cp^*_2PR ($Cp^* = C_5Me_5$) have been described in the literature[1]. We have synthesized a series of novel phosphanes **2** and phosphoranes **4** by the following routes :

$$\underset{\mathbf{1}}{Cp^*_2PCl} \xrightarrow{R^-} \underset{\mathbf{2}}{Cp^*_2PR} \quad (R= H, N_3, Me, OMe, SMe)$$

$$\underset{\mathbf{3}}{Cp^*_2PR'} \xrightarrow{(X)} \underset{\mathbf{4}}{Cp^*_2P(X)R'} \quad (R= Cl, H;\ X= O, S, Se)$$

The crystal structure analyses of several compounds prepared **2** (R= H, OMe, SMe [2]), **4** (R'= Cl, X= S; R'= H, X= O) have been carried out and the bond length and angles are discussed.

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SULFENYLATION REACTION OF SOME α-PHOSPHORYL SULFOXIDES.

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MARIAN MIKOLAJCZYK
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Lódz, Sienkiewicza 112, Poland.

Abstracts Some α-methylsulfanyl phosphorylsulfoxides were obtained by sulfenylation reaction in homogeneous phase.

Key words S-methyl methanethiolsulfonate, α-phosphorylsulfoxides, Horner-Wittig.

In the course of our studies of sulfenylation of sulfoxides and sulfones[1,2] we became interested in investigating the sulfenylation reaction of α-phosphorylsulfoxides. Previous reports on the alkylation,[3] Horner-Wittig reactions[4] and chlorination[5] of the latter compounds indicated high reactivity of the corresponding carbanions with eletrophiles and, therefore, a successful sulfenylation reaction was expected to occur. In fact, when some α-phosphoryl sulfoxides 1a-c were treated with BuLi/THF, followed by addition of S-methyl methanethiolsulfonate, the corresponding α-sulfenylated derivatives 2a-c were obtained in 50-75% yields.

$$\underset{\underline{1}}{(MeO)_2PO\text{-}CH_2SOR} \xrightarrow[MeSSO_2Me]{BuLi/THF,\ -78^0} \underset{\underline{2}}{(MeO)_2PO\text{-}CH(SMe)SOR}$$

R = Me (a); C_6H_5 (b); p-Me-C_6H_4

Preliminary attempts using NaH/DMSO/$MeSSO_2Me$ or K_2CO_3/$MeSSO_2Me$ under PTC were unsuccessful.

When sulfenylation was performed with the optically active α-dimethylphosphoryl methyl p-tolyl sulfoxide (-)S the optically active α-sulfenylated derivative, containing two chiral centres, was obtained. The latter compound is of interest as it would lead, through the Horner-Wittig reaction with carbonyl compounds, to the optically active ketene dithioacetal S-oxides, useful reagents for asymmetric Michael additions[6] and Diels-Alder reactions[7].

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Acknowledgment: This work was supported by FAPESP and CNPq.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 187
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NEW ROUTES TO *(E)*-HALOPHOSPHAALKENES

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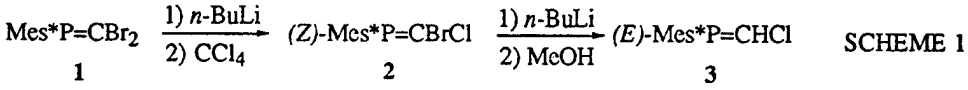
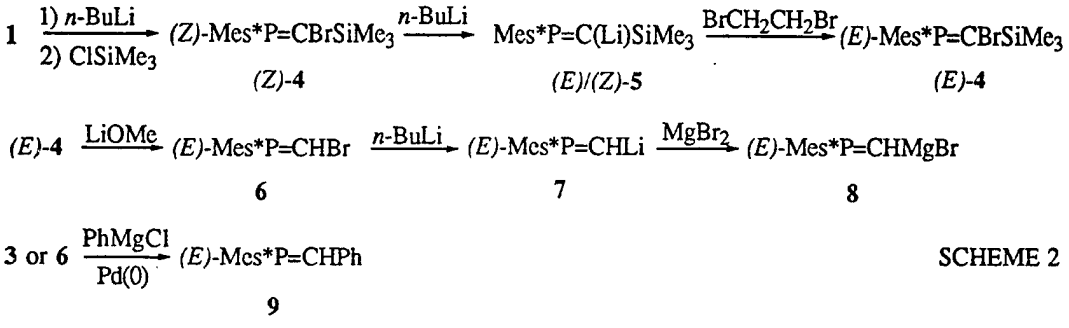
Starting from dihalophosphaalkenes Mes*P=CHal$_2$ (Hal = Cl, Br, I) we have been developing methodologies for the synthesis of *(E)*-Mes*P=CHHal, which can be converted to reactive phosphaalkenyl metal reagents. Dibromophosphaalkene **1** was reacted with *n*-butyllithium at -120 °C, furnishing **2** after chlorination of the intermediate carbenoid. Compound **2** was transformed to the *(E)*-chlorophosphaalkene **3** as shown (SCHEME 1).



SCHEME 1

(E)-Bromophosphaalkene **6** was obtained from **1** via **4** and *(E)*/*(Z)*-**5** as illustrated in Scheme 2. Compound **6** was obtained in 54 % yield with respect to **1**.



SCHEME 2

Halogen-lithium exchange of **6** furnished **7** which was converted to the stable phosphaalkenyl-Grignard reagent **8**. Phosphaalkenes **3** and **6** were subjected to Stille-type cross coupling reactions with phenylmagnesium chloride; *trans*-phosphastilbene **9** was isolated in 76% yield from **3** and in 90% yield from **6**. In both cases, **9** was obtained with 100% isomeric purity (SCHEME 2).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 188
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STERICALLY AND ELECTRONICALLY STABILIZED ORGANO-PHOSPHORUS COMPOUNDS

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Abstract The dialkylamino groups and the methoxy group were employed in a protective group and attempts were made to prepare dithioxo- and selenoxo-phosphoranes.

We have been successful in stabilizing unusual phosphorus compounds in low-coordination states by using the 2,4,6-tri-*t*-butylphenyl group.[1,2] Some bulky groups containing dimethylamino group were utilized in stabilizing $RP(=X)_2$ and RP(=X), where X=S or Se. The lone pair electrons in the amino group seem to stabilize the phosphorus with intramolecular coordination, which was confirmed by X-ray crystallography, ^{31}P NMR, and ^{77}Se NMR.[3] On the other hand, the methoxy group in place of amino does not lead to stabilization but rather to destabilization, activating such phosphoranes or intermediates to serve as sulfurization or selenation reagent of carbonyl compounds.[4]

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 189
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A NEW TECHNIQUE FOR THE GENERATION OF ALKYL METATHIOPHOSPHATES

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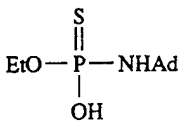
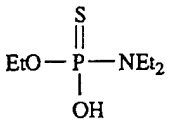
We have recently described a technique for the generation of alkyl metaphosphates, $ROPO_2$, by thermolysis of phosphoramidic acids of structure ROP(O)(OH)NHR (**1**) [1]. We have now successfully shown that alkyl metathiophosphates, ROP(S)(O), which have received but little previous consideration [2], can be generated by the same approach. Compounds **2** (Ad = 1-adamantyl) and **3** were synthesized for this study. Both were easily fragmented on heating in an inert solvent. When an alcohol trapping agent was present each gave EtO–P(S)(OR)(OH) consistent with EtOP(S)(O) as an intermediate. In the absence of a trap, **2** was cleanly converted to the pyrophosphate derivative **4** in a process established to follow first-order kinetics, thus proving that decomposition of **2** proceeded by elimination of EtOP(S)(O). Compound **3** decomposed by mixed first and second order kinetics, and gave a more complex mixture of products. EtOP(S)(O) generated from **2** phosphorylated the OH groups on the surface of silica gel, a process previously demonstrated for $ROPO_2$. With a monoester of phosphoric acid, the mixed monothiopyrophosphate EtOP(S)(OH)-O-P(O)(OH)(OR) was formed in a new synthetic approach to these valuable compounds.



(**2**)



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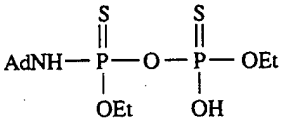

(**4**)

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 190
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REACTION OF TRIALKYLPHOSPHINE CARBON DISULFIDE ADDUCTS WITH CYCLOPENTADIENONES

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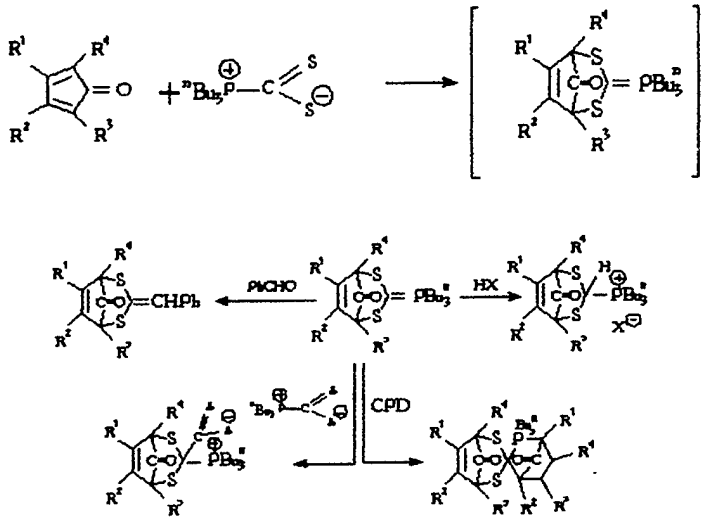
It has been known more than for 100 year that triethylphosphine forms the 1:1 adducts with carbon disulfide and isothiocyanates. However, little is know on the reaction of the adducts and the formation of reactive alkylidenephosphoranes was recently reported by the reaction of adducts with electron-poor double bonds.

We have undertaken a detailed study of the cycloaddition reactions of adducts with a wide range of different cyclopentadienones (CPD). Reaction of the CS_2/tri-n-butilphosphine adducts with one equivalent of cyclopentadienon in C_6H_6 or CH_2Cl_2 resulted in a slow reaction to produce a new adducts, alkylidenphosphoranes and phosphoranes, isolated after flash cromatography.



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THE REACTION OF α-AMINO-SUBSTITUTED DIPHENYLPHOSPHINE OXIDES WITH ELEMENTAL SULFUR AND SELENIUM. A NEW ROUTE TO THIO- AND SELENOAMIDES.

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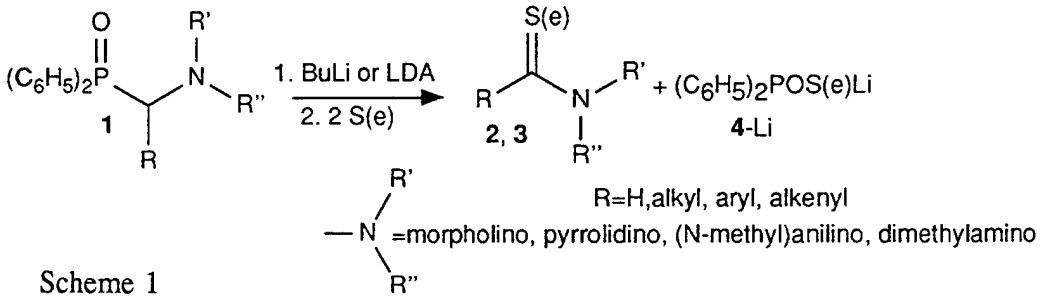
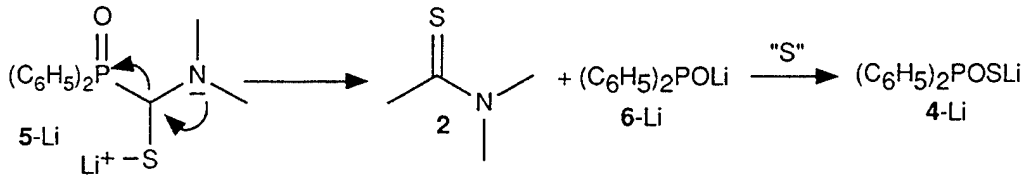
Lithiated α-amino-substituted diphenylphosphine oxides **1** showed an interesting reactivity towards sulfur and selenium, leading to the formation of thioamides **2** and selenoamides **3**, which could be isolated in good yields. Two equivalents of the chalcogene were found to be needed for complete conversion of the phosphine oxide anions. In the case of sulfur, diphenylphosphinothioic acid **4** was isolated as a side product, thus explaining the stoichiometry of the reaction (Scheme 1).

The optimal reaction conditions were found to depend both on the nature of the substituent R in **1** and on the chalcogene. If R=H, aryl or alkenyl, the reaction with sulfur was carried out routinely at 0°C. In the case of R=alkyl, deprotonation of the newly formed thioalkanamide by **1**-Li (R=alkyl), resulted in low yields. This deprotonation could be suppressed by lowering the temperature to -20°C. Markedly increased yields of thioalkanamide could be obtained. The reaction of **1**-Li with selenium required room temperature.



Scheme 1

The mechanism of the reaction of **1**-Li with sulfur was deduced from a ^{31}P NMR study. First, an α-phosphinoyl thiolate **5**-Li is formed. Thioamides **2** result from elimination of lithiated diphenylphosphine oxide **6**-Li from **5**-Li, triggered by the nitrogen lone pair. Subsequently, **6**-Li reacts with a second equivalent of sulfur to **4**-Li. The selenoamides are thought to be formed by a similar mechanism.



Scheme 2

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ARYLSULPHONAMIDES OF AMIDOTHIOPHOSPHONIC ACIDS

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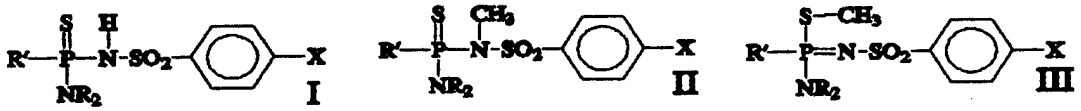
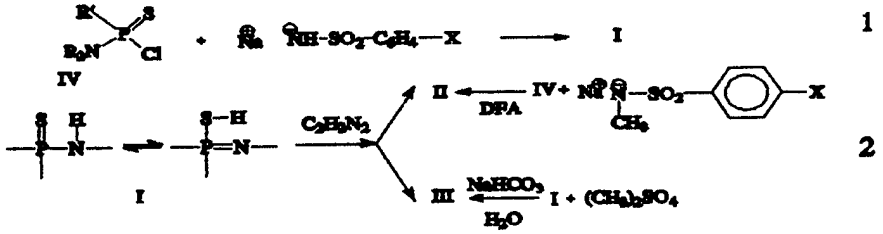
Chemical structure-antimicrobian activity correlation in a thyophosphoric arysulphonamide class were estabilished[1]. The aim of this paper is to present new compounds of same type: p-substituted arylsulphonylamides of amidothiophosphonic acids, I; N-methyl and S-methyl derivatives of them, II and respectively III, synthesyzed by schemes 1 and 2(R'=cC$_6$H$_{11}$, C$_6$H$_5$; NR$_2$=N(CH$_3$)$_2$, N(C$_2$H$_5$)$_2$, N(C$_2$H$_4$)$_2$O; X=F, Cl, Br, H, CH$_3$, OCH$_3$).



For structure I there are thionamido-thiolimido tautomeric equilibrum wich lies far on the site of the thiono form. The two nucleophilic centers from correspondent ambident anion selectively reacts with electrophyles as the methyl iodide or dimethylsulphate.



The physico-chemical characteristics of the new isolated compounds was estabilished by means of IR, ^{1}H-NMR, ^{31}P-NMR and MS. The fragmentation pathways for the three series of compounds were estabilished[2,3]. The compounds I-III were tested to evaluate their inhibitory effects on carbonic anhidrase and some bacterial strains.

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SYNTHESIS AND REACTIONS OF THE NOVEL DIPHOSPHINE, *i*PrN= C[$CH_2P(NiPr_2)_2$]$_2$

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The aldimine *n*BuN=CH*i*Pr and phosphorus trichloride react to give phosphorus(III) amides in a 1:1 and 2:1 molar ratio. An imine-enamine tautomerism is proposed. In a [4+1] cycloaddition reaction diacetyl-(N-*n*-butyl)diimine and $\lambda^3\sigma^3$P-species, $RPCl_2$ or $EtOPCl_2$, form 1,2,3$\lambda^5\sigma^4$-diazaphospholenes[1]. The same diimine and $(Et_2N)_2PCl$ is furnishing annellated azaphospholenes[1]. A 1,3,4$\lambda^5\sigma^4$-diazaphospholanium is formed from a $\lambda^3\sigma^2$-phosphenium and *i*PrN=CMe_2[2]. Phosphorus(III) amides $P(NR_2)_3$ (R= Me, Et) and O-trimethylsilylated diacetyldioxime give rise to yield the first monocyclic pentaazaphosphoranes .

O-trimethylsilylated diacetyldioxime and the phosphenium $(iPr_2N)_2P^+$ give a 1,3,2$\lambda^5\sigma^4$-diazaphospholenium ring system. For the phosphorus(III) triamide $P(NiPr_2)_3$ which was prepared from $ClP(NiPr_2)_2$ and $HNiPr_2$ the reaction takes a completely different pathway, namely to furnish a bis(hydroxylamine) and diphosphine **1**.

During the course of the reaction probably *i*PrN=CMe_2 is formed which undergoes an imine-enamine tautomerism to give the phosphine $(iPr_2N)_2PCH_2C(=NiPr)CH_3$, precursor for diphosphine **1**. Surprisingly enough, $ClP(NiPr_2)_2$ and LDA in a 1:1 molar ratio react to form $HP(NiPr_2)_2$ and *i*PrN=CMe_2 and not the expected $P(NiPr_2)_3$ which itself in the presence of catalytic amounts of LDA decomposes to furnish the same products. LDA acts as a hydride transfer agent . The ketimine *i*PrN=CMe_2, $ClP(NiPr_2)_2$ and LDA yield compound **1** or, if *i*PrN= CMe_2 and $P(NiPr_2)_3$ is reacting successively.

If $ClP(NiPr_2)_2$ and LDA is reacted in a 1:2 ratio besides compound **1**, $HP(NiPr_2)_2$ and $(iPr_2N)_2PP(NiPr_2)_2$ are obtained .

In diphosphine **1** P-C bonds are cleaved by bis(hexafluoropentadionato)palladium(II) to yield a phosphido-bridged complex **2**. The second product originates from transfer of the $CF_3C(O)CH=C(CF_3)O$ moiety on to the *i*PrN=$C(CH_2)_2$ fragment.

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MECHANISM OF THE REACTION OF NUCLEOPHILES >P-O⁻ WITH THE C-Br BOND. BROMOPHOSPHATE AS AN INTERMEDIATE.

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Abstract The reaction of the ions >P-O⁻ and >P-S⁻ with α-bromocarboxylic esters proceeds through the nucleophilic displacement on bromine which results in the release of an enol anion as a nucleofuge.

The anions of the type >P-O⁻ and >P-S⁻ in reaction with α-bromocarboxylates yield debrominated products. ^{31}P NMR spectra of the products of the reductive debromination reaction as well as the reaction of bromophosphate with the phosphite anion present the same picture. Methyl 1-bromo-2,2-diphenylcyclopropane-carboxylate with dibenzylphosphine oxide at the presence of sodium methanolate also yields the debrominated product and methyl dibenzylphosphinate. On the other hand, bromophosphate is captured by an enolate of α-bromoamide to form N-phosphorylated amide. The debromination of methyl 1-bromo-2,2-diphenyl-cyclopropanecarboxylate with 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinan sodium salt yields 2-bromo-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan. These suggest that the X-philic substitution operates in the reaction in focus.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 195
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NUCLEOPHILIC ADDITION TO CARBONYL COMPOUNDS. COMPETITION BETWEEN HARD (AMINE) AND SOFT (PHOSPHITE) NUCLEOPHILE

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[1]Institute of Organic Chemistry, Biochemistry and Biotechnology [2]Institute of Organic Technology and Plastics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland.

In the reaction mixture of carbonyl compound, amine and diethyl phosphite several different reactions are observed. The formation of aminophosphonate (Kabachnik- Fields reaction) is frequently accompanied with the formation of hydroxyphosphonate (Pudovik reaction) or product of its rearrangement.[1-3] This is due to the presence of one electrophile (carbonyl compound) and two nucleophiles (amine and phosphite) in the reaction mixture, which may compete for the electrophilic center.

We have studied the reaction for various carbonyl compounds by means of the ^{1}H and ^{31}P NMR and also by performing the kinetic experiments. We have measured the formation of imine in the reaction of carbonyl compound with excess of butylamine and also the formation of hydroxyphosphonate in the reaction of carbonyl compound with diethyl phosphite in the presence of tertiary amine.

Analyzing the data obtained from kinetic experiments and NMR studies we have observed that the preference of hydroxyphosphonate path over the imine path becomes stronger once we move from aliphatic to aromatic aldehydes or ketones.

We have found that this can be neither due to the changes of electrophilicity of the carbonyl center nor to the steric factors. The only parameter consistent with the observations is the Pearson's hardness and softness parameters.[4]

Thus the competition between two reactions can be explained as the interaction of soft phosphorus nucleophile with soft aromatic carbonyl compound and hard nitrogen nucleophile with hard aliphatic carbonyl compound. Aliphatic carbonyl compounds form predominantly imines and aminophosphonates. The change toward formation of hydroxyphosphonates are observed after replacing the aliphatic substituent into aromatic one. Hydroxyphosphonates are formed predominantly for bisaromatic ketones. We have found a good correlation between our data and the softness parameters calculated by GRINDOL[5] program.

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STEREOSELECTIVE SYNTHESIS OF TRISUBSTITUTED OLEFINS

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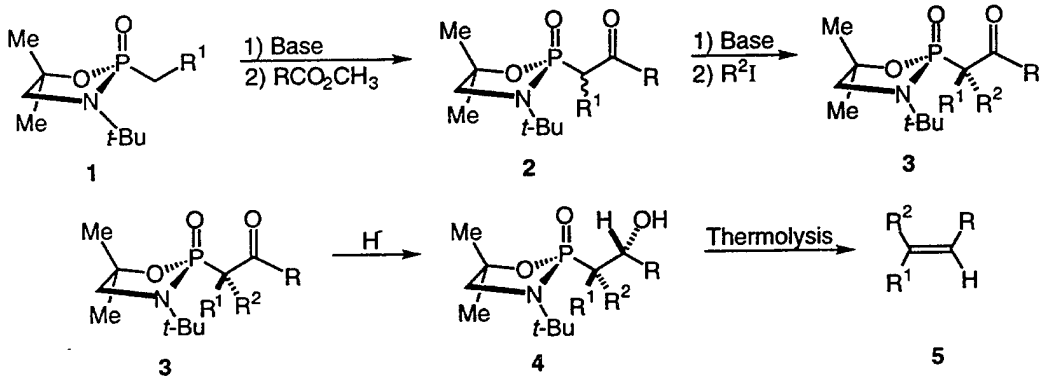
A new method for the highly stereoselective synthesis of trisubstituted olefins is presented. The method involves the stereoselective construction of various β-hydroxy phosphonamidates followed by their thermolysis to provide trisubstituted olefins in extremely high geometrical purity (>99/1).

The stereoselective construction of β-hydroxy phosphonamidates could be accomplished through three main synthetic transformations. The first involves the acylation of various parent 1,3,2-oxazaphospholidines (**1**) to provide monoalkylated β-keto phosphonamidates (**2**) in good yield. The second step is the alkylation of the β-keto phosphonamidates to provide α,α-dialkylated β-keto phosphonamidates (**3**) in high yield and very high diastereoselectivities. Finally, the highly diastereoselective reduction of the dialkylated β-keto phosphonamidates could be accomplished through the use of a variety of reducing agents to give β-hydroxy phosphonamidates (**4**) in high yield and high diastereoselectivities.



Thermolysis of the diastereomerically pure β-hydroxy phosphonamidates gave a variety of trisubstituted olefins (**5**) in high yield and stereoselectivity. This methodology has also been applied towards the stereoselective synthesis of tetrasubstituted olefins.

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MONOCYCLIC AND FUSED 4-IMINO(4-OXO)-1,3,2-DIAZAPHOSPHOLANES AND - PHOSPHORINANES. SYNTHESIS AND SOME PROPERTIES

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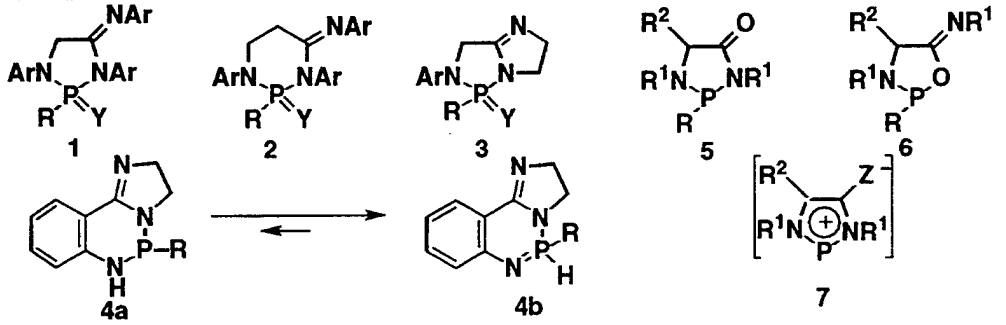
In contrast to the great variety of well known phosphorus heterocycles with exocyclic C=O double bond the number of ones containing exocyclic C=N bond is unusually modest. We elaborated the convenient method of preparation of various N,P,N-heterocycles with exocyclic C=N bond (**1-4**) from the readily available corresponding amino acid amidines and appropriated dichlorides or diamides of phosphorus (III) acids. Rings' **1-3** with P(III) are easily converted into (thio)phosphoryl derivatives, while the direct phosphorylation of amino amidines by $RP(Y)Cl_2$ is unusually ineffective. Tricycles **4** - derivatives of 2-(2-amino phenyl)imidazoline - mainly exist in the more conjugated hydrophosphazo tautomeric form **4b** (>90 %).



N,P,O-Heterocycles **6** with C=N bond together with concomitant N,P,N-isomers **5** are formed in the reactions of amino acid amides $R^1NHCHR^2C(O)NHR^1$ with $RPCl_2$. The course of preferential phosphorylation is strongly dependent on the nature of R, R^1 substituents in reagents. Decrease of $RPCl_2$ electrophility and increase of sterical hindrance on amide nitrogen are favoured to formation of **6**. In the case of R^1= Ar or if R^1=Me, R=Cl only oxo-isomers **5** were obtained. EI mass-spectra of 2-chloro derivatives **1** (Y= l.e.p.) and **5** (R^1=R^2=Me) are indicative of these ones potential ability to be a potential precursors of the true phosphorus mezoionics such as **7** (Z=NAr, O). Mezoionic intermediate **7** (Z=O) was proposed to participate in a role of powerful oxidant in the reactions of chloride **5** with amines or HMDSNa.

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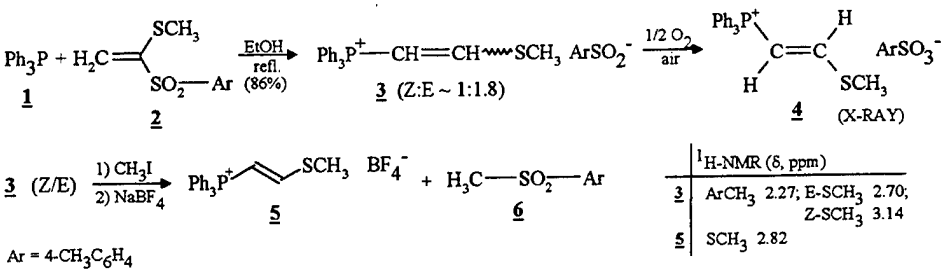
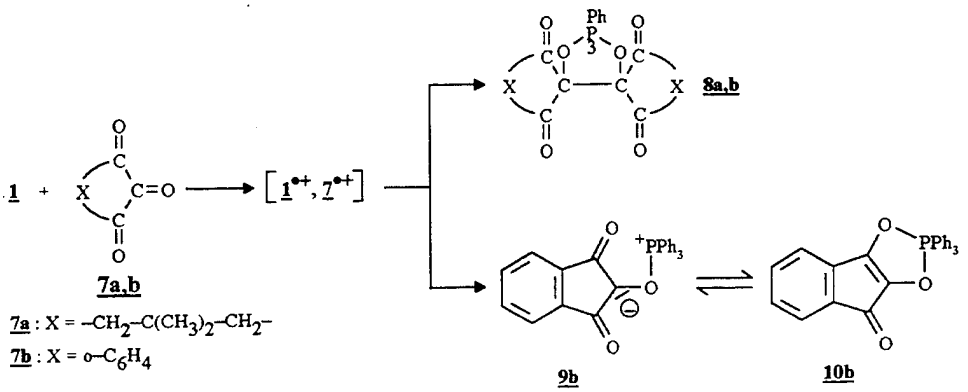
TRIPHENYLPHOSPHINE IN SOME NUCLEOPHILIC ADDITIONS TO DOUBLE BONDS CONTAINING ELECTROPHILIC CARBON

KURT SCHANK, STEPHAN BÜGLER, ROBERT LIEDER and NORBERT SCHOTT
Department of Organic Chemistry, University of Saarbrücken, Germany

Abstract Phosphorus (III) componds like **1** possess basic and nucleophilic properties (phosphonium salt formation) as well as SET properties (i.e. reduction of peroxides). Typical examples of both reaction types are discussed in schemes I and II.



SCHEME I: *Nucleophile-Electrophile interaction between triphenylphosphine (**1**) and 1-methylthiovinyl-4-tolylsulfone (**2**) and subsequent reactions*



SCHEME II: *REDOX-Interactions of **1** with cyclic vicinal triketones **7a,b***

Oxodimedone (**7a**) and indantrione (**7b**) form 2:1-adducts with **1** via intermediate SET and apparent "Umpolung" of midstanding carbonyl carbons. Only in the case of **7b** 1.3-dipole **9b** could be observed in equilibrium with **10b**.

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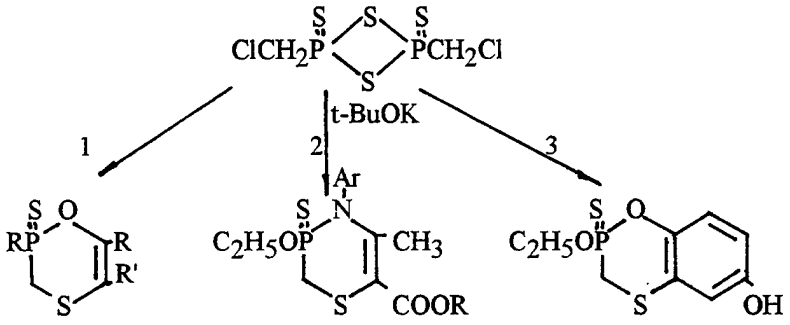
1,4,2-OXATHIA- AND -AZATHIAPHOSPHORINES

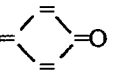
VLADIMIR KOZLOV, SVETLANA CHURUSOVA, SERGEY YAROVENKO, LEV BOGELFER, VALERIY ZAVODNIK
Institute of Plant Protection Chemicals, Moscow 109088, Russia

Abstract New heterocyclic 1,4,2-oxathia- and -azathiaphosphorines were obtained and their structure was investigated.

Key Words *Heterocyclic phosphororganic compounds, oxathia- and azathiaphosphorines.*

The method of synthesis of new phosphoruscontaining heterocyclic compounds - 1,4,2-oxathiaphosphorines and -azathiaphosphorines is suggested. Alcoholysis or aminolysis of dithiadiphosphetidines and following reaction with α-halogencarbonylic compounds (1), β-halogenenamines (2) or benzoquinone (3) resulted in phosphorines.



1. $C_2H_5OH+Et_3N$, (Et_2NH), RC(O)CHR'Hal
2. $C_2H_5OH+Et_3N$, CH_3-C(ArNH)=C(Cl)COOR
3. C_2H_5OH, O=  =O

The structure of the obtained compounds is confirmed by the data of NMR spectroscopy and X-rays analysis. Oxathiaphosphorines are detected to exist in crystalline form in the conformation of "semychair" with the removed from the plane methylene fragment. The dihedral angle between the planes is 131.7 °.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 200
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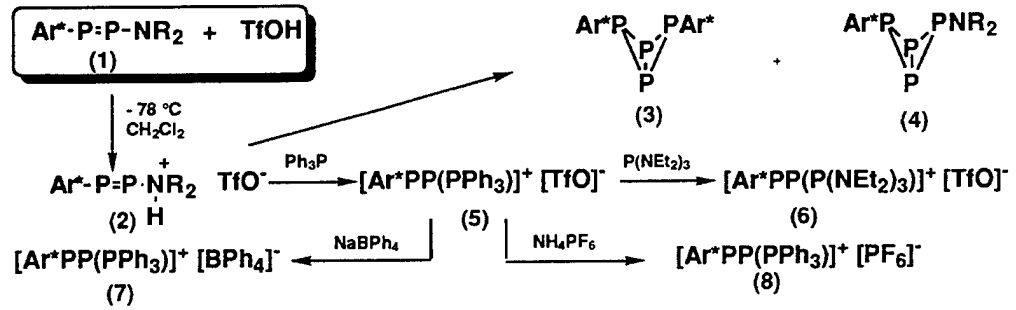
THE FIRST EXAMPLES OF DONOR-STABILIZED PHOSPHANETRIYL-PHOSPHONIUM $[RP_2]^+$ IONS.

VADIM D. ROMANENKO[a], VALENTIN L. RUDZEVICH[a], EDUARD B. RUSANOV[a], ALEXANDER N. CHERNEGA[a], ANNA SENIO[b], JEAN-MARC SOTIROPOULOS[b], GENEVIEVE PFISTER-GUILLOUZO[b] and MICHEL SANCHEZ[c]

[a]*Institute of Organic Chemistry of the National Academy of Sciences, 253660 Kiev 94, the Ukraine ;* [b]*Laboratoire de Physico-Chimie Moléculaire CNRS URA 474, Université de Pau et des Pays de l'Adour, 64000 Pau, France ;* [c]*Laboratoire de Synthèse et Physico-Chimie Organique CNRS URA 471, Université Paul Sabatier, 31062 Toulouse, France.*

Abstract Synthesis of the first donor-stabilized phosphanetriylphosphonium ion $[Ar^*PP{<}{-}{-}PPh_3]^+$ via trifluoromethanesulfonic acid (TfOH) induced reaction of P-dialkylaminodiphosphenes, $Ar^*P{=}PNR_2$ (Ar^* = 2,4,6-tri-tert-butylphenyl) with triphenylphosphane has been described.

We found that in contrast with Ar*P=PAr* which has undergone a P/P bond cleavage upon the low temperature reaction with strong acids (A. Cowley, 1983), a selective protonation of the nitrogen center takes place when diphosphenes (**1**) are treated with TfOH in CH_2Cl_2 at -78°C. Upon warming the solutions of (**2**) to 20°C the latter decompose to form *ca.* 50/50 mixture of bicyclotetraphosphanes (**3**) and (**4**). Addition of TfOH (2 equiv.) to a mixture of diphosphene (**1**) and Ph_3P results in near quantitative yield of the donor-acceptor adduct (**5**). The Ph_3P ligand of $[Ar^*PP(PPh_3)]^+$ readily participates in nucleophilic substitution reactions affording a novel entry to donor-stabilized phosphanetriylphosphonium cations. The structure of (**7**) has been elucidated by X-ray diffraction study [1].



Reference

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UNUSUAL TRANSFORMATIONS OF 2-CYANOACRYLATES IN REACTIONS WITH TRIVALENT PHOSPHORUS COMPOUNDS

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Russian Academy of Sciences,
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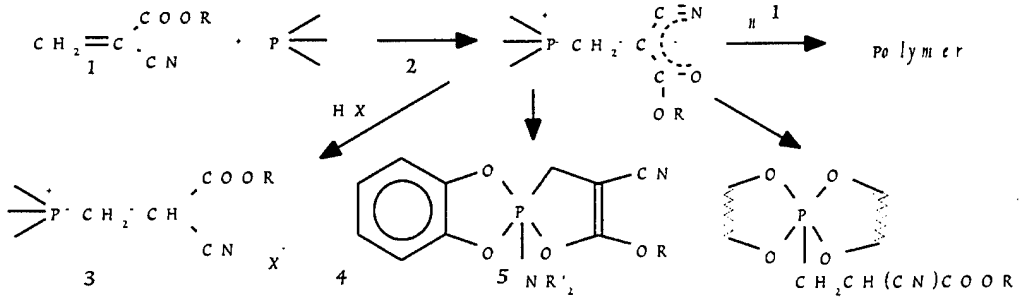
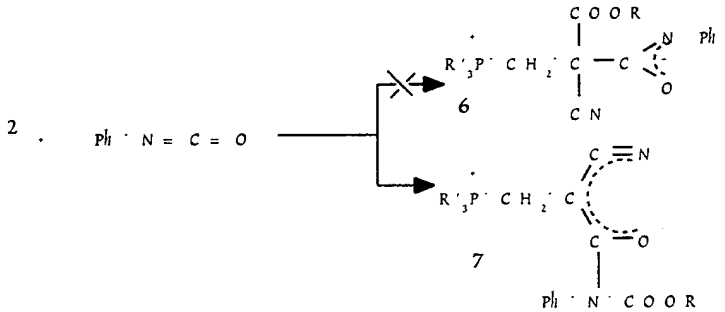
Cyanoacrylates **1** have existed for 40 years, but up till [1] only polymerization processes, effected by various nucleophiles, including trivalent phosphorus compounds, have been known. We have shown that under established conditions **1** (**a R=Me , b R=Et**) reacts with trivalent phosphorus compounds not only *via* the anionic polymerization pathway, but depending on the structure, it forms stable adducts **2**,**4** or **5**.



Only strong nucleophiles react to form stable betaines **2**. Weak nucleophiles, e.g. Ph_3P, react reversible with **1**, and the equilibrium is shifted to the left. The reaction zwitter-ions **2** with electrophile, that locks a good leaving group, e.g. Ph-N=C=O, affords not the expected adduct of C-alkylation **6**, but isomeric zwitter-ion **7**.



The second possibility of the stabilization of the anionic charge is closing unsaturated ring **4**. Stereoeffects play an important role in its stabilization. Carboxylic acid esters with P-C bond, which are intramoleculary phosphorylated at oxygen, were unknown.Stabilization of the primary formed zwitter-ion is possible not only its intramolecular spirocyclization, but also by "trapping" of the anionic charge by an active hydrogen of the starting nucleophiles (adducts **5**). Trapping of the anionic charge in the initially formed zwitter-ion **2** can be carried out with introduction of an acid (adduct **3**).

[1] I.I. Kandror, I.O. Bragina, M.A. Galkina and Yu.G.Gololobov, *Izv. Akad. Nauk. Ser.Khim.*, 2798 (1990).

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 202
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SYNTHESIS OF 4,5-DIHYDROISOXAZOLES BEARING PHOSPHONATE MOIETY

Chengye Yuan and Chaozhong Li
Shanghai Institute of Organic Chemistry, Chinese Academy of Science,
Shanghai 200032, CHINA.

Introduction of phosphoryl group usually leads to the improvement of biological activity of the parent molecule. A facile synthetic route was introduced based on an intramolecular silylnitronate-olefin cycloaddition (ISOC) reaction. Thus, 3-(β-diethoxyphosphoryl)-ethyl-5-methoxycarbonyl - 4,5 -dihydroisoxazole (1), 3-(α-diethoxyphosphoryl- α-substituted methyl) - 5 - methoxycarbonyl - 4,5 - dihydroisoxazole (2) and 3 - methyl - 4 -alkyl(aryl) - 5 - bisphosphoryl - 4,5 - dihydroisoxazole (3) were prepared from diethyl methylphosphonate, diethylphosphite and methylene bisphosphonate respectively after treatment with BuLi or LDA and appropriate nitroalkene followed by $ClSiMe_3$. Condensation of but - 3 - en - 1 - yl phosphonate with nitroalkene, followed by $ClSiMe_3$, led to the stereoselective synthesis of fused carboisoxazole derivatives (4). In the case of aryl substituted α- nitroalkene, the reaction undergoes stereoselectively due to the formation of transition state of the least steric hindrance during the Michael addition step, which gave rise to the exclusive formation of erythro isomers. With alkyl substituted α- nitroalkenes, the diastereoselectivity was not obvious as the result of minor steric difference of the related groups. It seems necessary to point out that the stereochemistry involved in the ISOC reaction is quite different from an intramolecular nitrile - oxide olefin cycloaddition (INOC) process presumably due to the formation of transition states with diverse steric environments. Since 4,5-dihydroisoxazole derivatives are synthetic equivalent of β- hydroxy ketones, 1,3 - diketones, γ- aminoalcohols, α β- unsaturated ketones, the present contribution should expand the field of applications of 4,5 -dihydroisoxazole derivatives in the natural products synthesis by building block strategy.

The Project was supported by National Natural Science Foundation of China.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 203
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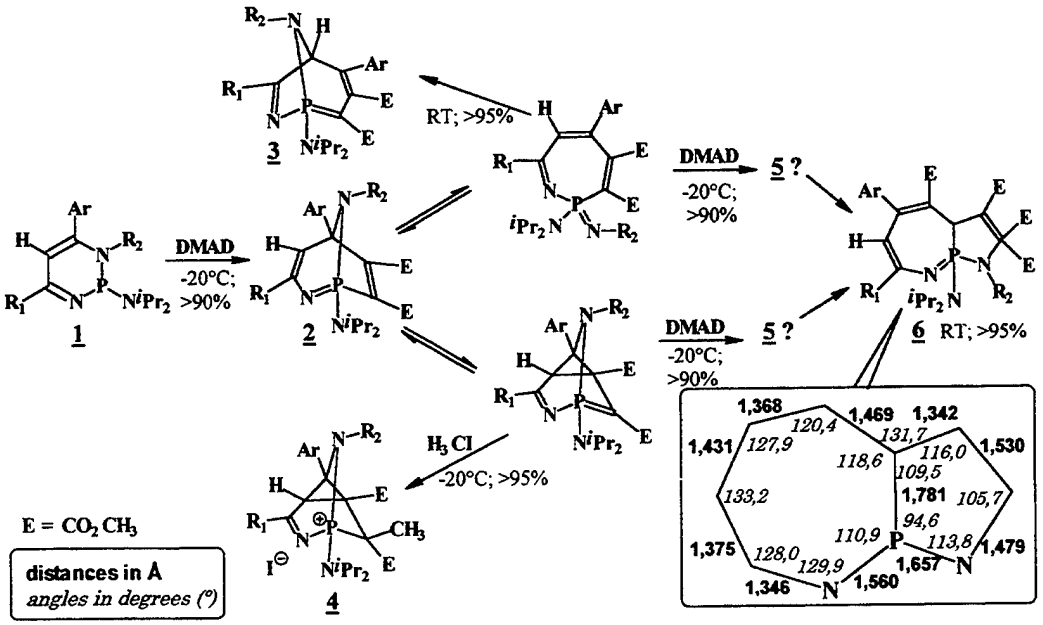
UNEXPECTED BUT EASY SYNTHESIS OF A DIHYDROPHOSPHADIAZAAZULENE

KLAUS BIEGER, MIGUEL TOMÁS, JOSÉ BARLUENGA,
RAFAEL SANTIAGO[§], SANTIAGO GARCÍA-GRANDA[§]
Depto de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo

Abstract The title compound is the main product of the 2:1 reaction of DMAD with diazaphosphinines. The supposed mechanisms with intermediates and related products will be presented.

A dihydrodiazaphosphaazulene **6** was the surprising final product of the 1:2-reaction of **1** with DMAD. It could be shown, that the bicyclophosphadiazaoctatriene **2** is an intermediate of the reaction. Two reaction pathways seem to be possible according to the thermal and nucleophilic reactivity of **2**, leading to the formation of **3** or **4** respectively. An other intermediate **5** has been observed. Its structure still has to be established by x-ray diffraction, allowing to decide, which mechanism is the right one.



Acknowledgements: Thanks are due to the E.C. for a grant to K.B. and to the University of Oviedo for financial support of this work.

§ X-ray structure determination

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ORGANOANTIMONY RINGS COMPARED WITH ANALOGOUS PHOSPHORUS HOMOCYCLES

HANS J. BREUNIG,
University of Bremen, FB 2, D-28334 Bremen, Germany

Analogous ring systems $(RE)_n$ (E = P, Sb) [1,2] with R = Et, Ph, Tol, tBu, $(Me_3Si)_2CH$ are different with respect to ring-ring-reactions.

Phosphorus homocycles like $(EtP)_3$, $(EtP)_4$, $(EtP)_5$ are independent species at room temperature whereas the analogous antimony rings $(EtSb)_4$ and $(EtSb)_5$ exist only in equilibria in solution.

Phenyl phosphorus rings are the pentamer $(PhP)_5$ and the hexamer $(PhP)_6$. Both rings exist as well in solution as in the crystalline state. Phenyl antimony is hexameric only in the crystalline state. On dissolution pentamers and tetramers are formed. Similar reactions are also observed with o-, m-, and p-tolyl antimony rings. Equilibria between phosphorus rings are observed however at elevated temperatures.

With bulky substituents the behaviour of analogous phosphorus and antimony rings becomes similar. The rings $(RE)_4$ (E = P, Sb; R = tBu, $(Me_3Si)_2CH$). preserve the ring size in various phases.

Structures of analogous phosphorus and antimony rings are related. In the crystalline state the four membered rings are folded and the substituents adopt trans positions. The six membered rings have chair conformations in the crystal with equatorial substituents. Generally folding is more pronounced in antimony rings

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2. H. J. BREUNIG in The chemistry of organic arsenic, antimony and bismuth compounds, edited by S. Patai , (J. Wiley, Chichester, 1994), Chap. 14, pp. 563 - 577 and literature cited therein.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 205
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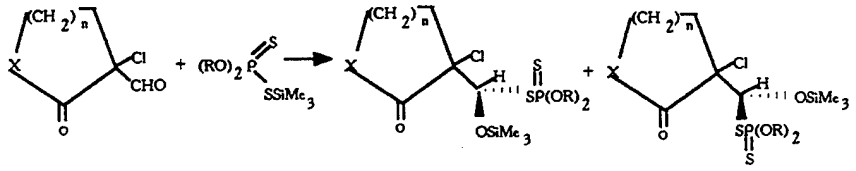
REACTIONS OF α-FORMYL-α-CHLORCYCLONONES AND γ-BUTYROLACTONE WITH S-TRIMETHYLSILYL ESTER OF DIALKYLDITHIOPHOSPHORIC ACID

F.I.GUSEINOV, R.N.BURANGULOVA, V.V.MOSKVA
Department of Organic Chemistry, Kazan State Technological University,
Kazan, 420015, Russia

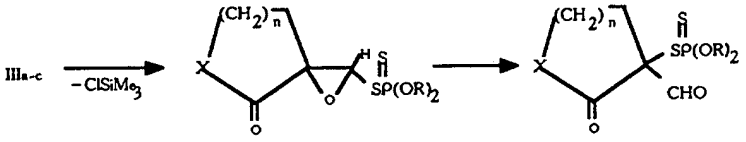
Abstract α-Formyl-α-chlorsubstituted cyclonones or α-formyl-α-chlor-γ-butyrolactone react with O,O-diizopropyltrimethylsilyldithiophosphate to give adducts which rearrange thermaly to α- dithiophos phoryl contained β-dicarbonic compounds.

In our previous studies we have shown that silyl esters of semithioacetals of α-chlor-β-oxo and α-phosphoryl-α,α-dichlorosubstituted aldegydes rearrange to 1,3- and 1,2-dicarbonic compounds[1] or α-ketophosphonates contained chlorthioesters[2], respectively. The main reason for our current interest is the reactions of α-formyl-α-chlorcyclonones (Ia, b) and α-formyl-α-chlor-γ-butyrolactone (Ic) with dialcoxy-S-trimethylsilyldithiophosphates (II). Stable adducts (IIIa, c) are formed by reactions of oxoaldegydes (Ia, c) with dithiophosphates (II).



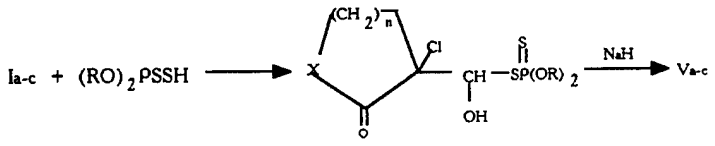
Ia-c II IIIa-c

The spectral date (IIIa, c) are consistent with the mixture stereomers (^{1}H NMR: two dublets (CH) J=15Hz). Upon heating, (IIIa, c) rearrange to α-dithiophosphoryl substituted 1,3-dicarbonic compounds (Va, c) followed by elimination of trimethylchlorsilan and migration of phosphoryl group. We suggest the formation of oxiranes (IVa, c) in this reaction.



IVa-c Va-c

The interaction of chlorcontained hydroxydithiophosphate (VIa, c) obtained from the reaction of (Ia, c) and dithiophosphoric acids, with natrium hydrid affords isomeric adducts (Va, c), instead of oxiranes (IVa, c).



VI VIIa-c

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Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, pp. 207–216
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AUTHOR INDEX

17th International Symposium on the Organic Chemistry of Sulfur

Tsukuba, Japan July 7-12, 1996

Scientific Programme

The purpose of this Symposium is intended to cover all aspects of the organic chemistry of sulfur.

A. Synthesis of organic sulfur compounds and organosulfur mediated synthesis.

B. Theoretical, mechanistic and stereochemical aspects of the organic chemistry of sulfur.

C. Heterocyclic sulfur compounds.

D. Bio-organic and medicinal sulfur chemistry.

E. Advanced materials: organic conductors, polymers, etc.

F. Ecological aspects of organic sulfur compounds.

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XI[th] International Symposium on

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8th INTERNATIONAL SYMPOSIUM ON INORGANIC RING SYSTEMS

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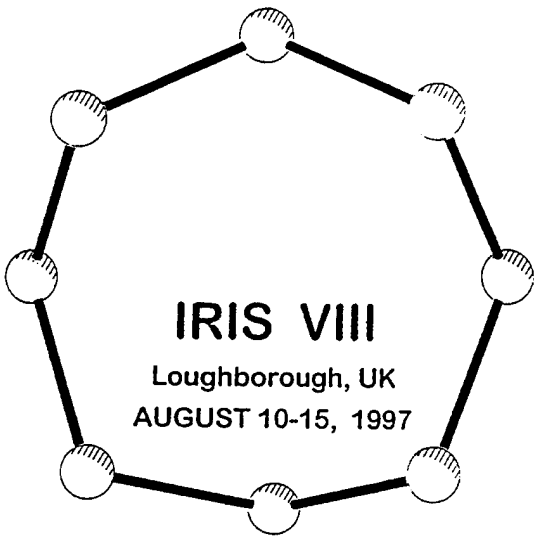

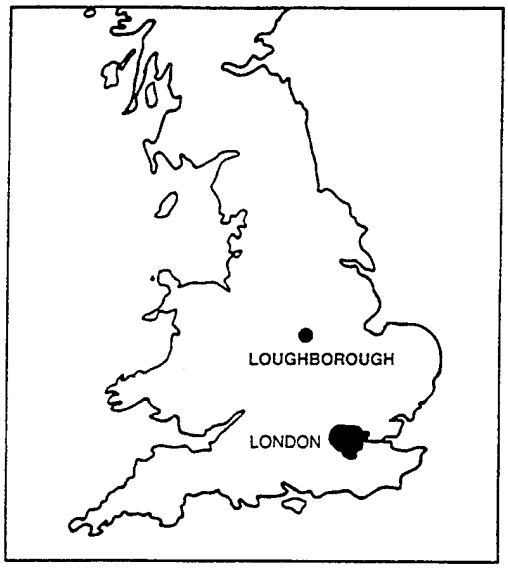

IRIS meetings are the primary symposia for the discussion of work describing synthesis, structure and reactivity of Inorganic Ring Systems, as well as inorganic cages and solids.

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Key Words: Authors should include at the end of the abstract a list of six key words suitable for use in indexing and database entry.

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PREEDF 111(1–4) 1–216 (1996) ISSN 1042-6507

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ON PHOSPHORUS CHEMISTRY (XIIIth ICPC)
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