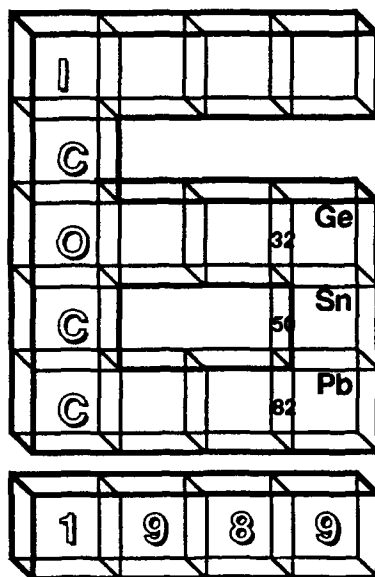
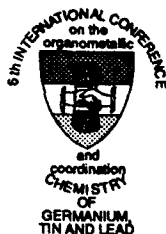


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**SIXTH INTERNATIONAL CONFERENCE
ON THE ORGANOMETALLIC AND COORDINATION CHEMISTRY
OF GERMANIUM, TIN AND LEAD**

July 23-28, 1989

Brussels, Belgium

Under the auspices of
the "Vrije Universiteit Brussel"
the "Federation of the European Chemical Societies" (124th event of FECS)



the "Vlaamse Chemische Vereniging"
the "Société Royale de Chimie"
the "Université Libre de Bruxelles"

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Jean-Claude Maire	Université d'Aix-Marseille	France
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Mario Onyszchuk	Mc Gill University, Montreal	Canada
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Valery Petrosyan	Moscow State University	USSR
Peter J. Smith	International Tin Research Institute, Uxbridge	U.K.
Giuseppe Tagliavini	Università di Padova	Italy

Local Organising Committee

Marcel Gielen (Chairman), Ann Delmotte and Rudolph Willem, Vrije Universiteit Brussel
G.P. Van der Kelen, Rijksuniversiteit Gent
Bernard Mahieu, Université Catholique de Louvain
Logistic Support: Public Relations, Vrije Universiteit Brussel

Conference Information

The 6th International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead will be held from July 23 to July 28, 1989 on the campus of the Vrije Universiteit Brussel (Oefenplein), entrance 13 (Pleinlaan) or entrance 6 (Triomflaan) at Aula Q, conference room C. Parking near Aula Q will be available for the participants.

The registration desk will be open from Sunday, July 23, from 2 to 6 p.m., on Monday, July 24, from 8.30 a.m. till noon, and on Thursday, July 27, from 8.30 a.m. till noon. The Conference Secretariate will be open every day during morning, poster and afternoon sessions.

Telex: 61051 VUBCO B

Telefax University: 32 (2) 641 22 82

Practical Information

The official language of the conference will be English.

No formal dresses are required at the Congress.

Participants are kindly requested to wear their badge throughout the Conference as to recognise them as participants on the Conference site and during social events.

Participants and accompanying persons may phone from the Conference Secretariate to Wasteels-Brooke for any information concerning tourist trips.

Scientific Programme

The Conference is open to theoretical, spectroscopic, mechanistic and synthetic aspects of coordination and organometallic chemistry of germanium, tin and lead compounds, toxicology, release, pathways and fate in the environment, applications in organic chemistry, polymer stabilization, catalysis, etc.. Thursday July 27th 1989 will be devoted to the "Tin Day".

General Schedule of the Conference

	Sunday July 23	Monday July 24	Tuesday July 25	Wednesday July 26	Thursday July 27 "Tin Day"	Friday July 28
8.15 a.m.		Registration			Registration	
8.45 a.m.		Opening address				
9.00 a.m.		Rahm	Koleshnikov	Mironov	Kumar Das	Guibé
10.00 a.m.		C O F F E E				B R E A K
10.30 a.m.		Papers	Papers	VISIT TO BRUGGE	Papers	Papers
12.00		L U N C H			L U N C H	
		POSTER VIEWING			POSTER VIEWING	
2.30 p.m.	Registration	Holmes	Takeuchi		Mitchell	Stille
3.30 p.m.		COFFEE BREAK			COFFEE	
4.00 p.m.		Papers	Papers		Papers	
7.00 p.m.	WELCOME COCKTAIL				BANQUET	

Publication Information

The plenary lectures will be published in a special issue of **Main Group Metal Chemistry** that will be sent to all active participants to the Conference **free of charge**. This work relates the Department of Navy Grant N00014-89-J-9014 issued by the Office of Naval Research European Office. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein

General Information

International currency is freely changed at any bank. A bank is located on the campus of the University, between building F and the campus restaurant. Credit cards are accepted in most shops and restaurants, not in banks. Tickets are required for all social events and will be requested for admission. On Wednesday, at 1p.m., coaches will leave the Conference site for the visit of the city of Brugge.

Scientific Information

Oral Presentation

Slides of 5x5cm will be used exclusively to ensure trouble-free projection. Authors are kindly requested to place their slides, arranged upside down for insertion in the projector, in the box available from the projectionist in the lecture room at least 30 minutes before the beginning of the Contributed Papers Session. The slides must be collected from the projectionist at the end of the session. For clarity, use of overhead projectors is not encouraged, although such facilities will be available.

Poster Session

The posters should be displayed from Monday morning throughout the Conference to facilitate presentation and discussions. Posters can be mounted on Sunday, from 2 p.m., in room Q-2 where the secretariate-registration-information desk is located and should be removed before 2.30 p.m. on Friday. Posters left after 2.30 p.m. on Friday will be discarded.

Registration - Information Desk

The Conference Bag containing the booklet with program, abstracts, list of participants, badge, meal tickets and any other useful information may be collected at the Registration-Information Desk in Room Q-2 at the Conference site from 2 till 6.30 p.m. on Sunday, July 23, from 8.30 a.m. till noon on Monday, July 24 and, for the participants to the "Organotin Day", from 8.30 till 9.00 a.m. on Thursday, July 27.

Lunches

The University Cafeteria is open for breakfast from 8 to 9 a.m. every Conference day, and, for lunch, from noon till 1.30 p.m.. No meals can be obtained free of charge without the tickets provided.

Sponsorship

The Organising Committee acknowledges the following Institutions and Companies for financial and other support:

The Office of Naval Research European Office

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**The Conference is sponsored by the Office of Naval Research European Office.
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policy of the United States Government and no official endorsement should be
inferred.**

SUNDAY, JULY 23, 1989

7.00 p.m. : Mixer

Room Q-2

MONDAY, JULY 24, 1989

AULA Q, Conference Room C

8.45 a.m.: Opening Address by the Conference Chairman

Morning Session

9.00 a.m.: Plenary lecture. Chairman: **Stille, John K.** (Fort Collins, Colorado, U.S.A.)

PL1 Rahm, Alain

Université de Bordeaux I, F - 33405 Talence Cedex, France

Recent Developments in Organotin Chemistry under High Pressure

10.00: Coffee Break in room Q-2

Contributed Papers. Chairman: **Glockling, Frank** (Oxford University, U.K.)

10.30 a.m.

SL01 Jousseau, Bernard and Villeneuve, Patrice

Université de Bordeaux I, F - 33405 Talence Cedex, France

Reversal of Selectivity in S_E2 Cleavage of Mixed Tetraorganotins by Halogens

11.00 a.m.

SL02 Molloy, Kieran C.; Waterfield, Philip C. and Mahon, Mary F.

University of Bath, Bath BA2 7AY, U.K.

3+2 Cyclisation Reactions using Organotin Azides: Synthesis of New Organotin Heterocycles

11.30 a.m.

SL03 Jurkschat, Klaus

Martin Luther Universität Halle Wittenberg, Halle/Saale, GDR

Kuivila, Henry; Liu, Shungcheng and Zubieta, Jon A.

State University of New York at Albany, Albany, New York 12222, USA

Bidentate Behavior of a Cyclic Tridentate Lewis Acid

12.00: Lunch in the University Restaurant

Poster viewing. Room Q-2

Afternoon Session

2.30 p.m.: Plenary Lecture. Chairman: **Pereyre, Michel** (Talence, France)

PL2 Stille, John K.

(Fort Collins, Colorado, USA)

Coupling Reactions of Organotin Reagents with Organic Electrophiles: A Facile Method of Carbon-Carbon Bond Formation

3.30 p.m.: Coffee Break in room Q-2

Contributed Papers. Chairman: **Jones, Colin H.W.** (Burnaby, BC, Canada)

4.00 p.m.

SL04 Boyce, M.; Cashin, B.; Cunningham, D.; McGinley, J. and Sheerin, D.

University College, Galway, Ireland

Novel Classes of Organotin(IV) Heterobimetallics

4.30 p.m.

SL05 Sita, Lawrence R. and Bickerstaff, Richard D.

Carnegie Mellon University, Pittsburgh, Pennsylvania 15213-3890, USA

Isolation and Molecular Structure of the First Bicyclo[2.2.0]hexastannane

5.00 p.m.

SL06 Ashby, Janet R. and Craig, Peter John

School of Chemistry, Leicester Polytechnic, P.O. Box 143, Leicester LE1 9BH, U.K.

Speciation for Analysis of Organometals and Organometalloids

5.30 p.m.

SL07 Köhler, Frank H.; Hertkorn, N. and Blümel, J.

Anorganisch-Chemisches Institut der Technischen Universität München, D - 8046

Garching, FRG

Mobile Stannyl Groups in Bi- and Tricyclic Hydrocarbons

6.00 p.m.

SL08 Sharma, Ramadar

R.D. & D.J. College, Qr. 3, Munger 811 201, India

Tin(IV) Complexes of Triazene-1-oxides

TUESDAY, JULY 25 1989

AULA Q, Conference Room C

Morning Session

9.00 a.m.: Plenary lecture. Chairman: **Takeuchi, Y.** (The University of Tokyo, Japan)

PL3 Koleshnikov, Stanislav P.

Institute of Organic Chemistry of the USSR Academy of Sciences, Moscow, USSR
Recent Advances in Trichlorogermane Chemistry

10.00 a.m.: Coffee Break in room Q-2

Contributed papers. Chairman: **Onyszchuk, Mario** (McGill University, Montreal, Canada)

10.30 a.m.

SL09 Karsch, Hans H.; Baumgartner, Gustav and Müller, Gerhard
Anorganisch-chemisches Institut der Technischen Universität München,
D - 8046 Garching, FRG
Novel Low Valent Germanium Compounds with Organophosphorus Ligands

11.00 a.m.

SL10 Escudié, Jean; Couret, Claude; Satgé, Jacques; Ranaivonjatovo, Henri;
Lazraq, Mohamed; Anselme, G.; Ramarijaona, O.
Université Paul Sabatier, F - 31062 Toulouse Cedex France
and Dräger, M.
Institut für Anorganische und Analytische Chemie der Johannes Gutenberg Universität
D - 6500 Mainz, FRG
Germanes $>Ge=C<$ and Germaphosphenes $>Ge=P-:$ New Aspects of their Reactivity

11.30 a.m.

SL11 Veith, Michael; Lisowsky, Richard; Hobein, Peter and Koch, Jürgen
Universität des Saarlandes, D - 6600 Saarbrücken 11, FRG
Why Do Ge(II)-amides, -alcoholates or -thiolates Differ from the Corresponding Sn(II)- and Pb(II)-derivatives?

12.00: Lunch in the University Restaurant

Poster Viewing in room Q-2

Afternoon Session

2.30 p.m.: Plenary Lecture. Chairman: **Veith, Michael** (Universität des Saarlandes, Saarbrücken, FRG)

PL4 Takeuchi, Y.

(The University of Tokyo, Japan)

Physical Organic Chemistry of Germacycloalkanes and Related Compounds

3.30 p.m.: Coffee Break in room Q-2

Contributed Papers. Chairman: **Krebs, Adolf** (Universität Hamburg, FRG)

4.00 p.m.

SL12 Kupce, Eriks and Lukevics, Edmund

Institute of Organic Synthesis, Latvian SSR Academy of Science, 226 006 Riga 6, USSR

^{73}Ge NMR of Penta- and Hexacoordinate Germanium Derivatives

4.30 p.m.

SL13 Lukevics, Edmund and Ignatovich, Lubov

Institute of Organic Synthesis, Latvian SSR Academy of Science, 226 006 Riga 6, USSR

Synthesis and Properties of Biologically Active Organogermanium Compounds

5.00 p.m.

SL14 Bregadze, Vladimir I.; Kampel, Vladimir Ts.; Petriashvili, Manana V. and Godovikov, Nikolai N.

USSR Academy of Sciences, 117813 Moscow B-334, USSR

Organogermanium and -Tin Compounds Containing a Carborane Cage

5.30 p.m.

SL15 Egorov, Mikhail P.; Kolesnikov, Stanislav P.; Nefedov, Oleg M.,

Institute of Organic Chemistry of the USSR Academy of Sciences, Moscow, USSR

Dvornikov, Alexander S. and Kuzmin. Vladimir A.

The Institute of Chemical Physics, USSR Academy of Sciences, Moscow, USSR

Dimethylgermylene from 7-Germanorbornadiene: UV Spectrum, Reactivity and Complexation

6.00 p.m.

SL16 Singh, R.V.

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

Synthetic, Structural and Biological Aspects of the Coordination Compounds of Germanium Derived from Heterocyclic Thio-imines

WEDNESDAY, JULY 26, 1989

AULA Q, Conference Room C

Morning Session

9.00 a.m.: Plenary lecture. Chairman: **Nefedov, Oleg M.** (Moscow, USSR)

PL5 Mironov, V.F.

(Moscow, USSR)

Synthetic Investigations in the Field of Organogermanium Compounds. 1955-1988

10.00: Coffee Break in room Q-2

Contributed Papers. Chairman: **Böhland, Heinz** (Mülhausen, GDR)

10.30 a.m.

SL17 Srivastava, G. and Rustagi, G.K.

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

Synthesis and Reactions of Chlorodiorganotin Dialkyl Phosphates

11.00 a.m.

SL18 Narula, Suraj Prakash; Bharadwaj, Shashi K.

Department of Chemistry, Panjab University, Chandigarh 160014, India

and

Mairesse, Gaetan; Barbier, Pierre and Nowogrocki, Guy

Equipe de Cristallochimie, Ecole Nationale Supérieure de Lille

F - 59652 Villeneuve d'Ascq Cedex, France

Solid State Structure of di-n-butyl-di(aminobenzoato)tin(IV) Compounds

11.30 a.m.

SL19 Sharma, Raj Pal and Bhatti, S.S.

Department of Chemistry, Panjab University

Chandigarh: 160 014 India

Preparation and Characterization of some Lead(II) phenoxides

12.00: Lunch in the University Restaurant

1.00 p.m.: Visit to the City of Brugge

THURSDAY, JULY 27, 1989

AULA Q, Conference Room C

TIN DAY

Morning Session

9.00 a.m.: Plenary lecture Chairman: **Smith, Peter J.** (Uxbridge, U.K.)

PL6 Das, V.G. Kumar

(Kuala Lumpur, Malaysia)

Some Recent Structural and Biological Work on Organotin(IV) Compounds

10.00: Coffee Break in room Q-2

Contributed Papers. Chairman: **Thayer, John S.** (Cincinnati, Ohio, USA)

10.30 a.m.

SL20 Sherman, Larry R. and Kellner, Ginny L.

Department of Chemistry, University of Scranton, Pennsylvania 18510-2096, USA

Gender Related Toxicity of Tri-n-butyltin Chloride

11.00 a.m.

SL21 Wharf, Ivor

Dawson College, Montreal, Que., H3Z 1A4 Canada

Reeleder, Richard

MacDonald College, Ste-Anne-de-Bellevue, Que., H9X 1C0 Canada

and Simard, Michel G.

Université de Montréal, C.P. 6128, Succ. A, Montréal, Qué., H3C 3J7 Canada

The Correlation of Fungicidal Activity and Structural Variation for Triaryl tin Acetates, Oxides and Hydroxides

11.30 a.m.

SL22 Harrison, Philip G., Ashworth, A. and Clark, E.N.

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

Pathways in the Thermolysis of Organotin Compounds

12.00: Lunch

Poster viewing in room Q-2

Afternoon Session

2.30 p.m.: Plenary Lecture. Chairman: **Das, V.G. Kumar** (Kuala Lumpur, Malaysia)

PL7 Mitchell, Terence Nigel

Universität Dortmund, Postfach 500 500, D - 4600 Dortmund 50, B.R.Deutschland
Some New Organotin Synthons

3.30 p.m.: Coffee Break in room Q-2

Contributed Papers. Chairman: **Jurkschat, Klaus** (Martin-Luther-Universität Halle, GDR)

4.00 p.m.

SL23 Jones, Colin H.W.; Gay, I.D. and Sharma, R.D.

Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Multinuclear Solid-State NMR of Organotin Chalcogenides

4.30 p.m.

SL24 Sebald, Angelika

Bayerische Geo-Institut, Universität Bayreuth, D - 8580 Bayreuth, B.R.Deutschland

High-resolution Solid State ^{119}Sn and ^{207}Pb NMR: a New Analytical Tool in Organotin and Organolead Chemistry

5.00 p.m.

SL25 Dräger, Martin and Behrends, Kerstin

Institut für Anorganische Chemie und Analytische Chemie der Universität

Joh.-Joachim-Becher-Weg 24, D - 6500 Mainz, B.R. Deutschland

$\text{Ph}_3\text{Pb}(\text{Sn-t-Bu}_2)_n\text{-PbPh}_3$, $n = 1-4$, Organometallics with Opto-electronic Properties

7.00 p.m

Social Dinner in the restaurant "Les Fourches", rue Eugène Cattoir, 14, near the Conference site. The conference badge is needed to attend the banquet without having to pay.

FRIDAY, JULY 28 1989

AULA Q, Conference Room C

Morning Session

9.00 a.m.: Plenary lecture. Chairman: **Holmes, Robert R.** (Amherst, Massachusetts, U.S.A.)

PL8 Guibé, François

(Orsay, France)

Palladium-Catalysed Hydrostannolytic and Hydrostannation Reactions and their Applications in Organic Synthesis

10.00 a.m.: Coffee Break in room Q-2

Contributed papers. Chairman: **Petrosyan, Valery S.** (Moscow, USSR)

10.30 a.m.

SL26 Cochran, John C.; Bronk, Brian S.; Terrence, Kathleen M. and Phillips, Harmony K.

Colgate University, Hamilton, New York 13346, USA

Carbonyl Substituted Vinylstannanes: Preparation and Protodestannylation

11.00 a.m.

SL27 Neumann, Wilhelm P.; Kobs, Uwe; Lube, Andreas; Nußbeutel, Udo and Thies, Olaf

Universität Dortmund, Postfach 50 05 00, D - 4600 Dortmund 50, B.R. Deutschland

Stannyl-mediated Aromatic Substitutions of High Regioselectivity

11.30 a.m.

SL28 Parrain, Jean-Luc ; Duchène, Alain and Quintard, Jean-Paul

Faculté des Sciences de Nantes, F - 44072 Nantes Cedex 03, France

α -Tributylstannylacetals: Preparation and Use as "d1 Umpolung" Reagents

12.00: Lunch in the University Restaurant

Poster Viewing in room Q-2

Afternoon Session

2.30 p.m.: Plenary Lecture. Chairman: **Nagle, Jeffrey K.**, Brunswick, Maine, USA

PL9 Holmes, Robert R.

University of Massachusetts Amherst, Massachusetts 01003, USA

Cluster Chemistry of a New Class of Organo Oxotin Compounds

3.30 p.m.: Closing Address

Posters

P01 Vasnin, Sergei Vasilevich

Department of Inorganic Chemistry, Patrice Lumumba Peoples' Friendship University
Ordjonikidze Street 3, Moscow 117 923, USSR

Geanangel, Russel

University of Houston, Houston, Texas 77204-5641, USA

Vasilenko, Tatiana; Molodkin, Aleksei

Department of Inorganic Chemistry, Patrice Lumumba Peoples' Friendship University
Ordjonikidze Street 3, Moscow 117 923, USSR

The Investigation of Tin(II, IV) Chloride Interaction with Some Representatives of the Azole Series

P02 Shcherbakov, Vladislav I.; Sarycheva, N.A., Grigor'eva, I.K.; Zakharov, L.N.; Bochkova, R.I. and Razuvaev, G.A.

Institute of Chemistry Academy of Sciences, Tropinina Str. 49

603600 Gorky, GSP-445, USSR

The First Organotin Analog of Bunte Salt and its Structure

P03 Sall, A.S. and Diop, Libasse

Laboratoire de Chimie Minérale, Faculté des Sciences, Université Cheikh Anta Diop

Dakar, Sénégal

Infrared Characterization of some Mono- and Polyorganotin Adducts

P04 Slock, Marc; Hoste, S. and Van der Kelen, G.P.

Laboratorium voor algemene en anorganische chemie, R.U.G., Krijgslaan 281

B-9000 Gent, Belgium

Spectral Characteristics and Formation Constants for Electron Donor Acceptor Complexes of Organotin Compounds with Tetracyanoethylene

P05 Dakternieks, Dainis

Division of Chemical & Analytical Sciences, Deakin University, Geelong 3217, Australia
and Rolls, Carolyn L.

Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

NMR Investigation of Diorganoyltin(IV)dihalide and Triorganoyl(IV)halide Complexes with Secondary Phosphines and Diorganoylphosphino-N-phenyl(thioformamido) Ligands

P06 Sita, Lawrence R.; Bickerstaff, Richard D.; Lee, Steven P.

Department of Chemistry Carnegie Mellon University, 4400 Fifth Avenue
Pittsburgh, PA 15213-3890, USA and

Gordon, Mark S. and Boatz, Jerry

Department of Chemistry, North Dakota State University, Fargo, ND, 58105, USA

Structural and Electronic Requirements for the Interaction of Stannylenes with Carbon-Carbon Multiple Bonds

P07 Cano Esquivel, Mercedes and Campo, Jose Antonio

Dpto. Química Inorgánica, Facultad Ciencias Químicas, Universidad Complutense
28040 Madrid, Spain

The Reactions of Tin Halides with Carbonylmolybdenum Complexes. Cleavage of Molybdenum-Tin and Molybdenum-Mercury Bonds

P08 Tudela, David

Departamento de Química (C-VIII), Universidad Autónoma de Madrid, 28049 Madrid, Spain

The Repeat Distance in Triorganotin(IV) Polymers

P09 Reuter, Hans

Anorganisch Chemisch Institut, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, B.R. D.

Novel Crystalline Hydrolysis Products of a Monoorganotin Trihalide

P10 Pombrik, Sophya I.; Golovchenko, L.S.; Peregudov, A.S. and Kravtsov, D.N.

Institute of Organoelement Compounds, USSR Academy of Sciences

Vavilov Str. 28, 117813 Moscow B-334 USSR

Synthesis and ^{19}F NMR Study of Unsymmetrical Triaryltin Chlorides and their Adducts with Pyridine

P11 Kokunov, Yu. V.; Gorbunova, Yu. E. and Buslaev, Yu. A.

Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, Leninsky prospect 31, Moscow B-71, GSP-I 117907 USSR

The Preparation and Structure of some Tin(II) Fluorocomplexes

P12 Faraglia, Giuseppina

Dipartimento di Chimica Inorganica, Via Loredan 4, I - 35100 Padova Italy

Sitran, Sergio and Fregona, Dolores

Istituto di Chimica e Tecnologia del C.N.R., Corso Stati Uniti, I - 35020 Padova, Italy

Tin and Organotin Halide Complexes with Carbonyl and Thiocarbonyl Donors

P13 Voronkov, Mikhail G.; Baryshok, Viktor; Ovchinnikova, Zinaida and Lazarev, Igor

Institute of Organic Chemistry, Siberian Branch of the USSR Academy of Sciences

1 Favorsky Street, 664 033 Irkutsk, USSR

3,7,10-Trimethyl-1-Arylstannatranes

P14 Feshin, Valentin; Dolgushin, Gennadii; Lazarev, Igor and Voronkov, Mikhail G.

Institute of Organic Chemistry, Siberian Branch of the USSR Academy of Sciences

1 Favorsky Street, 664 033 Irkutsk, USSR

Electronic and Molecular Structure of Tetrachlorostannane Complexes with Esters of the Series RCOOR' from ^{133}Cl NQR

P15 Lee, F.L.; Gabe, E.J.

Chemistry Division, N.R.C., Ottawa K1A 0R6, Canada

Khoo, L.E.; Leong, W.H.

School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

Eng, G.

Chemistry Department, University of the District of Columbia, Washington, D.C. 20005, USA and

Smith, Frank E.

Chemistry Department, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

Synthesis and Structural Studies of Diorganotin Iminodiacetates

P16 Petrosyan, Valery S. and Reutov, Oleg A.

Chemistry Department, M.V. Lomonosov University, Moscow 119899, USSR

Trans-strengthening Effects in the Coordination Organotin Compounds

P17 Machell, J.; Mingos, D.M.P. and Stolberg, Tonie Louis
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.
Reactive Cyclic Stannylenes

P18 Jurkschat, Klaus; Klaus, Carmen; Dargatz, Manfred; Tzschach, Alfred
Martin Luther University, Postfach, DDR - 4010 Halle/S., German Democratic Republic
Meunier-Piret, Jacqueline and Mahieu, Bernard
Université Catholique de Louvain, Louvain-la-Neuve, Belgium
The Reaction of 3-Dimethylamino-(1,1-dimethyl)propyl magnesium chloride with Tin(II) chloride. Stabilization of a SnCl^+ Cation in the New Tin Cluster $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me})_2\text{SnCl}]_3\cdot\text{SnCl}_2$

P19 Pan, Huade; Hu, Chun; Fu, Fang-xin; Zhang, Zhen-Quan and Sun, Yun-Hong
Chemistry Department, Northeast Normal University, Changchun, Jilin
Peoples' Republic of China
Investigation on Synthesis and Properties of Di(α -substituted alkyl)tin Dibromides and their Complexes with some Nitrogen Ligands

P20 Rafii, Esfandiar; Faure, Robert; Pellet, Isabelle; Lena, Louis and Metzger, Jacques
Ecole Supérieure d'Ingénierie, de Pétrochimie et de Synthèse Organique Industrielle,
Av. Escadrille Normandie Niemen, F-13397 Marseille Cedex 13, France
Synthesis of Mono(trialkyl)phosphonates from Dialkylphosphonates

P21 Shiryaev, Vladimir Iljitch; Grachev, Andrey and Androsenko, Sergey
State Scientific Research Institute of Chemistry and Technology of Organoelement
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P22 Molloy, Kieran C.; Brown, Paul and Mahon, Mary F.
School of Chemistry, University of Bath
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P23 Roe, S. Mark and Alcock, Nathaniel W.
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Veith, Michael and Huch, Volker
Institut für Anorganische Chemie der Universität des Saarlandes,
D-6600 Saarbrücken, B.R. Deutschland
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P26 Tandura, Stanislav N.; Gurkova, Svetlana N. and Gusev, Alexay I.
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P27 Tanaka, Katsumi and Takeuchi, Yoshito
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The University of Tokyo, Komaba, Meguro-ku, Tokyo, Japan 153
**Mass Spectrometry of Organogermanium Compounds. Mechanism of Fragmenta-
tion Processes of 1-Germacyclohexane and their Methyl Derivatives**

P28 Kolesnikov, Stanislav P.; Egorov, Mikhail P.; Galminas, Anton M. and Nefedov,
Oleg M.
Institute of Organic Chemistry of the Academy of Sciences
Leninsky Prosp., 47, B-334 Moscow 117913, USSR
Reactivity of 7-Germanorbornadiene towards Olefins

P29 Kolesnikov, Stanislav P.; Povarov, Sergei L. and Nefedov, Oleg M.
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Hydrogermylation of Aromatics by a New Super-acidic system HGeHal₃-AlHal₃

P30 Barrau, Jacques; Ben Hamida, Najib and Satgé, Jacques
Laboratoire de Chimie des Organominéraux, UA 477, Université Paul Sabatier,
118 route de Narbonne, F - 31062 Toulouse Cedex, France
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P31 Castel, Annie; Rivière, Pierre; Satgé, Jacques; Ko, Young Hoon and Desor, Daniel
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P32 Neumann, Wilhelm P.; Billeb, G.; Brauer, H.; Köcher, J. and Viebahn, S.
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P33 Breunig, Hans Joachim; Ates, Mustafa; Gülec, Sabahittin
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P34 Mazerolles, Pierre; Laurent, Christian and Faucher, Alfreda
Laboratoire des Organométalliques, Université Paul Sabatier, 118, route de Narbonne
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P35 Reynès, Alex; Morancho, Roland
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**Synthesis and Thermolysis of Organometallic Precursors of Amorphous Thin
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P36 du Mont, Wolf-W.; Lange, Lutz and Sewing, Dirk
Fachbereich Chemie der Universität Oldenburg, Postfach 2503, D - 2900 Oldenburg
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P37 Khabashesku, Valery N.; Boganov, Sergey E.; Kerzina, Zoya A.; Nefedov, Oleg M.
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Tamás, J.; Gömöry, A.; Besenyei, I.

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Budapest, H-1525 Hungary

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P38 Bochkarev, M.N.; Pankratov, L.V.; Nevodshikov, V.I.; Lineva, Albina Nikolaevna;
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49, Gorky, GSP-445 603600, USSR

**1,1,2,2-Tetrakis(pentafluorophenyl)digermanedihydride in the Synthesis of Pol-
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P39 Seleznev, Aleksandr; Bravo-Zhivotovskii, Dmitrii A.; Vyazankin, Nikolai and Vo-
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Organogermanium Cyclo-imines

P40 Biltueva, Irina; Bravo-Zhivotovskii, Dmitrii A.; Vyazankin, Nikolai and Voronkov,
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The Structure and Reactions of Thermally Stable Silaenolate Anions

P41 Sidorkin, Valerii; Balkhchi, Georgii; Pestunovich, Vadim and Voronkov, Mikhail G.
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**Theoretical Analysis of Heterolytic Cleavage of the X-M-N Hypervalent Bond in
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P42 Pestunovich, Vadim; Kalikhman, Inna; Baukov, Yuri; Bannikova, Olga; Belousova, Lyudmila; Kramarova, Eugenia; Shipov, Aleksandr and Voronkov, Mikhail G.
Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, 1 Favorsky Street, 664 033 Irkutsk, USSR
(N-M) and (O-M) Chelate $C(Me)_2MCH_2$ Derivatives (M = Ge, Sn) of N-Methylacetamide and Lactams

P43 Borisova, Alla I.; Medvedeva, Alevtina and Voronkov, Mikhail
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The Role of Triorganogermyl(silyl)propynal Heteroatom in the Orientation of S, N-Nucleophile Addition

P44 Vyazankina, Olga; Gendin, Dmitri and Vyazankin, Nikolai
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Method for Preparing Esters of α -Germylated Carboxylic Acids and O-Silylated Ketene Acetals

P45 Mochida, Kunio
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Photochemistry of Phenyl-substituted Trigermanes

P46 Mochida, Kunio; Kikkawa, Haruhiko
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Nakadaira, Yasuhiro
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P47 Taraban, Marc B.; Maryasova, Vera I. and Leshina, Tatyana V.
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P48 Nagar, Rajesh
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Synthetic, Structural and Thermal Studies of N-Pyridino Benzamide-2-carboxylic Acid and its Lead Complex

P49 Thayer, John S.
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 - 0172, U.S.A.
Dissolution of Tin and Lead by Aqueous Alkyl Halides

P50 Nagle, Jeffrey K.
Department of Chemistry, Bowdoin College, Brunswick, Maine 04011, USA
Interactions between Sn^{2+} and Pb^{2+} Ions and a Platinum(II) Dimer in Aqueous Solution

P51 Pachevskaya, Valentina; Golovchenko, L.S. and Kravtsov, D.N.
A.N. Nesmeyanov Institute of Organoelement Compound, USSR Academy of Sciences
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¹⁹F NMR Study of Intramolecular Coordination in Organotin and -Lead Derivatives of o-Substituted Phenols

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Via Bolognola, 7, I - 00138 Roma, Italy
Ion Pair Formation between Lead(II) Chloride Complexes and Tertiary Amines in Xylene

P53 Rzaev, Zakir Magerlam O. and Mamedova, Svetlana G.
Institute of Organochlorine Synthesis. Samed Vurgun Str., 124
Academy of Sciences of the Azerbaijan SSR, 373200 Sumgait, USSR
Tin Effect in Complex Radical Reaction Formation of Tin-containing Polyfunctional Macromolecules

P54 Praet, Anne; Dewaele, Chris; Verdonck, Ludo and Van der Kelen, Gustaaf P.
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HPLC of Organotin Compounds

P55 Verdonck, Ludo; Vanderyse, Leen; Bossuyt, Antoine R. and Van der Kelen, Gustaaf P.
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Tin-Based Tungsten Carbonyl Precursors in the Catalysis of Olefin Metathesis

P56 Eng, George; Coddington, Stephen and Stockton, Laura
Department of Chemistry University of the District of Columbia
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Tolerance of Ceratocystis ulmi to Organotin Adducts

P57 Maillard, Bernard; Degueil-Castaing, Marie; Navarro, Charles and Bitit, Najib
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Reactivity of Allyltins towards Unsymmetrical Alkyl Dihalides

P58 Verlhac, Jean-Baptiste and Pereyre, Michel
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351 Cours de la Libération, F - 33405 Talence, France
Synthesis and Reactivity of Functionally Substituted Vinyltins

P59 Tagliavini, Giuseppe and Marton, Daniele
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I - 35131 Padova, Italy
Organoalkoxytin Dihalides as Intermediates in Organic Synthesis

P60 Zhil'tsov, Sergey F.; Soboleva, Emma B. and Shustov, Sergey B.
The State Pedagogical Institute, Ulyanovsk 1, 603 005 Gorky, USSR
The Application of Initiating Systems Based on Organic Compounds of Tin and Lead for Synthesis of Bioresistant Polymers

P61 Semchikov, Yuri D.; Mazanova, Lyudmila M.
The Chemistry Institute at N.I. Lobachevsky State University, Gagarin Avenue 23,
Block 5, Gorky, GSP-43, 603600, USSR and
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The Preparation of Bioresistant Polymers on Organometallic Catalysts Including Tin and Lead Compounds

P62 Dumartin, Gilles; Delmond, Bernard; Pereyre, Michel and Rahm, Alain
Laboratoire de Chimie Organique et Organométallique, Université de Bordeaux I
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Synthesis and Utilization of Polymer-supported Organotin Reagents

P63 Delmond, Bernard; Andrianome, Marc and Häberle, Karl
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Hydroxylation and Oxidation of Terpenic Structures via Allyl- and Benzyistannanes

P64 Gupta, K.L. and Srivastava, P.
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Preparation and Lewis Acid Behaviour of Ethyl(iso-propyl)tin dichloride towards some Nitrogen Donors

P65 Liepinsh, Edvards; Birgele, Irena; Lukevics, Edmund; Bogoradovsky, Evgenii
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 ^{13}C Isotope Shifts in ^{119}Sn and ^{29}Si NMR Spectra of Stannyl- and Silylacetylenes and -allenes

P66 Das, Mrinal K. and De, Somnath
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Diorganotin(IV) Complexes of Some Dihydroxamic Acids

P67 Böhland, Heinz and Berg, Irene
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Coordination Chemistry of Triphenyltin Isothiocyanate

P68 Varshney, A.K. and Varshney, S.

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Synthesis and Structural Studies of Coordination Compounds of Tin(II) with Sulphur Donor Benzothiazolines

P69 Lycka, Antonin; Holecek, Jaroslav and Tkác, Ivan

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^1H , ^{13}C , ^{15}N , and ^{119}Sn NMR Spectra of Some Organotin(IV) Oxinates and Thiooxinates

P70 Agarwal, Suresh Chandra; Varshney, V. K.; Umesh Chandra and Sharma, R.C.

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Synthesis and Biological Study of Pb^{2+} and Sn^{4+} Complexes with some Schiff-bases

P71 Sherman, Larry R. and Kellner, Ginny L.

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The Effect of Polysorbate 80 on the Toxicity of Organotin Compounds

P72 Ng, Seik-Weng

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Structures of Organotin Carboxylates

P73 Wojtowski, R.; Bowes, C. L.; Hamtak, Peter; Wharf, Ivor and Onyschuk, Mario

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6 and Simard, M

Département de Chimie, Université de Montréal, Montréal, Québec Canada H3C 3J7

Molecular Adducts and Complex Anions of Phenyltin and Phenyllead Azides

P74 Harrison, Philip G. and Oquab, D.

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FT-IR Study of the Thermal Decomposition of Diorganotin Dicarboxylates

P75 Harrison, Philip G. and MacManus, J.

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Kinetics and Mechanism in the Thermolysis of Trimethylstannane

P76 Arakawa, Yasuaki

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Sciences, The University of Shizuoka, 395 Yada, Shizuoka-shi, Shizuoka 422, Japan

Visualization of Intracellular Distribution of Dibutyltin Compounds

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Thermal Decomposition of Organotin Compounds

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**Diorganotin(IV) Derivatives of Thiodiglycolic Acid: Synthesis, Spectroscopic
Characterization and in vivo Antitumour Activity**

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**Diorganotin(IV) Derivatives of Substituted Iminodiacetic Acids: Synthesis,
Spectroscopic Characterization, X-Ray Structure Analysis, in vitro and in vivo
Antitumour Activity**

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**In vitro and in vivo Antitumour Activity of Diorganotin(IV) Derivatives of the Type
Bu₂Sn(O-XY-O)**

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**Synthesis and Characterization of a Series of Diorganotin(IV) Compounds of the
Type R₂Sn(O-C₆H₄-o-NH-CH₂CH₂-NH-C₆H₄-o-O)**

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Synthesis and Characterization of a Series of Substituted 2,2-Di-n-butyl-4-oxo-benzo-1,3,2-dioxastannines

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Bis(bis(trimethylsilyl)methyl)tin(II)-bis(ethene)nickel(0)

P84 Doidge-Harrison, Solange S.M.V.; Cox, Philip J.

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Co-ordination Chemistry of Functional Substituted Organotin Compounds

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Chlorostannation of Carbonyl Activated Double Bonds in Aromatic Systems

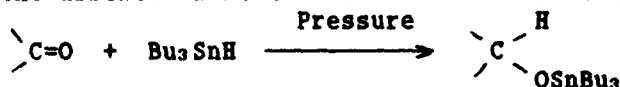
RECENT DEVELOPMENTS IN ORGANOTIN CHEMISTRY UNDER HIGH PRESSURE

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Organotin compounds are playing an increasing role in organic synthesis (1). We have been looking for new aspects of the organotin chemistry, using the high pressure technique (2).

Tin alkoxides have been prepared by hydrostannation of ketones in the absence of Lewis acids or free radical initiators (3).

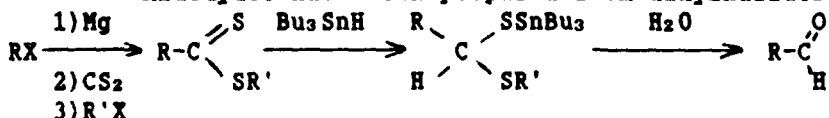


Very good yields were obtained even with sterically hindered ketones, or with cyclopropyl- and α,β -epoxy ketones (preservation of the three membered ring).

Alkenes were hydrostannated in high yields under high pressure and side reactions such as ring opening could also be avoided. 1,3-Dienes also added tin hydrides (4).

New chemoselectivities have been observed. Thus, with tin hydride, chloroketones gave chloroalkoxytins under pressure and dechlorinated ketones under classical conditions (5). Similarly, chloroalkenes gave either addition on the double bond (HP conditions) or substitution of the chlorine atom (classical conditions) (6).

Aldehydes have been prepared from alkylhalides :



The hydrostannation step is much more efficient under high pressure than under free radical conditions (steric hindrance, chemoselectivity) (7).

Alkenyltins can react as dienophiles with substituted 1,3-dienes. The thermal isomerization of 2- β -(tributylstannyl)-styrene was avoided by the use of the high pressure (8). With the optically active menthyl 3-tributylstannylacrylate, the diastereoselection was strongly dependent on the pressure (9).

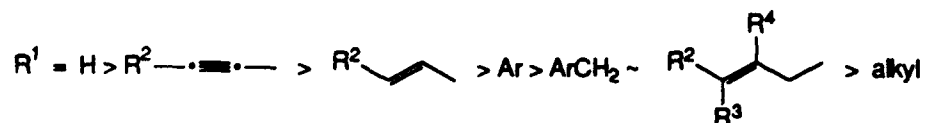
1 H. PEREYRE, J.P. QUINVARD and A. RAHM, "Tin in Organic Synthesis", Butterworths, Londres (1987). 2 A. RAHM, "Organometallic Chemistry" in "High Pressure Organic Chemistry", le MOULLE, editor, Elsevier, (1988). 3 H. BOCHEIL-CASTAING, A. RAHM and H. DANA, J.Org.Chem., **51**, 1672 (1986). 4 a) A. RAHM, H. BOCHEIL-CASTAING and H. PEREYRE, J.Organometal., **1**, 232, C 29 (1982). b) A. RAHM and R. AMARDEIL, submitted for publication. 5 H. BOCHEIL-CASTAING, D. MAILLARD and A. RAHM, J.Organometal.Chem., **287**, 49 (1985). 6 A. RAHM and R. AMARDEIL, in preparation. 7 A. TOUTILLIER, R. AMARDEIL and A. RAHM, in preparation. 8 A. RAHM, P. FERROUS, J. JURCIAN and S. PITUL, in preparation. 9 A. RAHM, P. FERROUS, H. BOCHEIL-CASTAING, J. JURCIAN and A. COLENTONCHI, Synth.React.Inorg.Nat.Org.Chem., **17**, 937, (1987).

Coupling Reactions of Organotin Reagents with Organic Electrophiles; A Facile Method of Carbon-Carbon Bond Formation

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The generation of a new carbon-carbon bond by the palladium catalyzed coupling reaction of organotin reagents with a variety of organic electrophiles, both in the absence and presence of carbon monoxide, has become a valuable synthetic procedure. This high yield reaction takes place regio- and stereospecifically while tolerating a variety of functional groups on either coupling partner, including unprotected carboxylic acid, aldehyde, alcohol, ester, amide, nitrile, nitro, methylene ketone, etc. Most importantly the organotin reagents can be purified and are stable--until subjected to the reaction conditions. Consequently, this reaction is valuable for the synthesis of complex organic molecules.

In this transformation, only one of the groups on tin enters the coupling reaction. Fortunately, different types of groups transfer selectively from tin, the simple alkyl group having the slowest transfer rate. Thus the necessary and important organotin reagent is an unsymmetrical one containing three alkyl groups such as methyl or butyl and a fourth group such as acetylenic, vinyl, aryl, benzyl or allyl.



When the reaction is carried out under a moderate pressure (1-3 atm) of carbon monoxide, a ketone is obtained, resulting from cross-coupling accompanied by carbon monoxide insertion.



The synthesis of a number of more complex organic molecules that utilize this coupling reaction as a key step will be illustrated.

RECENT ADVANCES IN TRICHLOROGERMANE CHEMISTRY

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High reactivity and variety of reactions of trichlorogermane are of particular interest. Numerous molecular and radical reactions of $\text{HGe}^{\text{IV}}\text{Cl}_3$, ionic reactions of $\text{H}^+\text{Ge}^{\text{II}}\text{Cl}_3^-$ and carbene-like reactions of $:\text{GeCl}_2$ demonstrate the ability of trichlorogermane to act in different way, often unpredictably but always excitingly.

The mechanisms of reactions, structural data of reactive intermediates as well as synthetic application of the reactions and possible practical uses of germaniumorganic compounds obtained will be discussed.

PHYSICAL ORGANIC CHEMISTRY OF GERMACYCLOALKANES AND RELATED COMPOUNDS

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In the study of physico-chemical properties of organic compounds, the stereochemistry, both static and dynamic, has an important role. The stereochemistry is affected by many factors. The replacement of a carbon atom in organic compounds with a germanium atom will be expected to afford informations concerning the effect of small change in one particular bond length to the structures of organic molecules. This is particularly appropriate since the germanium atom is tetravalent and its nature is close to carbon.

In this study we firstly aimed to elucidate the dynamic, and as a prerequisite, the static structure of a variety of organogermanium compounds. During this study, it was found, however, that the structural study of organogermanium compounds has so far not been systematic nor comprehensive. Consequently a considerable amount of efforts have been directed to the development of application of standard methodologies of physical organic chemistry to the study of organogermanium compounds.

The methodologies which was extensively if not firstly applied includes:

NMR spectroscopy (particularly ^{73}Ge NMR)

Molecular mechanics calculations

Molecular orbital calculations (MNDO and *ab initio*)

Electron spectroscopy (ultraviolet photoelectron and Auger electron)

The compounds investigated are variously substituted germacyclohexanes, germacyclopentanes and vinylgermanes. In this lecture the results for germacyclohexanes will mainly be discussed. Some chemistry of germacyclopentanes will also be treated in relation to the six-membered analogues.

STUDIES IN THE FIELD OF ORGANIC GERMANIUM COMPOUNDS

V.F. Mironov

State scientific-research institute of chemistry and technology of organoelement compounds, Moscow, USSR

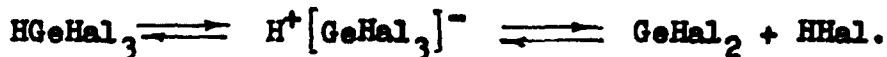
Our studies in the field of organic chemistry of germanium presented in more than 200 issues (including two monographs) were commenced in 1955 and are still in progress.

The comparative studies of chemical conversions of analogous compounds within the Group IVB elements in single-type reactions made it possible to conclude that in the chemistry of Group IVB elements (C, Si, Ge, Sn, Pb), after obvious substantial change between chemical properties during transition from carbon to silicon there is another, less pronounced, change between germanium and tin, i.e. the chemistry of germanium and silicon derivatives despite the fact that it has much common features differs greatly from the chemistry of organic derivatives of tin and lead.

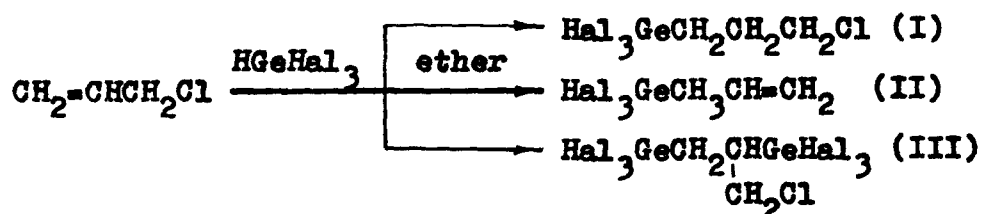
Initially the chemistry of trihalogermanes (HGeHal_3) received primary emphasis. It has been found that with conjugated dienes the reaction proceeds as follows:



i.e. it was for the first time found that trihalogermanes can be a source for reactive germanium dihalogenides of carbene-type:

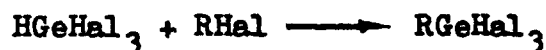


With ethers or amines in reaction medium giving ethers or aminates with HGeHal_3 the above equilibrium moves to the right and the hydrogermylation reaction (I) for example, in the case of allyl chloride is displaced by hitherto unknown condensation (II), double germylation (III) and polymerization (IV) reactions:

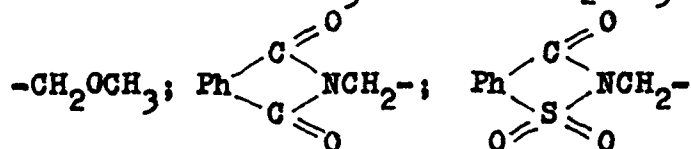


Hydrogermylation reaction proceeds essentially with any compounds containing multiple bonds. It opened the broad possibilities to obtain carbofunctional organic germanium compounds previously unknown. The tendency to reactions (II), (III) and (IV) increases from Cl to I. These reactions proceed often without ether or amine.

Iodides and other organohalogenides capable to reaction according to $\text{S}_{\text{N}}1$ mechanism enter actively into condensation reaction (II):

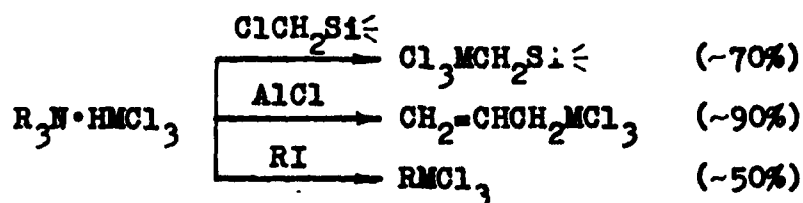


where R = t-Bu; $\text{Ph}_3\text{C}-$; Ad-; $-\text{CH}_2\text{SiR}_3$; $\text{CH}\equiv\text{CCH}_2-$; PhCH_2- ;



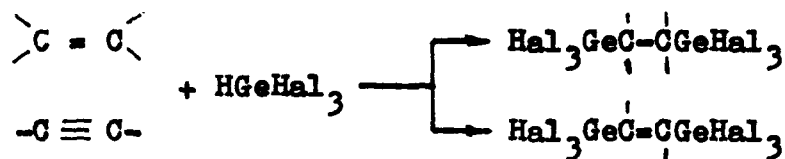
The amine complexes of trihalogermanes can also enter in this reaction.

The comparative studies of $\text{HGeCl}_3 \cdot \text{R}_3\text{N}$ and $\text{HSiCl}_3 \cdot \text{R}_3\text{N}$ revealed their close similarity and opened new preparative methods for the germanium and silicon compounds hitherto non-available:

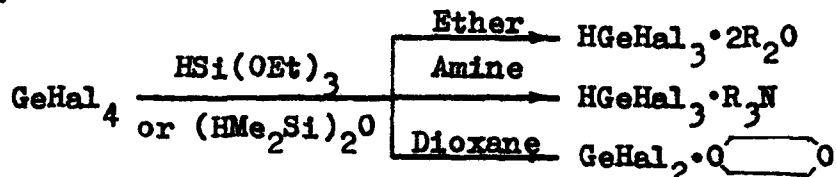


where M = Ge and Si.

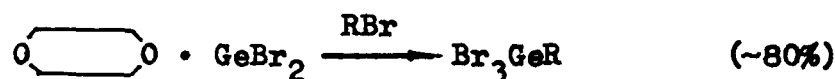
The original double germylation reaction (III) proved also to be enough conventional, it proceeds with some olefinic and acetylenic compounds:



The simple preparative methods for trihalogermane etherates and aminates obtaining as well as GeHal_2 dioxanates from available hydrosilanes and GeHal_4 have been found:

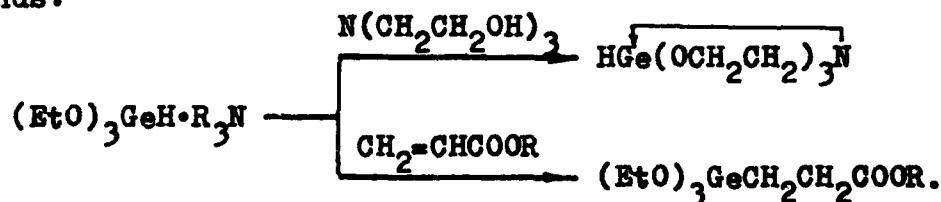


Dibromogermanium dioxanate became to be the most convenient one in series of synthesis. It is established that it reacts with practically any organobromides:

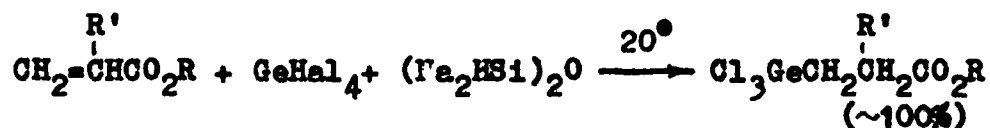


where $\text{R} = \text{Ad-}; \text{Ar-}; -\text{CH}_2\text{Br}; -(\text{CH}_2)_n\text{COOMe}; -\text{CH}=\text{CH}_2; -\text{CH}=\text{CHPh}; -\text{CH}=\text{CHBr}$ etc.

Trialkoxygermane aminates (new complex germanium compounds) have substantially extended the synthetic possibilities in the chemistry of germanium organic compounds:

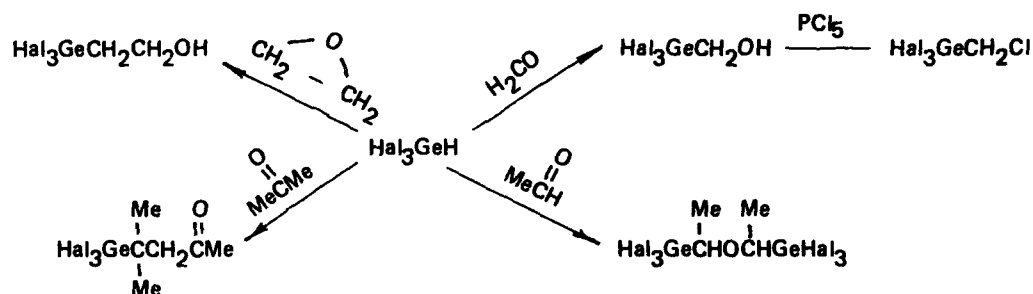


In the case of α, β -unsaturated carbonyl compounds it is unnecessary to prepare separately trichlorogermanes and their etherates; it is sufficient to mix three starting reagents:

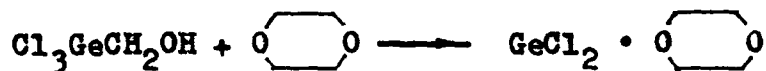


where $\text{R} = \text{H}, \text{Alk}, \text{Cl}; \text{R}' = \text{H}, \text{Me}; \text{Hal} = \text{Cl}, \text{Br}.$

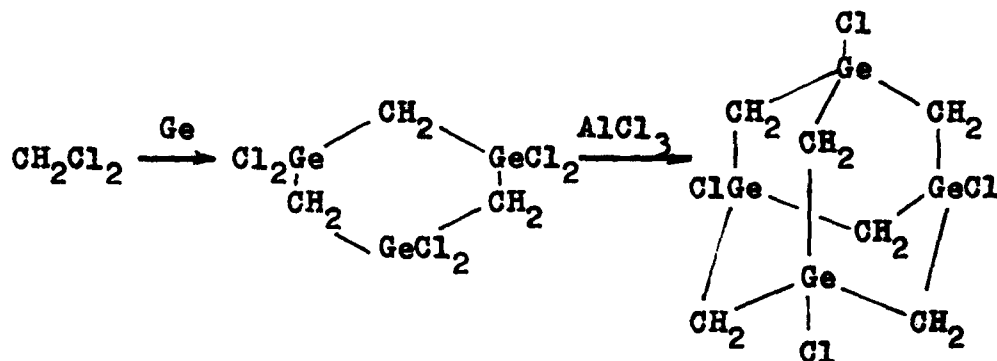
Trihalogermanes enter into unexpected reactions with ketones, aldehydes and ethylene oxide:



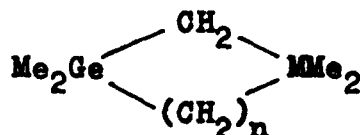
Trichlorogermylmethanol can be a source for GeCl_2 :



The direct synthesis i.e. interaction of elementary silicon with organohalogenides have been attracted much attention. The first unsaturated organic compounds of germanium have been prepared by this method. By involving of α -halomethylgermanes and -silanes in synthesis the different bridged cyclic compounds have been prepared; on base of them germaadamantanes have been synthesized:

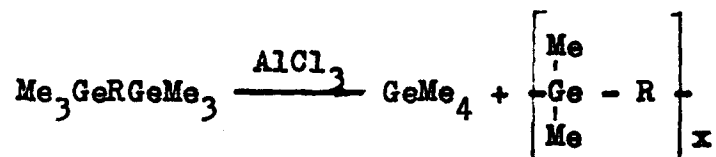


1,3-Digermacyclobutanes and other germacycloalkanes of type:



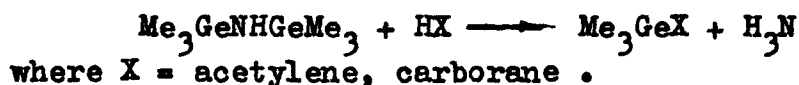
where M = Si, Ge, have been synthesized both by direct and organometallic synthesis.

The bridged germanium compounds in contrast to their silicon analogues showed more tendency to the following reaction:

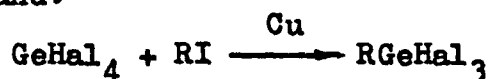



where R = CH₂; C₂H₄; O; NH .

Germazanes are proved to be more reactive than silazanes with protonated compounds:

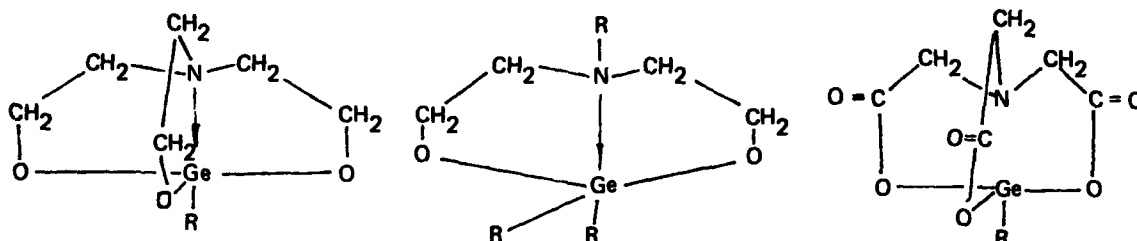


Finally, one more new reaction for Ge-C bond formation has been found:

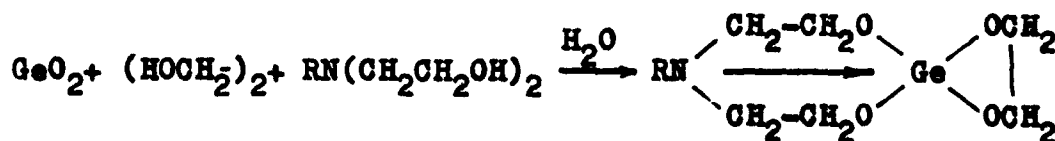


where R = Me, Pr, CH₂I, Ph , n-PhI, Bu, All, α-Naf, m-MePh-.

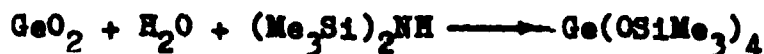
The chemistry of biological active five-coordinated germanium compounds (so-called germatranes and their analogues) as well as germyladamantanes and C-germylcarboxylic and hydroxamic acids received the particular attention.



Involving germanium dioxide in synthesis has substantially simplified the preparation of some germatranes and germacynes, for example:



Germanium dioxide react also with hexamethyldisilazane:



The extensive studies of biological activity of organic germanium compounds have been showed that because of low toxicity they exhibit high biological activity and favourably affect the different living organisms. Besides, in contrast to silicone compounds germanium compounds turned to be less toxic among the structure-like compounds.

Quite possibly germanium plays an independent role as a biochemical trace element and its deficiency could doubtlessly make itself felt in all living organisms as well as that among organic germanium compounds will be find that ones of great value for use in medical preparations.

SOME RECENT STRUCTURAL RESULTS AND BIOLOGICAL WORK ON
ORGANOTIN(IV) COMPOUNDS

V.G. Kumar Das*

Department of Chemistry, University of Malaya,
59100 Kuala Lumpur, Malaysia.

The presently available commercial triorganotin crop protectants have not made a major impact in the agricultural sector as they are generally less selective in their toxic action and exert appreciable levels of phytotoxicity in many applications. The challenge to develop newer products has been synthetically addressed in our laboratories by considering several commonplace and novel variations in the ligand groupings attached to tin, and evaluating the resultant chemotherapeutic potency of the compounds against a wide range of fungal pathogens of tropical crops as well as against some economically important insect pests of rice and cruciferous vegetables. A selection of the screening results which point to specificity of fungitoxic action, reduced phytotoxicity, antifeedant and chemosterilant activities and pesticide synergism will be presented and briefly discussed in the context of their importance in integrated pest management schemes.

In the area of structural work, some recent crystallographic results will be presented which include examples of intra- and intermolecular coordination to tin as well as of competitive inner-sphere coordination by solvent or externally introduced ligands.

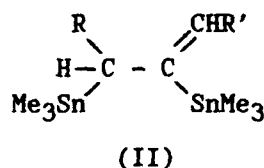
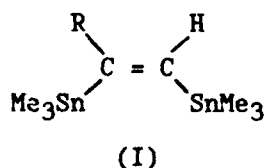
* In collaboration with A.J. Kuthubutheen (Department of Botany, University of Malaya), S. Balasbakaran (Department of Biochemistry, University of Malaya) and Ng Seik Weng (Institute of Advanced Studies, University of Malaya).

SOME NEW ORGANOTIN SYNTHONS

Terence N. Mitchell

Universität Dortmund, Postfach 50 05 00, D-4600 Dortmund, BRD

Though the chemistry of vinyl- and allyltins has been studied very thoroughly over the past 25 years, compounds containing two vinylic organotin residues or one vinylic and one allylic organotin residue have only recently become readily available, and their chemistry is only now being explored in some detail. This lecture will include results obtained using substrates of types (I) and (II), which are prepared by palladium-catalysed addition of ditins to alkynes and allenes.

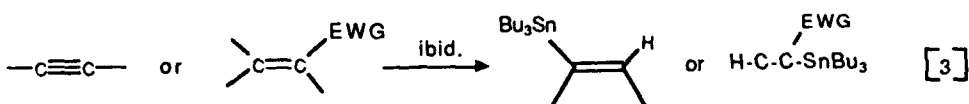
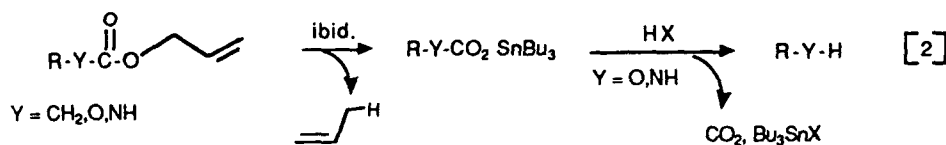
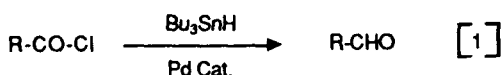


The second major topic to be covered involves the formation and reactions of functionally substituted organotins in which the functional substituent is a diphenylphosphino residue; these compounds are of interest not only from the preparative point of view but also but also because of their NMR-spectroscopic properties, which will be discussed within the framework of long-range element-element coupling constants.

PALLADIUM-CATALYZED HYDROSTANNOLYTIC AND HYDROSTANNATION REACTIONS AND THEIR APPLICATION IN ORGANIC SYNTHESIS

E. Guibé, Institut de Chimie Moléculaire d'Orsay, Laboratoire de Chimie Organique des Eléments de Transition, URA 255, Bât 420, 91405 ORSAY Cedex (France)

Various soluble palladium complexes such as $\text{Pd}(\text{PPh}_3)_4$ or $\text{PdCl}_2(\text{PPh}_3)_2$ are very efficient catalysts for the hydrostannolytic cleavage of acyl chlorides (eq. 1), allylic carboxylates (eq. 2) phosphates and phenoxides as well as for the hydrostannation of triple bonds and activated double bonds (eq. 3).



All these reactions are virtually instantaneous at room temperature ; they proceed via a polar (non-radical) mechanism ; that is tributyltin hydride acts formally as an hydride donor in the presence of the palladium catalyst.

The present lecture will cover more specifically two topics : firstly the application of the catalytic hydrostannolytic cleavage of allylic and propargylic esters in protective group chemistry and in peptide synthesis ; secondly the application of the palladium (and molybdenum) catalyzed hydrostannation of alkynes as a possible route to regio and stereodefined alkenylstannanes.

CLUSTER CHEMISTRY OF A NEW CLASS OF ORGANO OXOTIN COMPOUNDS

Robert R. Holmes, Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts, 01003 U.S.A.

We have uncovered an entirely new area of organotin chemistry by synthesizing new structural classes of organo oxotin carboxylates, phosphates, and phosphinates.¹ These materials form stable oligomers, varying in the number of tin atoms from two to seven. Some of the new structural forms can be characterized as drums, open-drums or ladders, oxygen-capped clusters, crowns, and cubane-like²⁻⁶ substances. In general, they form from the reaction of organostannonic acids with the appropriate phosphorus acid or carboxylic acid. X-ray studies have revealed that tin in most of these clusters is hexacoordinated and that the (Sn-O)₂ ring represents one of the basic building blocks. Although the structural forms are retained in solution, as revealed by ¹¹⁹Sn and ³¹P NMR measurements, some of them interconvert with each other. Further, as new cluster compositions were uncovered, analogies became apparent with other cluster chemistries, particularly those involving aluminum-nitrogen and iron-sulfur systems, suggesting possible useful correlations among common structural units. Some of the organotin cluster compounds have been found to be effective transesterification catalysts and potential exists for catalytic activity in polymerization processes.

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2. Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1985**, *24*, 1970-1971.
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SL01

REVERSAL OF SELECTIVITY IN SE_2 CLEAVAGE OF MIXED
TETRAORGANOTINS BY HALOGENS

Bernard Jousseume and Patrice Villeneuve, Laboratoire de Chimie Organique et Organométallique, UA 35 CNRS, Université de Bordeaux I, 351, Cours de la Libération, F-33405 Talence Cedex (France)

Numerous data on electrophilic cleavage of metal-carbon bonds is now available. These studies have been developed primarily because the very high selectivity of electrophilic demetallation allows useful synthetic applications. The ease of cleavage by halogens of mixed organotin derivatives follows the sequence : benzyl > aryl \approx vinyl > methyl > higher alkyl. For mixed tetraalkyltin compounds, a cyclic or an open SE_2 transition state, or a charge-transfer mechanism has been proposed to account for selectivity, solvent effects and configurational changes at the cleaved organic group, whereas an open SE_2 transition state with assistance of the solvent or another molecule of electrophile is generally accepted for aryl or vinyltin derivatives.

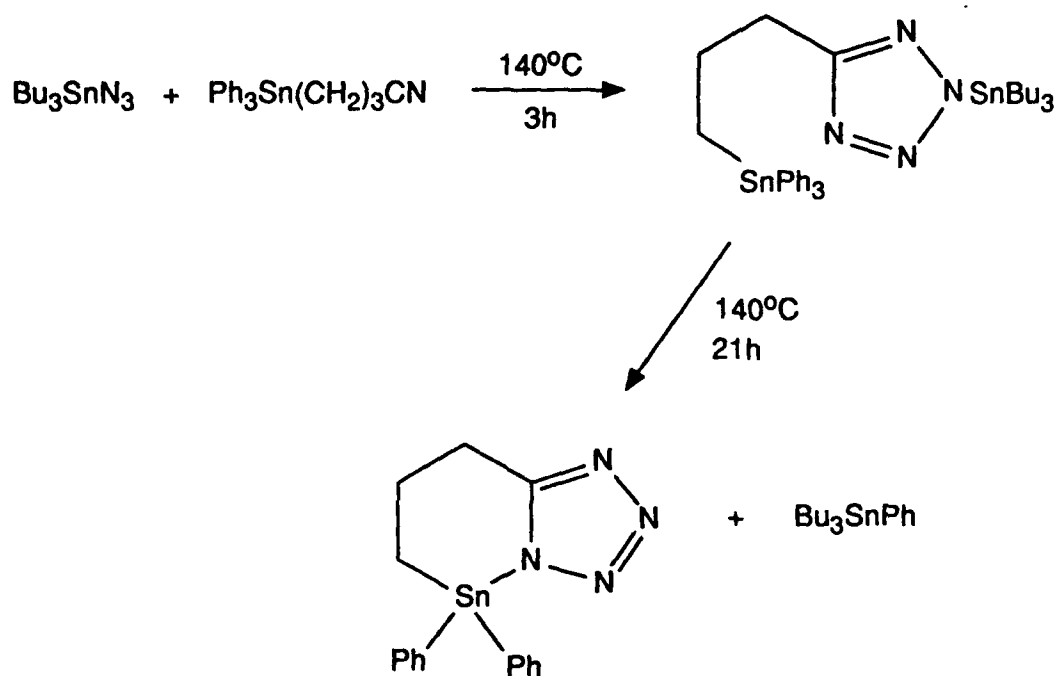
We present examples of halogenodemetallation where the usual sequence of reactivity is reversed, i.e. where alkyl groups are cleaved preferentially to aryl, vinyl or benzyl groups in mixed tetraorganotin derivatives and propose an interpretation of these unexpected results.

3 + 2 CYCLISATION REACTIONS USING ORGANOTIN AZIDES : SYNTHESIS OF NEW ORGANOTIN HETEROCYCLES

Kieran C Molloy, Philip C Waterfield and Mary F Mahon

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U K

Organotin tetrazoles can be synthesised by the thermal cyclisation of a nitrile and an organotin azide. Under appropriate conditions, the organotin tetrazole can be used to construct new bicyclic organotin compounds by nucleophilic ring closure between tetrazole nitrogen and a pendant electrophile.



The structures of both the mono- and bicyclic heterocycles will be discussed, along with other examples of this synthetic approach.

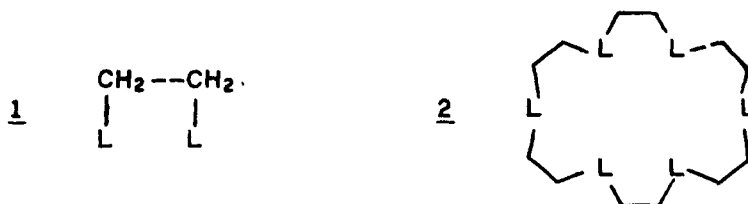
SL03

BIDENTATE BEHAVIOR OF A CYCLIC TRIDENTATE LEWIS ACID.

Klaus Jurkschat, Martin Luther Universität, Halle
Wittenberg, D.D.R.

Henry G. Kuivila, Shungcheng Liu and Jon A. Zubieta;
Department of Chemistry, State University of New York at
Albany, Albany, NY 12222.

Bi- and multidentate ligands such as ethylenediamine (1), the crown ethers (2) in which L is a donor atom have long been familiar in coordination chemistry.



Their Lewis acid counterparts in which L is an acceptor, however, have received very little attention to date. This report concerns the synthesis of the potentially tridentate 1,5,9-tristannacyclododecane system. The 1,1,5,5,9,9-trimethyl, the 1,5,9-trichloro-1,5,9-trimethyl and 1,1,5,5,9,9-trichloro analogs have been synthesized and their complexation behavior with chloride ion have been studied. The results of these studies and the novel structure of a complex with chloride ion as determined by X-ray single crystal diffractometry will be described. These and other results will be discussed in relation to chelation by multidentate Lewis acids in general.

By M. Boyce, B. Cashin, D. Cunningham*, J. McGinley and D. Sheerin,
Chemistry Department, University College, Galway, Ireland.

Exhaustive crystallographic studies of the products from reactions of organotin halides and pseudohalides with $M(3\text{-MeOsalen})$, $M = \text{Co, Ni, Cu, and vanadyl}$; $3\text{-MeOsalen} = \text{N,N'-ethylenebis(3-methoxysalicylidene-iminate)}$, and closely related complexes, have revealed three classes of heterobimetallic complexes.

1. Complexes in which the organotin halide co-ordinates to a water molecule which is hydrogen bonded to the transition metal Schiff-base complex. These include examples of $\text{SnMe}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ with five co-ordinate tin and also with six co-ordinate tin, as a result of intermolecular chloride bridging, thus clearly establishing the effects of intermolecular Sn-Cl bonds.
2. Intimate ion-paired heterobimetallics $[\text{SnR}_2]^{2+} [\text{MX}_2\text{SB}]^{2-}$ ($R = \text{alkyl group}$; $X = \text{halide or pseudohalide}$; $\text{SB} = \text{Schiff-base ligand}$), $[\text{SnR}_2\text{Cl}_4] \{[\text{SnR}_2]^{2+} (\text{NiClSB})^-\}_2$ ($R = \text{alkyl group}$) and $[\text{SnPh}_2(\text{NCS})]^+ [\text{NiNCS}(\text{SB})]^-$. In most cases the location of the organotin cation is such as to give seven co-ordinate tin.
3. Complexes $\text{SnR}_n\text{Cl}_{4-n} \cdot \text{VO}(3\text{-MeOsalen})$ ($n = 2 \text{ or } 3$; $R = \text{organo group}$) in which the vanadyl group forms a donor bond to tin thus establishing the first heterobimetallics in which vanadyl assumes this role.

SL05

ISOLATION AND MOLECULAR STRUCTURE OF THE FIRST
BICYCLO[2.2.0]HEXASTANNANE

Lawrence R. Sita and Richard D. Bickerstaff, Department of
Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213,
USA.

Recent advances in the field of polysilanes have led to the isolation and characterization of a wide range of structurally unique polycyclic frameworks. These compounds represent not only challenging synthetic and theoretical benchmarks, but they also serve to provide insight for the design of new solid state materials. With regard to polystannanes, linear and cyclic structures have been known for some time, however, reports of polycyclic polystannanes have not yet been documented. Accordingly, our efforts directed towards the development of a general synthetic strategy for the construction of polycyclic polystannanes will be discussed, as well as, the isolation of the first representative of this new class of compounds, the bicyclo[2.2.0]hexastannane derivative, 1. The formulation of new advanced materials based on the molecular and electronic structure of 1 will also be considered.

SPECIATION FOR ANALYSIS OF ORGANOMETALS AND ORGANOMETALLOIDS

J.R. Ashby and P.J. CraigSchool of Chemistry, Leicester Polytechnic, P.O. Box 143, Leicester.
LE1 9BH. U.K.

Recent developments in the analytical chemistry of organometallic compounds will be discussed, with an emphasis on the analysis from environmental matrices (viz. water, sediments). Analytical work with tin, lead, arsenic, antimony, germanium, selenium, mercury and sulphur will be covered. The main techniques involve a derivitisation with either hydride or ethyl generating reagents so as to produce a volatile organometallic analyte capable of chromatography, produced from a non-volatile environmental organometallic compound. The following compounds were reacted to produce analysable derivatives by the ethyl generation method referred to above - SnCl_2 , MeSnCl_3 , Me_2SnCl_2 , Me_3SnCl , Et_2SnCl_2 , Pr_3SnCl , BuSnCl_3 , Bu_2SnCl_2 , Bu_3SnCl , Ph_3SnCl , Ph_2SnCl_2 , PhSnCl_3 , cHex SnBr_3 , $\text{cHex}_2\text{SnBr}_2$, cHex_3SnBr , PbCl_2 , Me_2PbCl_2 , Me_3PbCl , Me_3PbOAc , HgCl_2 , MeHgCl , Me_3GeCl , Na_2Se , SeO_2 , Na_2SeO_3 , Na_2SeO_4 . The detection techniques used to identify the analytes were atomic absorption and mass spectrometries.

Some results will also be presented for the levels of butyl tin species in various U.K. sediments, using the methods described above.

References

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3. S. Clark and P.J. Craig, *Appl.Organometal.Chem.*, **2**, 33, 1988.
4. J. Ashby and P.J. Craig, *Sci.Total Environ.*, 1989 (in press).
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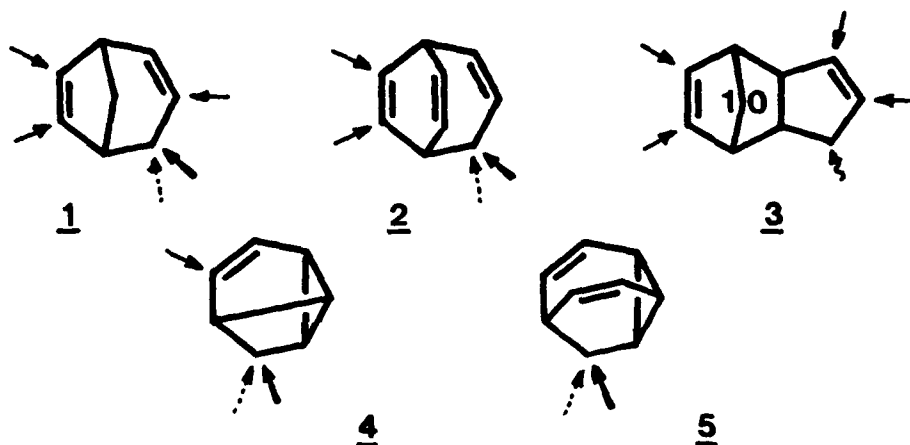
MOBILE STANNYL GROUPS
IN BI- AND TRICYCLIC HYDROCARBONS

SL07

Frank H. Köhler, Norbert Hertkorn, and Janet Blümel

Anorganisch-chemisches Institut, Technische Universität
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Stannyl groups have been introduced into the bi- and tricyclic hydrocarbons 1, 2, and 3. The isomers formed contain one or two stannyl groups in the positions indicated



in the figure by arrows. The stereochemistry follows from ^{119}Sn , ^{13}C , and ^1H NMR spectroscopy. Some of these new compounds are stable, others rearrange: stannyl derivatives of 4 and 5 are obtained from 1 and 2, whereas for 3 a stannyl group moves to the 10-position leaving the skeleton unchanged or a fragmentation of 3 occurs. 4 may react further to give stannylated styrene. The stannyl group is essential for these reactions the pathways of which will be discussed.

TIN (IV) COMPLEXES OF TRIAZENE-1-OXIDES

SL08

Ramadhar Sharma
P.G. Dept. of Chemistry
R.D. & D.J. College, Munger-811201, India.

Derivatives obtained by interacting organotin (IV) and tin (IV) halides with variedly substituted triazene-1-oxides (TH) are described. The derivatives are invariably six coordinate octahedral but orthohalo substituent to the N-C (Ar) bond of the triazene-1-oxides give five coordinate trigonal bipyramidal complexes. The aryl substituent effects on coordination potentialities of variably substituted bidentate/tridentate triazene-1-oxides are also discussed. The structure of the complexes has been deduced by using (i) elemental analyses, (ii) conductance measurements in nitromethane, (iii) molecular complexities in freezing benzene and, (iv) i.r. spectral studies in the range $20-4000\text{ cm}^{-1}$ at RSIC, Madras. A trans-halo bis (triazene-1-oxidato) tin (iv) complex for $\text{Sn T}_2\text{I}_2$ and a cis-halo bis analogue in the case of $\text{Sn T}_2\text{Cl}_2$ has been assigned.

Organotin (IV) compounds as also triazene-1-oxides are found to possess bactericidal properties. A comparative estimate of the biocidal activity of binary tin (IV) compounds, organotin (IV) compounds, various triazene-1-oxides and their tin/organotin (IV) has also been carried out using agar-agar plate diffusion-zone inhibition technique.

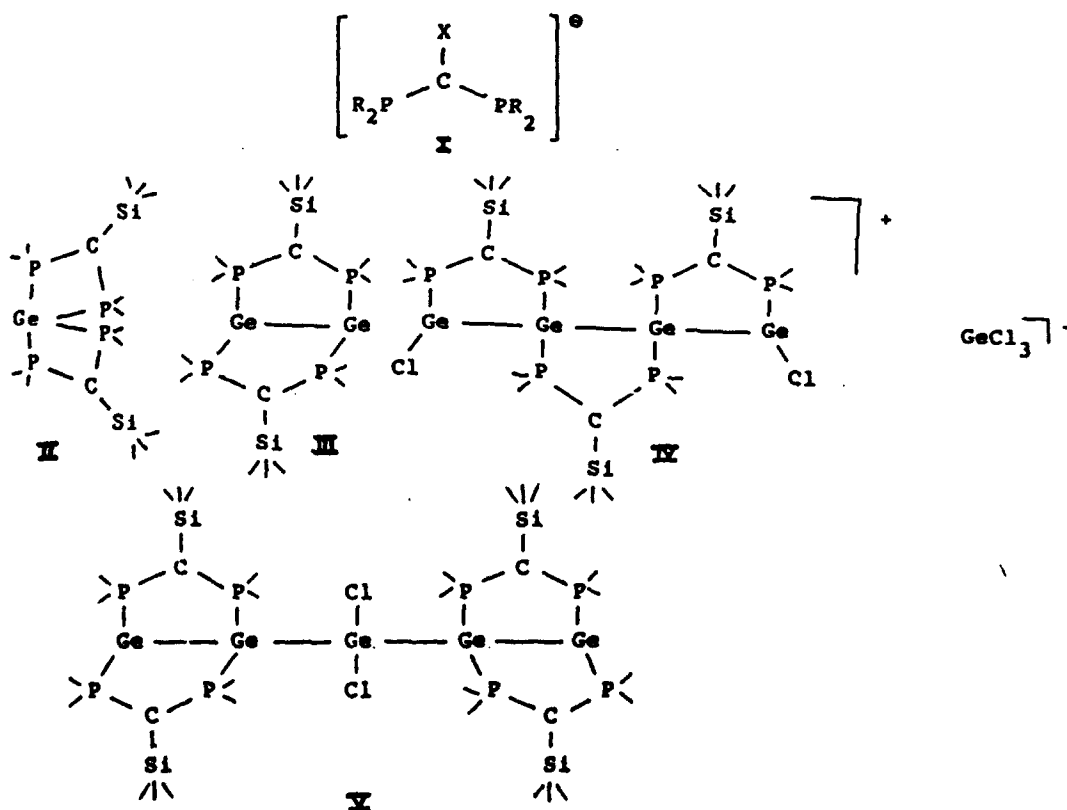
NOVEL LOW VALENT GERMANIUM COMPOUNDS WITH ORGANOPHOSPHORUS LIGANDS

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Anionic diphosphinomethanide ligands of type I are used to synthesize a variety of novel low valent germanium complexes, which are virtually unprecedented. These include e.g. mononuclear (II), dinuclear (III), tetranuclear (IV) and pentanuclear (V) species. Particular interesting by its novelty and unusual chemistry is III (formal oxidation state +1), which is not only an excellent ligand to transition metals, but exhibits also outstanding donor capacity to main group acceptors. Compound III thus mimics trends in phosphine coordination chemistry, giving rise to novel compounds with main group element-germanium bonds.

Some representative examples, including compounds with B-Ge, Al-Ge, Sn-Ge, Ge-Ge, S-Ge, I-Ge, and Cr-Ge, are given and the reactivity of III is compared to that of II.



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Mes: , CR₂: 

$$\text{Mes}_2\text{Ge}=\text{CR}_2 + \text{N}_2\text{CR}_2 \longrightarrow \left[\text{Mes}_2\text{Ge}=\text{N}-\text{N}=\text{CR}_2 \right] \xrightarrow{\times 2} \begin{array}{c} \text{Mes}_2\text{Ge}-\text{N}-\text{N}=\text{CR}_2 \\ | \quad | \\ \text{R}_2\text{C}=\text{N}-\text{N}-\text{GeMes}_2 \end{array}$$
$$\begin{array}{ccc} \text{RR}'\text{Ge}-\text{PAr} & \xrightarrow{\text{tBuLi}} & \text{RR}'\text{Ge}=\text{PAr} \\ \text{6} \quad \text{F} \quad \text{H} & & \text{4, 5} \end{array} \quad \text{Ar: } \text{C}_6\text{H}_4 \text{ with substituents X and Y} \quad , \text{RR}': \text{tBu}_2 \text{ 4} \\ \text{tBu, Mes} \text{ 5}$$
$$\text{tBu}_2\text{Ge}=\text{PAr} \xrightarrow{\quad} \text{tBu}_2\text{Ge}-\text{PAr} \xrightarrow{\text{solvent}} \text{tBu}_2\text{Ge(H)}-\text{P(H)Ar}$$

4

New aspects of the reactivity of 4, 5 and of previous synthesized germaphosphene $\text{Mes}_2\text{Ge}=\text{PAr}$, as well as original routes to novel unsaturated species of germanium and phosphorus, will be presented.

WHY DO Ge(II)-AMIDES, -ALCOHOLATES OR -THIOLATES DIFFER
FROM THE CORRESPONDING Sn(II)- AND Pb(II)-DERIVATIVES?

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Compounds of Ge(II), Sn(II), and Pb(II) which are similar in composition are often very different in their chemical behaviour as well as in their structures. For example, the polycyclic $Si_2(N^tBu)_6El_2$ with $El = Ge$ contains distinct dicoordinate germylene units while if $El = Sn$ the tin atoms are bonded to three nitrogen atoms. In the alcoholate series $[El(O^tBu)_2]_n$ with $El = Ge$ and Sn the molecules are dimeric ($n = 2$) whereas where $El = Pb$ the degree of polymerization is represented by $n = 3$. The thiolates $[El(S^tBu)_2]_n$ are even more versatile with regard to their structures: if $El = Ge$ the molecule is a centrosymmetrical dimer, soluble in benzene ($n = 2$), for $El = Sn$ the substance is polymeric and unsoluble in benzene ($n = \infty$), and with $El = Pb$ the compound is composed of three formula units and is again soluble in nonpolar solvents ($n = 3$). In the unsymmetrically substituted germylene and stannylene $GeCl(O^tBu)$ and $SnCl(O^tBu)$, which are coordination dimers, the chlorine atoms are "syn" with respect to the Ge_2O_2 plane while they are "anti" to the corresponding Sn_2O_2 plane in the tin derivative.

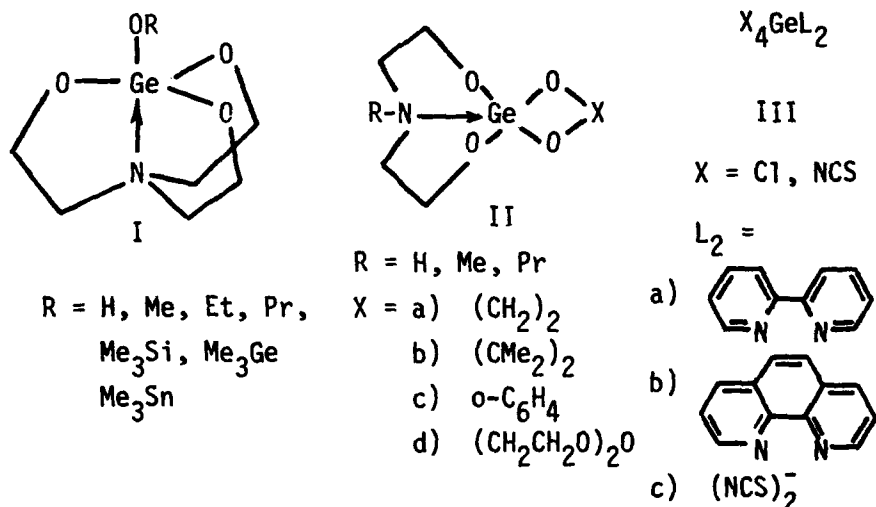
Syntheses, structures (X-ray) and the chemistry of these mostly new compounds will be discussed.

^{73}Ge NMR OF PENTA- AND HEXACOORDINATE Ge DERIVATIVES

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Until recently, germatranes (I) have been the only derivatives of hypervalent germanium studied by ^{73}Ge NMR. In the present study, ^{73}Ge resonance was observed for a series of new pentacoordinate Ge derivatives - 1,3-dioxa-6-aza-2-germacyclooctanes (germocanes, II) and ^{73}Ge chemical shifts of hexacoordinate Ge were determined for the first time in compounds of type III.



It was found that the transition of Ge atoms to the pentacoordinate state in II results in an upfield shift of the ^{73}Ge resonance by ca. -12 ppm relative to the tetracoordinate model compound $\text{Ge}(\text{OEt})_4$. This shift is smaller, as compared to that observed earlier for I (ca. -24 ppm). An increase in donor-acceptor $\text{N} \rightarrow \text{Ge}$ bond strength in II is accompanied by a remarkable broadening of the ^{73}Ge signal, making its detection difficult. Significantly increased ^{73}Ge shielding in compound IId ($\delta = -94$ ppm, R = H) suggests a pseudohexacoordinate state of the Ge atom.

In hexacoordinate Ge derivatives the ^{73}Ge shielding is increased by ca. 340 ppm relative to the tetracoordinate parent compounds. An additional upfield shift was observed when going to anion IIIc. ^{73}Ge and 2D EXSY ^{14}N NMR spectra indicate a decrease in ligand exchange rate in III, as compared to the tetracoordinate analogues. Additional data regarding the structure of compounds studied were obtained by ^1H , ^{13}C , ^{14}N , ^{15}N and ^{17}O NMR spectroscopy.

SYNTHESIS AND PROPERTIES OF BIOLOGICALLY ACTIVE
ORGANOGERMANIUM COMPOUNDS

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Three methods are proposed for the development of biologically active organogermanium derivatives. They involve modification of biologically active organic compounds by introducing organogermanium substituents, preparation of germanium analogues of drugs, and study of biological activity of structurally specific organogermanium compounds lacking organic analogues.

It was shown that representatives of many classes of organogermanium compounds were characterized by low toxicity (germesquioxanes, adamantylgermanes, many alkyl-, hetaryl- and carbofunctional germatranes). Thienylgermatranes were more toxic. Thereby, 2-substituted derivatives in the thiophene series showed the highest toxicity, whereas in the furan series, on the contrary, 2-substituted derivatives were less toxic than the 3-substituted ones. Organogermanium compounds in most cases possess lower toxicity than the corresponding organosilicon compounds and sometimes their carbon analogues. Toxicity of B-Me₃M-substituted propio- and isobutyrohydroxamic acids decreases in the sequence:



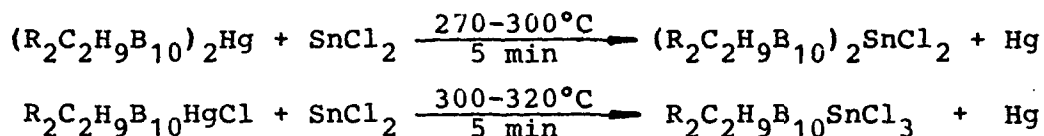
Their protective effect at hypoxia increases in the same sequence.

Germatranes possessing antitumour and neurotropic activity of the depressant type were synthesized.

Thienylgermatranes act as psychostimulants.

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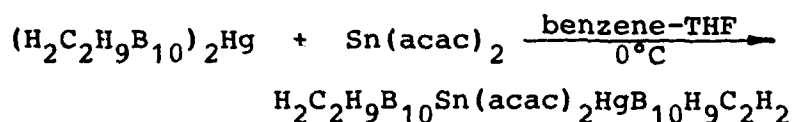
The derivatives of carborane containing sigma-bond between boron and tin atoms were obtained by the interaction of B-mercurated carboranes with fused stannous chloride:



Contrary to C(carborane)-Sn bond the B-Sn bond in carbora-nyltin chlorides is stable towards nucleophilic reagents, which makes it possible to replace chlorine atoms by the oxo-group under the action of an alkali in aqueous-etherial medium and by alkyl groups under the action of Grignard reagents.

Using gamma resonance spectroscopy method it was shown that the influence of the B(9)-carboranyl group is close to that of a methyl group.

The bimetallic Sn-Hg derivatives of carboranes were obtained by the insertion of tin(II) acetylacetonate into B-Hg bond¹:



The interaction of pentafluorophenyl derivatives of germanium with carboranylmcury compounds results in the formation of carboranyl compounds containing B-Hg-Ge-Ge-Hg-B, B-Hg-Ge or Ge-Hg-B-B-Hg-Ge chains².

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DIMETHYLGERMYLENE FROM 7-GERMANORBORNADIENE: UV-SPECTRUM,
REACTIVITY AND COMPLEXATION

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Dimethylgermylene ($\lambda_{\max} 380\text{nm}$, $\epsilon = 1.3 \cdot 10^3 \text{ l/mol} \cdot \text{cm}$) has been
detected in liquid phase in the flash photolysis of 7,7-
dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorbornadie-
ne (I) (heptane, 20° , $5 \mu\text{s}$) /1/.

The rate constants of reactions of Me_2Ge with (I) ($k = 1.2 \cdot 10^7 \text{ l/mol} \cdot \text{s}$), Me_3SnCl ($3.5 \cdot 10^8$), MeOH ($3 \cdot 10^7$), 2,2,6,6-tetra-
methyl-4-thiacycloheptyne (II) ($5 \cdot 10^8$), styrene ($7 \cdot 10^7$),
 CCl_4 ($1.2 \cdot 10^7$), O_2 ($2 \cdot 10^7$) have been determined.

The spectral and kinetic proofs of the formation of mole-
cular complex $\text{Me}_2\text{Ge} \cdot \text{PPh}_3$ (III) have been obtained. The
electronic absorption spectrum of (III) has a band with
 $\lambda_{\max} 370\text{nm}$. The molar extinction coefficient of (III)
($7.5 \cdot 10^3 \text{ l/mol} \cdot \text{cm}$) is more than that of Me_2Ge . The lifetime
of (III) ($2 \cdot 10^{-3} \text{ s}$, $[(\text{I})] = [\text{Ph}_3\text{P}] = 5 \cdot 10^{-5} \text{ mol/l}$) is ~ 5 times
more than the lifetime of Me_2Ge ($4 \cdot 10^{-4} \text{ s}$). The disappea-
rance of (III) is subordinated to the kinetic law of the
second order ($2k = 1.5 \cdot 10^9 \text{ l/mol} \cdot \text{s}$). The rate constants of
the reaction between (III) and Me_3SnCl ($1.0 \cdot 10^8$), (II) ($7 \cdot 10^7$), CCl_4 ($3 \cdot 10^6$) are less than those of Me_2Ge .

The photolysis of (I) in hydrocarbon glass (3-methylpenta-
ne, toluene, 77K) has been studied to compare spectral
data of Me_2Ge in solution and in matrix. However, in above-
mentioned conditions (I) does not generate Me_2Ge . The
yellow colour ($\lambda_{\max} 420\text{nm}$) originated in the matrix photo-
lysis could be explained by the formation of radicals,
which were detected by the ESR-technique.

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and O.M.Nefedov *Izv. Akad. Nauk SSSR, Ser.Khim.*, 1987,
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SYNTHETIC, STRUCTURAL AND BIOLOGICAL ASPECTS OF THE
COORDINATION COMPOUNDS OF GERMANIUM DERIVED
FROM HETEROCYCLIC THIO-IMINES

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ABSTRACT

The Synthesis and Structural aspects of some trigonal bipyramidal and octahedral complexes of germanium with thio-imines are described. These were derived by the condensation of 2-furaldehyde, 2-thiophene-carbaldehyde, 2-pyridinecarbaldehyde and 3-indolecarbaldehyde with 2-mercaptoaniline. The newly synthesized compounds have been characterized by elemental analysis, conductance measurements, molecular weight determinations and electronic, infrared, mass, ^1H and ^{13}C NMR spectral studies. Two representative ligands and their germanium complexes have been tested for their antifungal activity against *Helmenthosporium gramineum* and *Rhizopus oryzae*. The growth inhibition percentage has been calculated on the basis of the average diameter of the fungal colony.

SYNTHESIS AND REACTIONS OF CHLORODIORGANOTIN
DIALKYL PHOSPHATES

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Chlorodiorganotin dialkyl phosphates, $\text{ClR}_2\text{SnOP(O)(OR')}_2$ ($\text{R} = \text{Me, Bu, Ph}$; $\text{R}' = \text{Me, Pr}^n, \text{Pr}^i$), have been prepared in high yield by the insertion reactions of dialkyl phosphorochloridates with diorganotin oxides. These are hydrolytically stable, crystalline solids which are soluble in organic solvents and tend to disproportionate after melting into diorganotin dichloride and diorganotin bis(dialkyl phosphates) when heated under reduced pressure. All these compounds have been characterised by molecular weight, IR, multinuclear (^1H , ^{13}C , ^{31}P and ^{119}Sn) NMR and mass spectral data. These are strongly auto associated through bridging phosphato moieties and the degree of association is concentration dependent. As shown by the mass spectra, the association does not break completely even in the vapour state. The NMR parameters (e.g., chemical shifts and ^{119}Sn - ^1H , ^{119}Sn - ^{13}C , ^{119}Sn - ^{31}P coupling constants) have been correlated with the geometry around the tin atom in these compounds.

Various reactions of chlorodiorganotin dialkyl phosphates, such as adduct formation, insertion reaction and Sn-O-P bond cleavage etc. have been studied and a comparison with those of the corresponding dialkyl dithiophosphato derivatives of tin has been made.

Solid State Structure of Di-n-butyl-di(aminobenzoato) tin(IV) Compounds.

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&

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There are no reports on the structure of di-n-butyl di(aminobenzoato) tin(IV) compounds in solid state. Here, the structure of the compounds $n\text{-Bu}_2\text{Sn}(\text{O}_2\text{C}_6\text{H}_4\text{NH}_2)_2$, [where NH_2 group is at ortho, meta or para position] is investigated using infrared (νNH_2 , 3470, 3410; νCO_2 , 1620, 1380 cm^{-1}) Mass (pmi; $m/e = 506$), CP MAS ^{119}Sn NMR (-530.4 to -529.2 ppm) and Mössbauer (l.s. = 1.5 - 1.47; Q.S. = 3.80 - 3.57 mm sec^{-1}) spectral data. These studies suggest the solid diorganotin dicarboxylates to be monomeric, slightly intermolecularly hydrogen bonded, six coordinated tin compounds.

Single crystal x-ray diffraction data of the o-aminobenzoato derivative (298K); space group = $R\bar{3}$; $a = 16.029(9)\text{Å}$, $\alpha = 105.19(8)^\circ$ (for rhombohedral axes); ($a = 25.45(2)\text{Å}$, $c = 19.13(2)\text{Å}$ with hexagonal axes). $z = 6$, $D = 1.40\text{ Mg m}^{-3}$; $\lambda = 0.7107\text{ Å}$; $R = 0.062$; $RW = 0.063$ for 1131 unique reflections [$1 > 3\sigma(1)$] support highly irregular and strained octahedral geometry in the solid state. Such stereochemistry for diorganotin dicarboxylates is not yet reported.

Preparation and Characterization of some Lead (II) Phenoxides

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Abstract

Although metal alkoxides have been extensively studied over the years¹ but the chemistry of their analogues metal phenoxides remains relatively neglected². This paper describes the preparation and characterization of some lead(II) phenoxides.

4-Nitrophenol reacts with lead (II) carbonate or yellow lead (II) oxide in aqueous medium to form a yellow, water insoluble compound. This has been characterized as $Pb(OH)L$, where L = 4-nitrophenoxide ion) on the basis of elemental analyses, 1H NMR, ^{13}C NMR, electronic, reflectance and infrared spectra. Further, the identity of this compound has been confirmed by isolating the same compound obtained by the reaction of lead (II) acetate with sodium 4-nitrophenoxide in aqueous medium. In a similar way, a variety of lead (II) compounds $Pb(OH)L'$ where L' = 4-aldehydephenoxide, 4-chlorophenoxide, 4-methylphenoxide or 2,4-dichlorophenoxide ion) have been prepared and characterized. The experimental details and results shall be presented.

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GENDER RELATED TOXICITY OF TRI-n-BUTYLTIN CHLORIDE

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An initial study on the gender related acute toxicity of tri-n-butyltin chloride (TBTC_l) using Long Evans rats has indicated that the male morbidity is greater than the female death rate in standard acute testing. The TBTC_l was emulsified in corn oil (25 mg/mL) using a tissue grinder. Approximately 0.75 mL (0.26 mM/kg) of TBTC_l were administered to each rat. The animals were allowed to eat and drink ad libitum and observed for eight days. The morbidity of the male rats was nearly three times the death rate of female rats indicating that tri-butyltin compounds are more toxic towards male and female animals in acute studies.

THE CORRELATION OF FUNGICIDAL ACTIVITY
AND STRUCTURAL VARIATION FOR TRI-ARYLTIN ACETATES,
OXIDES, AND HYDROXIDES

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Several series of Ar_3SnOAc , $(\text{Ar}_3\text{Sn})_2\text{O}$, and Ar_3SnOH ($\text{Ar}=\text{p-ZC}_6\text{H}_4$) with $\text{Z}=\text{F}$, Cl , CH_3 , CH_3O , etc., have been synthesized for comparison with the well-known fungicides Brestan and Du-ter. Fungicidal activity was assessed by both radial growth and spore germination assays. In general, replacement of p-H by F, Cl, or CH_3 does not lead to a change in fungicidal activity although some slight decrease is noted in some cases. However, with $\text{Z}=\text{CH}_3\text{O}$, fungicidal activity effectively vanishes. While this may reflect the steric requirements of the active sites involved in the various fungicidal processes, the electronic changes caused by the p- CH_3O group cannot be neglected. Thus IR data show all Ar_3SnOAc are polymeric except for the p- CH_3O system which X-ray crystallography confirms as monomeric with an asymmetric chelating acetate group ($d(\text{Sn}-\text{O}_1)2.060\text{\AA}$; $d(\text{Sn}-\text{O}_2)2.747\text{\AA}$), like Cy_3SnOAc . Tin-119 NMR results confirm the strong electron-donating nature of the methoxy group in these compounds in agreement with earlier data for the halide analogues.

PATHWAYS IN THE THERMOLYSIS OF ORGANOTIN COMPOUNDS

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MOCVD is now firmly established as a synthetic method which produces thin films of materials the properties of which can be vastly different from those of the corresponding bulk. This is exemplified by tin(IV) oxide, which in the form of a gel or microcrystalline powder exhibit good ion-exchange and catalytic oxidation properties, but as a thin film on glass is very hard and mechanically strong. Thin films of tin(IV) oxide are most commonly laid down by MOCVD of organotin compounds. Several compounds have been employed for this purpose including tetramethyltin, methyltin chlorides, and dialkyltin diacetates, although the preferred precursor molecule is *n*-butyltin trichloride. In spite of the commercial importance, little is known of the fundamental chemistry of the reactions involved in these decomposition processes, and so here we describe the major reaction pathways we have identified.

Examination of the oxidative thermolysis of organotin compounds shows that the reactions do not usually take place in the gas phase. Rather they are invariably mediated by the available surface with which they are in contact, and proceed via an initial dissociative chemisorption step involving Sn-C bond fission forming surface organostannyl, R_3Sn-I , and surface alkoxy, $RO-I$, groups. Further loss of organic groups from the tin atoms of the surface R_3Sn-I groups occurs via two major routes depending on the nature of the organic group. Groups such as methyl, vinyl or phenyl, which do not possess a hydrogen at a sp^2 -hybridised β -carbon atom, undergo cleavage affording, respectively, methane, ethene and benzene. However, those which do, eg. ethyl, *n*-propyl, *iso*-propyl, *n*-butyl and *iso*-butyl, readily eliminate the corresponding alkene, ethene, propene, but-1-ene and *iso*-butene. With increasing Brønsted acidity of the available surface, mixtures of *cis* and *trans* but-2-enes are formed rather than but-1-ene, indicating the occurrence of a surface carbonium ion-promoted isomerization process. Concurrent to these two pathways is oxidation of the surface alkoxy groups to the corresponding surface carboxylate and ultimately to the desorption of carbon dioxide. Desorption at intermediate stages in this oxidation process gives rise to transiently-observed alcohols and carbonyl compounds. Additional reaction pathways are possible for functionally-substituted organotin compounds, and in particular reductive-elimination has been observed for organotin hydrides, chlorides and carboxylates.

MULTINUCLEAR SOLID-STATE NMR OF
ORGANOTIN CHALCOGENIDES

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The solid state NMR spectra, measured using MAS, will be reported for ^{13}C , ^{119}Sn and where appropriate for ^{77}Se or ^{125}Te for the compounds $(\text{Me}_2\text{SnE})_3$, $(\text{Me}_2\text{Sn})_3\text{E}_2$, $(\text{t-Bu}_2\text{SnE})_2$, $(\text{t-Bu}_3\text{Sn})_2\text{E}$, $\text{E} = \text{S}$, Se or Te . Excellent, high-resolution spectra were obtained using cross-polarisation techniques.

The solid state NMR data are interpreted in the light of the known crystal structures for these compounds, although a simple correlation between the NMR and structural parameters is not observed. In the case of $(\text{Me}_2\text{SnTe})_3$, the NMR data led us to a redetermination of the crystal structure since the NMR data was not consistent with the reported structure.

For ^{119}Sn and ^{125}Te , a correlation between NMR chemical shifts and quadruple coupling constraints observed in Mössbauer spectra will be discussed.

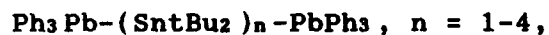
HIGH-RESOLUTION SOLID-STATE ^{119}Sn AND ^{207}Pb NMR - A NEW ANALYTICAL
TOOL IN ORGANOTIN AND -LEAD CHEMISTRY

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Over the last few years considerable improvement in probe construction and spectrometer hardware has made high-resolution solid-state NMR spectroscopy a truly multinuclear spectroscopy. Particularly, ^{119}Sn and ^{207}Pb appear to be attractive nuclei, owing to their favourable NMR-properties and to the rich chemistry of the respective elements. Especially in the field of organometallic chemistry the whole suite of high-resolution solid-state NMR techniques (CP, MAS, HPD) can be used to its full advantage for the observation of metal nuclei. Recently, we have investigated a whole range of different organotin and -lead compounds, using the above mentioned techniques [1-4], and reliable standard conditions for the routine use of these experiments are now established.

We would like to present some of our results concerning intra- and/or intermolecular association, polymorphism, observation of J-coupling in the solid state (including pulse experiments which allow further reduction of the observed linewidths), crystallographic inequivalences, anisotropy of the chemical shielding tensor. All these topics will be discussed using examples of ^{119}Sn and ^{207}Pb high-resolution solid-state NMR spectra of a variety of organotin and -lead compounds.

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ORGANOMETALLICS WITH OPTO-ELECTRONIC PROPERTIES

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Reaction of R_3PbLi with $\text{I}-(\text{SntBu}_2)_n-\text{I}$ gives the title series of compounds containing Pb-Sn bonds. To link this bonds, the usage of solvents with moderate ability to solvate (e.g. ether) gives better results than the usage of good coordinating solvents (e.g. thf). The former class of solvents forces back side reactions ultimately leading to products of fission or rearrangement.

The four chain compounds are reliably identified by means of nmr spectroscopy. ^{207}Pb - and ^{119}Sn -nmr spectra complement one another in yielding a unified frame of chemical shifts and coupling constants. Intense electronic absorption maxima (ϵ 40-60 \cdot 10⁵ cm²/mol) exhibit a distinct red-shift with increasing chain length (297-382 nm).

The terminal distances Pb-Sn extend from 2.82 to 2.85 and to 2.88 Å, and shorten again to 2.86 Å in the six-membered chain. The central distances Sn-Sn lengthen uniformly from 2.87 to 2.93 Å.

CARBONYL SUBSTITUTED VINYLSTANNANES: PREPARATION AND
PROTODESTANNYLATION

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In recent years there has been considerable interest in the chemistry of vinylstannanes. Our studies have centered on the preparation of a number of vinylstannanes, substituted at either the proximate or remote carbons of the double bond by a ketone or ester group. Compounds of these structures can be prepared with both regioselectivity and stereoselectivity by Pd(0) catalyzed hydrostannation of an appropriate conjugated carbonyl substituted alkyne. Ketones and esters generally lead to the same regioselectivity but opposite stereoselectivity. Free radical catalyzed hydrostannation results in the opposite regioselectivity and mixtures of stereoisomers.

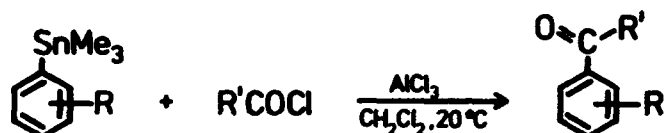
Protodestannylation appears to take place by two different mechanisms depending on whether the carbonyl is β to the stannyl group or α to the stannyl group. In the former case a normal S_E2 mechanism leads to products with retention of configuration at the double bond. In the latter case the proton apparently coordinates with the carbonyl oxygen and subsequent loss of the stannyl group results in formation of an allenol intermediate. Transfer to the proton from oxygen to carbon from either face gives a stereoisomeric mixture of products.

STANNYL-MEDIATED AROMATIC SUBSTITUTIONS OF HIGH REGIOSELECTIVITY

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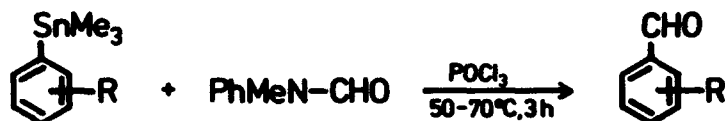
Stannyl cations proved to be powerful leaving groups¹⁾ from aromatic compounds. This allows ipso substitutions under mild conditions. Now, the scope of electrophilic aromatic substitutions is broadened up considerably, and directing influences of other substituents can be overcome. Regioselective substitutions at places not accessible for conventional S_E ar reactions so far can easily be carried out now. This will be demonstrated by a number of selected examples.

a) Friedel-Crafts acylation under very mild conditions:



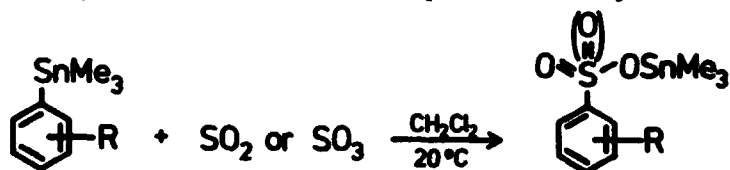
R = m-Me, p-Me, p-OMe, p-Cl; R' = Me, tBu, Ph

b) Stannyl-mediated Vilsmeier formylation:



R = H, o-Me, m-Me, p-Me, o-OMe, p-Cl

c) Sulfur electrophiles lead to stannyl esters of arylsulfonic or arylsulfonic acids²⁾ in quantitative yields:



R = H, o-Me, m-Me, p-Me, o-Et, o-OMe, m-OMe, p-OMe

- 1) Early work: C. Eaborn, J. Organomet. Chem. **100**, 43 (1975)
- 2) The stannyl cation is scavenged by the acid anion forming the ester. For SO_2 , this has been described as an insertion: U. Kunze, Rev. Si, Ge, Sn, Pb Comp. **2**, 251 (1977)

**α -TRIBUTYLSTANNYLACETALS : PREPARATION AND USE
AS "d¹ UMPOLUNG" REAGENTS**

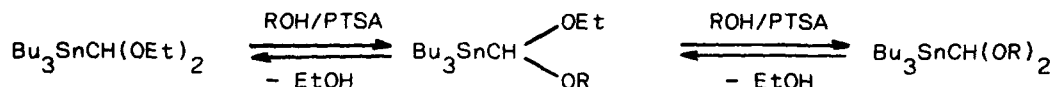
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Diethoxymethyltributyltin and dimethoxymethyltributyltin have been previously obtained from the reaction of orthoformates with tributylstannylmagnesium chloride (1) however, the presence of more labile alkoxy-groups appears to be useful for the access to hydroxy-derivatives when the α -tributylstannylacetals have been modified into α -stannylethers by reaction at the acetal function (2).

In this communication we report a route to increase the variety of available α -stannylacetals using a transacetalisation reaction :



The new α -stannylacetals have been obtained in 70-85 % yields and the behaviour of benzyloxy- and allyloxy-derivatives has been examined in substitutions at the acetal function. The reactivity of the obtained α -stannylethers has been explored (transmetallation with butyllithium or cross-coupling in the presence of palladium catalysts).

An interesting result is the generation and mainly the trapping of masked formylanions from α -tributylstannylacetals because after an initial successful attempt (1) we have failed during years to reproduce this result. Herein we analyze the suitable experimental conditions to trap "LiCH(OR)₂" by various electrophiles and we obtain reasonable yields in the expected products after substitution or addition reactions.

1 - J.P. QUINTARD, B. ELISSONDO and M. PEREYRE ; J. Organometal. Chem. 212 (1981), C31.

2 - J.P. QUINTARD, A. DUCHENE, G. DUMARTIN, B. ELISSONDO and J.B. VERLHAC ; Si, Ge, Sn and Pb Compounds 9 (1986), 241.

THE INVESTIGATION OF TIN (II, IV) CHLORIDE INTERACTION
WITH SOME REPRESENTATIVES OF AZOLES SERIES

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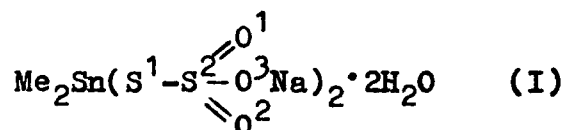
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29 new coordination compounds of 1:1 and 1:2 composition, isolated from THF, alcohol and benzene solutions, were obtained as a result of complexformation reactions of tin (II, IV) chloride with imidazole, triazole and their aliphatic and aromatic derivatives. All reactions were carried out under flowing dry nitrogen. The composition and individual properties of the synthesised adducts were determined by elemental and X-ray phase analyses. IR (4000 cm^{-1} - 200 cm^{-1}), NMR (^1H , ^{13}C , ^{119}Sn) and X-ray PES data indicate to the coordination of the pyridine-like nitrogen atom of the imidazole ring of ligands to the tin atom. This conclusion was confirmed by the results of X-ray structural investigation of monocrystals of adducts formed by tin (II) chloride with 1-vinylimidazole and 1-benzylimidazole. They showed the influence of the nature of derivatives in ligand molecules on the structural configuration of complexes and made possible to make an assumption about their dimer and polymer structure. The comparison of results of quantum-chemical calculation, carried out for a number of the synthesised compounds, with the IR and X-ray PES investigation data, confirms the conclusion about their tetrahedral structure.

THE FIRST ORGANOTIN ANALOG OF BUNTE SALT
AND ITS STRUCTURE

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Sodium S-alkylthiosulphonates type of $RS-SO_2-ONa$ (R-organic group, classical Bunte salts) are widely used in organic synthesis. Some other analoges with R-organometallic group are unknown. Dimethyltin 0,0'-dinatrium thiosulphonate (I) was synthesised as one of Bunte salts by the reaction of Me_2SnCl_2 with $Na_2S_2O_3$ in water-medium at room temperature (yield 40%):



The reaction also gives rise to dimethyltin sulphide and unsoluble substance (coordination polymer perhaps ?) brutto-composition of $C_2H_6O_{1,5}S_{0,8}Sn$. The scheme of this reaction and some properties of the compound I will be discuss. The structure of I has been confirmed by X-ray analysis (diffractometry, 1515 independent reflections with $J > 2\sigma$, refinement with anisotropic thermal parameters for all atoms, $R=0.048$). The Sn and S^2 atoms are bounded throught the S^1 atoms and have a distorted tetrahedral coordination. The Sn- S^1 , Sn-C and S^1-S^2 bond distances equal 2.473(2), 2.14(1) and 2.075(3) Å respectively. The O^2 , O^3 atoms and H_2O molecule with its symmetrical equivalents form a distorted octahedral at the Na atom. The Na-O distances in octahedral lies in range 2.305(7)-2.475(7) Å. Coordinative polyhedrons of the Sn- S^2 and Na atoms are connect by common faces and tops and form a three-dimentional tracery framework in crystal.

Infrared Characterization of some mono and polyorganotin adducts

by Abdou Salam SALL and Libasse DIOP^{*}

Laboratoire de Chimie Minérale

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Université Cheikh Anta DIOP

DAKAR - SENEGAL

Abstract

Adducts such as $\text{Sn}\phi_3\text{Cl Br}^-$, $(\text{Sn}\phi_3\text{Cl})_2\text{I}^-$, $(\text{Sn}\phi_3\text{Cl})_2\text{Cl}^-$, $(\text{Sn}\phi_3\text{Cl})_3\text{Cl}^-$ have been synthesized and structures proposed on the basis of their i.r spectra. The polynuclear compounds contain Sn-Cl-Sn bridges. Except the last compound, the SnC_3 skeleton is planar. $\text{Sn}\phi_3\text{X} \cdot n\text{Sn}\phi_3\text{Cl}$ ($\text{X} = \text{Br}, \text{I}$; $n = 1, 2, 3$) have been synthesized and structures proposed. In all these compounds $\text{Sn}\phi_3\text{Cl}$ behaves as a Lewis acid.

The compound $(\text{Sn}\phi_3\text{I})_2 \cdot \text{Sn}\phi_3\text{Cl}$ has been isolated and a structure proposed. In this compound $\text{Sn}\phi_3\text{Cl}$ plays a role of Lewis base.

SPECTRAL CHARACTERISTICS AND FORMATION CONSTANTS FOR ELECTRON DONOR
ACCEPTOR COMPLEXES OF ORGANOTIN COMPOUNDS WITH TETRACYANOETHYLENE.

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Charge-transfer absorption bands were observed in chloroform solutions of trialkyltiniodides (R_3SnI), tetraaryl tin compounds ($(XC_6H_4)_4Sn$) and methyltinaryl compounds of the type $(CH_3)_3SnC_6H_4X$ with tetracyanoethylene as acceptor.

Formation constants, K_c , for the formation of a 1:1 electron donor acceptor (EDA) complex were determined for all those complexes where the conditions demanded by Person's criterion were satisfied. From the charge transfer energy $h\nu_{CT}$, the formation constants and other spectral characteristics, and their dependence upon changing the alkyl moiety R, we were able to establish that the lone pair halide electrons are the preferential donor site in organotiniodides.

Using an appropriate deconvolution programme it was possible to determine two absorption maxima for EDA complexes of tetracyanoethylene with donors of the type $(XC_6H_4)_4Sn$ and $(CH_3)_3SnC_6H_4X$. The two charge transfer absorption maxima are ascribed to two transitions $h\nu_{CT1}$, $h\nu_{CT2}$ from two closely spaced energy levels in the donor molecule to the lowest unoccupied molecular orbital of the acceptor, rather than to the occurrence of the free tetracyanoethylene radical anion. The degree of energy splitting $h\nu_{CT2} - h\nu_{CT1}$ is explained by a mixing of molecular orbitals from the aromatic moiety and the substituents.

Using an experimental relationship between the charge-transfer energy and the ionisation potential I_p of the donor, we predict the unknown I_p for several substituted aromatic tin compounds.

Knowing the experimentally determined enthalpy of formation and the charge-transfer energy it was possible to derive the different energy contributions to the formation of these EDA-complexes and to their electrontransfers.

**NMR Investigation of Diorganoyltin(IV)dihalide and
Triorganoyltin(IV)halide Complexes with Secondary Phosphines and
Diorganoylphosphino-N-phenyl(thioformamido) Ligands**

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Phosphorus-31 and tin-119 NMR spectroscopies have been used to study the formation of a series of organoyltin(IV)phosphine and phosphido complexes $R_2SnX_2(HPR'_2)$, $R_2SnX(PR'_2)$ and $R_2Sn(PR'_2)_2$ (where $R = Ph, Me, Bu$; $R' = c-C_6H_{11}, Ph$; $X = Cl, Br$) in dichloromethane solution. Tin-119 chemical shifts indicate that $R_2Sn(PR'_2)_2$ are four coordinate whereas $R_2SnX_2(HPR'_2)$ and $R_2SnX(PR'_2)$ are five coordinated, the latter probably being dimeric via bridging halides. PhNCS inserts into the Sn-P bonds of $R_2SnX(PR'_2)$ and $R_2Sn(PR'_2)_2$ to give the new series of tin compounds $R_2SnX[R'_2PC(S)NPh]$ and $R_2Sn[R'_2PC(S)NPh]_2$ where ligand coordination is through the sulphur and nitrogen atoms resulting respectively, in five and six coordination about the tin atom. The series $R_2SnX[R'_2PC(S)NPh]$ and $R_2Sn[R'_2PC(S)NPh]_2$ may also be generated by reaction between diorganophosphino-N-phenylthio-formamide ligands, $R'_2PC(S)N(H)Ph$ and diorganoyltin(IV)dihalides; ligand deprotonation is spontaneous in one case (for $Ph_2SnX[(c-C_6H_{11})_2PC(S)NPh]$) whereas addition of base is necessary to generate the other members of the series.

The tin complexes $R_3Sn[R'_2PC(S)NPh]$ are always four coordinated when $R' = c-C_6H_{11}$, the ligand being S-bonded to tin. However where $R' = Ph$, the complexes $R_3Sn[R'_2PC(S)NPh]$ exist as both S- and N-bonded isomers when formed by reaction between R_3SnCl , $Ph_2PC(S)N(H)Ph$ and base, but only the S-bonded isomer is formed from the insertion reaction of PhNCS into R_3SnPPh_2 .

P06

STRUCTURAL AND ELECTRONIC REQUIREMENTS FOR THE INTERACTION OF
STANNYLENES WITH CARBON-CARBON MULTIPLE BONDS

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Recent interest in the chemistry of the Group IVB carbene
analogues, $R_2M:$ ($M = Si, Ge, Sn$), has centered on the reactions of
these species with carbon-carbon multiple bonds. Our synthetic
efforts directed towards the synthesis of stannacyclopropene and
stannacyclopropane derivatives from the reaction of diorgano
stannylidenes ($R_2Sn:$) with alkynes and alkenes, respectively, will
be discussed. Results obtained from *ab initio* molecular orbital
calculations concerning the molecular and electronic structure
and stability of the parent metallacyclopropene series, $c-$
 $[XH_2MC_2H_2]$ ($X = H, F$), will also be presented.

THE REACTIONS OF TIN HALIDES WITH CARBONYLMOLYBDENUM
COMPLEXES

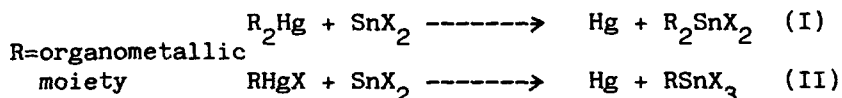
P07

CLAVEAGE OF MOLYBDENUM-TIN AND MOLYBDENUM-MERCURY BONDS

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Previously it has been shown that carbonyl compounds with metal-tin bonds could be synthesized by reaction of tin (II) halides and carbonyl complexes having mercury-metal bonds (eqns. I and II)(1,2,3).



However by reaction of tricarbonyl- π -cyclopentadienyl complexes of molybdenum with SnX_2 the $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{SnX}_3$ derivative was obtained by both routes (I and II).

The path of reactions is not clear; however it appears that the reactivity of mercurial compound with SnCl_2 depends of the stability and the nature of the mercury metal bond.

We are now studying related reactions of compounds containing HgOCOCF_3 groups.

We report the reactivity of $\text{Cp}(\text{CO})_3\text{MoHgOCOCF}_3$ with SnX_2 and SnX_4 . The $\text{Cp}(\text{CO})_3\text{MoHgOCOCF}_3$ was obtained in two different routes: by reaction of $[\text{Mo}(\text{CO})_3\text{Cp}]_2\text{Hg}$ or $\text{Cp}(\text{CO})_3\text{MoSnPh}_3$ with mercury trifluoroacetate. In the last reaction we have observed different compounds depending on the molar ratio of reactants and the reaction solvent.

We also report the reactivity with Sn(II) and Sn(IV) halides of carbonylmolybdenum complexes containing dpmm and dppe as P-P donor ligands and bpy, phen, dmp as NN donor ligands.

1. F. Bonati and G. Wilkinson; J.Chem.Soc. (1964), 179.
2. F. Bonati, S. Cenini and R. Ugo; J. Chem. Soc. A, (1967) 932.
3. P. Hackett and A.R. Manning; J. Chem. Soc., Dalton Trans., (1972) 2434.

THE REPEAT DISTANCE IN TRIORGANOTIN (IV) POLYMERS

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The repeat distance in carboxylate-bridged triorganotin (IV) carboxylate polymers has been defined as the ratio of the unit cell length that is parallel to the axis of propagation of the polymer to the number of monomeric units this length covers [1]. In the case of class 2 zig-zag polymeric chains [2] where triorganotin (IV) units are bridged by a second row atom such as F, O or N, the repeat distance is in a fairly narrow range with an average value of 4.25 Å. This value seems to be characteristic of class 2 polymers with second row bridging atoms (X) and angles Sn-X-Sn ranging from 128 to 150°. By means of the concept of repeat distance we can get interesting structural information just from the unit cell constants which can be obtained from powder X-ray diffraction data. That can be particularly useful when suitable single crystals cannot be obtained or when disorder prevents a full structure determination. In the case of triorganotin (IV) compounds, we can suspect that they are not class 2 polymers if their unit cell constants are not compatible with a repeat distance of ca. 4.25 Å. For those compounds, likely possibilities would be: i) a monomeric structure, ii) a class 1 polymeric chain with a linear Sn-X-Sn arrangement [2], and iii) bridging through two different atoms rather than a single one. These ideas will be applied to $(\text{Me}_3\text{SiCH}_2)_3\text{SnF}$, $\text{Ph}_3\text{Sn-NCO}$, $(\text{C}_6\text{H}_{11})_3\text{SnF}$ and $(\text{C}_6\text{H}_{11})_3\text{SnOH}$, in order to illustrate the structural information which can be obtained.

- [1] S.W. Ng, C. Wei and V.G. Kumar Das, J. Organomet. Chem., 345 (1988) 59.
[2] K.C. Molloy and K. Quill, J. Chem. Soc. Dalton Trans., (1985) 1417.

Novel Crystalline Hydrolysis Products of a Monoorganotin trihalide

P09

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In opposition to the tri- and diorganotin halides there is little known about the intermediates and final products in the hydrolysis of monoorganotin trihalides. Until now only the structures of two hydrated monohydroxy compounds $\text{RSn(OH)Cl}_2 \cdot \text{H}_2\text{O}$ were examined by X-ray diffraction methods.

In case of i-PrSnCl_3 it was possible for the first time to isolate and characterize not only the compound $\text{i-PrSn(OH)Cl}_2 \cdot \text{H}_2\text{O}$ (1) but also a $(\text{i-PrSn})_9\text{O}_8(\text{OH})_6\text{Cl}_5$ molecule (2) and the $[(\text{i-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion (3). Whereas 1 is formed when the trihalide is exposed to air, 2 and 3 could be prepared by 'recrystallisation' of $\text{i-PrSn(OH)}_2\text{Cl} \cdot 3/4\text{H}_2\text{O}$ in DMSO (2), DMF (3) or DMPU (3).

1 shows the same dinuclear molecular structure like the other monoorganotin hydroxide dihalide monohydrates: two octahedrally coordinated tin atoms are bridged by two hydroxyl groups. Within the four-membered rhombic Sn-O ring the bond lengths (204.6/217.1 pm) are depending from the position of the oxygen atom with regard to the organic group.

The pyramidal cage structure of 2 is built up of trigonal-bipyramidal and octahedral tin atoms linked by μ_3 -oxygen atoms and μ_2 -hydroxyl groups. With little exceptions the individual Sn-O bond lengths (196.9 - 218.1 pm) are determined by the position of the oxygen atom within the coordination polyhedra of the tin atoms. The crystal structure of 2 is completed by six DMSO molecules, from which four are involved in strong hydrogen bridges to hydroxyl groups of the organometallic molecule.

The football-shaped ion 3 is found in the compounds $\underline{3} \cdot \text{Cl}_2 \cdot 3\text{H}_2\text{O}$, $\underline{3} \cdot \text{Cl}_2 \cdot 2\text{DMF}$ and $\underline{3} \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{DMPU}$. Its tin atoms are distorted icosahedrally arranged and square-pyramidally and octahedrally coordinated, whereas the oxygen atoms are trigonal-planar or trigonal-pyramidal surrounded by three and the hydroxyl groups by two tin atoms. Sn-O bond lengths (201.7 - 215.5 ppm) show a similar dependence on the stereochemistry of the concerned atoms like those in 2, although they are influenced by secondary building units like six- or four-membered Sn-O rings.

SYNTHESIS AND ^{19}F NMR STUDY OF UNSYMMETRICAL TRIARYLTIN
CHLORIDES AND THEIR ADDUCTS WITH PYRIDINE.

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Earlier studying the role of coordination in electron transmission of metal-containing bridging systems it was established that the transfer from inert solvents to pyridine is accompanied by strong decrease of transmissive ability (TA) of $\text{Ar}_3\text{SnXC}_6\text{H}_4\text{F}-4$ (I, $\text{X} = \text{S}$) and weak decrease of TA of I ($\text{X} = \text{O}$). It was suggested that the distinctions observed were probably due to different intensity of coordination in solvatocomplexes $\text{Ar}_3\text{SnXC}_6\text{H}_4\text{F}-4 \cdot \text{Py}$ (II) formed in pyridine solutions. To clear up the question it was necessary to study TA of tin-containing compounds, forming in contrast to I strong undissociative complexes with pyridine.

In the present work the comparative ^{19}F NMR study of two series of compounds $\text{Ar}_2\text{Sn}(\text{Cl})\text{C}_6\text{H}_4\text{F}-4$ (III) and $\text{Ar}_2\text{Sn}(\text{Cl})\text{C}_6\text{H}_4\text{F}-4 \cdot \text{Py}$ (IV) was carried out in different solvents. For the synthesis of unsymmetrical triaryltin chlorides III the optimum scheme and conditions of synthesis were worked out. The structure of III and IV has been proved by the ^{19}F and ^{119}Sn NMR.

Analysis of statistical treatment of δF for III and IV allowed to make the conclusion that the electron transmission in both systems was similar. Therefore, the efficiency of transmission of substituent electron effects in tin-containing compounds, forming the strong complexes, does not depend on the participation of bridging tin atom in coordinating interactions. It was concluded that the low TA of I ($\text{X} = \text{S}$) in pyridine solution is the distinctive feature of weak coordinating interactions only and it arises from variation of ratio of complexes II and free molecules I in solution under the influence of substituents in Ar.

THE PREPARATION AND STRUCTURE OF SOME TIN (II)
FLUOROCOMPLEXES

P11

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Rapid exchange of fluoride ion among different tin fluorocomplexes has been shown by NMR ^{19}F study of $\text{Sn}^{2+}\text{-F}^{-}\text{-H}_2\text{O}$ system. With the increasing F/Sn ratio in the aqueous solution the complexes $\text{SnF}(\text{H}_2\text{O})_2^{+}$, $\text{SnF}_2(\text{H}_2\text{O})$ and SnF_3^{-} are formed.

The interaction of SnF_2 and SbF_3 in aqueous solution resulted in the formation of the compound $3\text{SnF}_2\cdot\text{SbF}_3$. The structural units in this compound are the neutral molecules SnF_2 and SbF_3 with the shortest distances of $2.063(8)\text{-}2.086(3)\text{\AA}$ for Sn-F and of $1.94(1)\text{-}1.990(9)\text{\AA}$ for Sb-F. The general structural pattern is described as the packing of SnF_2 molecules which formed polymeric chains by apical joining of SnF_3E and SnF_4E polyhedra, as well as of SbF_3 molecules.

Complexes of the composition $\text{M}(\text{H}_2\text{O})_6(\text{SnF}_3)_2$ ($\text{M}=\text{Zn}, \text{Cd}$) were prepared by addition of the fresh suspension of $\text{M}(\text{OH})_2$ to the aqueous solution of SnF_2 . These compounds have been shown to be isostructural and to realise monomeric pseudo tetrahedral complexes with the lone pair in the apex and strong covalent bonds Sn-F with the distance range $2.055(4)\text{-}2.057(4)\text{\AA}$ and angles $84.5(2)\text{-}86.1(2)^{\circ}$. On the side of lone pair there are three additional weak bonds Sn...F with fluorine atoms in the second coordination sphere, only one of them being at the distance less than 3\AA (Sn-F $2.97\text{-}3.47\text{\AA}$).

The tendency of lone pair for spatial association has determined the complex orientation towards the center of the symmetry in the structure. Zinc and cadmium cations filled the octahedral cavities formed by water molecules. The interaction of the last with tin complexes is accompanied by the formation of hydrogen bonds O-H...F with the distance range from $2.647(7)$ to $2.726(7)\text{\AA}$.

TIN AND ORGANOTIN HALIDE COMPLEXES WITH CARBONYL
AND THIOCARBONYL DONORS

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Coordination compounds of 2,6-dimethyl-4H-pyran-4-one (DMP) with various metal salts have been reported ¹, whereas the complexes of the analogue 2,6-dimethyl-4H-pyran-4-thione (DMTP) are practically unknown.

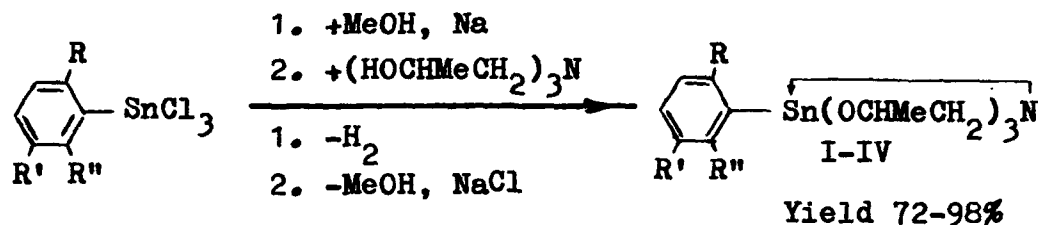
Recently we studied various lanthanide(III) nitrate adducts with DMP, of general formula $\text{Ln}(\text{DMP})_3(\text{NO}_3)_3$, in which the ligand coordinates through the carbonyl oxygen. Meanwhile we have reported platinum(II), palladium(II), rhodium(II) and rhodium(III) complexes with thiocarbonyl donors, with particular attention to their "in vitro" cytostatic activity.

In this note we extend the study to tin and organotin complexes. The adducts $\text{Sn}(\text{L})_2\text{Cl}_2$, $\text{Sn}(\text{L})_2\text{Cl}_4$ (L=DMP or DMPT), $\text{R}_2\text{Sn}(\text{DMP})\text{Cl}_2$ (R=Me or Ph), $\text{Me}_2\text{Sn}(\text{DMP})\text{Br}_2$, $\text{Me}_2\text{Sn}(\text{DMP})_2\text{Br}_2$, $\text{PhSn}(\text{DMP})\text{Cl}_3$, $\text{Ph}_3\text{Sn}(\text{DMP})\text{Cl}$ have been prepared and characterized by infrared and NMR (¹H and ¹³C) spectroscopy. The proton NMR spectra of ligands in deuterated chloroform contain the singlets due to the methyl (2.20 ppm) and ring CH (DMP, 6.01 ppm; DMPT, 6.93 ppm) protons. On coordination the CH proton signal undergo a downfield shift. As an example, it is observed at 6.55 ppm in $\text{Sn}(\text{DMP})_2\text{Cl}_2$ and at 7.30 ppm in $\text{Sn}(\text{DMTP})_2\text{Cl}_2$. Whereas the tin(II) and tin(IV) adducts are stable in benzene and in chlorinated hydrocarbons, the complexes containing organotin moieties tend to release ligand. All complexes dissociate either in acetone or in alcohols.

1 A.De Jager, J.J.De Vrieze and J.Reedijk, Inorg. Chim. Acta, 20, 59 (1976) and ref. therein.

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1-organylstannanes C-substituted in the stannatranyl skeleton were obtained by the reaction of aryltrichlorostannanes with sodium methylete and tris(2-hydroxypropyl)-amine:



R, R', R'' = H (I); R = CH₃O, R', R'' = H (II); R = CH₃O, R' = Me, R'' = H (III); R, R'' = CH₃O, R' = H (IV).

From ¹H NMR data 3,7,10-trimethylstannatrane (I) in CDCl₃ solution is associated in part, its phenyl ring substituted analogs (II-IV) being monomers. By analogy to the $\text{M}(\text{OCH}_2\text{CH}_2)_3\text{N}$ group (M = Si, Ge) a low resonance effect, σ_R^0 has been suggested for the stannatranyl group (M = Sn) [1]. The electronic effects of the $-\text{Sn}(\text{OCHMeCH}_2)_3\text{N}$ group (σ_R^0 and σ_I) were calculated by use of p- and m-carbon atom ¹³C chemical shifts of the phenyl substituent in the ¹³C NMR spectrum of (I). The 3,7,10-trimethylstannatranyl group shows the same weak π -acceptor properties ($\sigma_R^0 = 0.00 - 0.04$) as the silatranyl and geratranyl groups. However, in contrast to the $\text{M}(\text{OCH}_2\text{CH}_2)_3\text{N}$ group (M = Si, Ge), the 3,7,10-trimethylstannatranyl group displays a pronounced σ -acceptor effect ($\sigma_I = 0.28$).

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ELECTRONIC AND MOLECULAR STRUCTURE OF TETRACHLOROSTANNANE
COMPLEXES WITH ESTERS OF THE SERIES RCOOR' FROM ^{35}Cl NQR

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The electronic and molecular structure of SnCl_4 complexes with esters of the series $\text{Cl}_n\text{CH}_{3-n}\text{COOR}'$ ($n = 0-3$, $\text{R}' = \text{alkyl}$), $\text{XC}_6\text{H}_4\text{COOCH}_3$ ($\text{X} = \text{H}$, 2-, 3-, 4- CH_3 and Cl), etc. was examined by NQR at 77 K. Depending on the ratio of components and the ligand nature, octahedral 1:2 complexes or trigonal-bipyramidal 1:1 complexes are formed. The reaction of SnCl_4 with $\text{CH}_3\text{COOR}'$ ($\text{R}' = \text{CH}_3$, $\text{CH}(\text{CH}_3)_2$, $(\text{CH}_2)_2\text{Cl}$) and RCOOCH_3 ($\text{R} = \text{ClCH}_2$, BrCH_2 , Cl_2CH , 2- $\text{CH}_3\text{C}_6\text{H}_4$) leads to octahedral complexes whereas with 4- $\text{ClC}_6\text{H}_4\text{COOCH}_3$ trigonal-bipyramidal complexes are formed independently of the component ratio. In the reaction of SnCl_4 with $\text{ClCH}_2\text{COOC}_2\text{H}_5$ (1:2), 3- $\text{CH}_3\text{C}_6\text{H}_4\text{COOCH}_3$, 2- and 3- $\text{ClC}_6\text{H}_4\text{COOCH}_3$ (1:1) at low temperature a mixture of complexes of various structure is formed. This structure depends on the crystallization conditions. With the three latter B values in the B- SnCl_4 system there may be present complexes containing tin atoms with different coordination numbers (five and six). During the formation of octahedral $2\text{B} \cdot \text{SnCl}_4$ complexes a considerable redistribution of the electron density of all the chlorines attached to the tin atom occurs. The p_σ -electron density of the axial chlorine atom in trigonal-bipyramidal complexes is higher than in the corresponding octahedral complexes. In the complexes with esters it is also higher than in analogously built up SnCl_4 complexes with esters or carboxylic acid chloroanhydrides. Unlike the latter, in the formation of trigonal-bipyramidal SnCl_4 complexes with esters the electron density redistribution involves chlorine atoms which become equatorial.

SYNTHESIS AND STRUCTURAL STUDIES OF DIORGANOTIN
IMINODIACETATES

P15

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The success of cisplatin and its second generation derivatives^{1,2} as antitumour agents has led to the investigation of antitumour activity in a variety of organotin complexes³⁻⁵ structurally-related to these active platinum compounds. Recent reports of the activity of certain diorganotin derivatives of pyridine 2,10-dicarboxylic acid and some related compounds^{6,7} against the P388 lymphocytic leukemia tumour, both *in vitro* and *in vivo*, has led us to synthesise a series of diorganotin iminodiacetates, two of which are described herein. These are the compounds of formula $\text{HN}(\text{CH}_2\text{CO}_2)_2\text{SnR}_2$ with $\text{R} = \text{CH}_3$ or *n*- C_4H_9 . A full X-ray structural analysis of the dimethyltin compound has been carried out and the results are reported, along with a variety of spectroscopic data for both the dimethyl and di-*n*-butyl compounds.

The compounds of formula $\text{HN}(\text{CH}_2\text{CO}_2)_2\text{SnR}_2$ with $\text{R} = \text{CH}_3$ or *n*- C_4H_9 have been synthesised. The crystal structure of the dimethyltin compound is reported, along with some ^1H , ^{13}C and IR spectroscopic data for both the dimethyl and di-*n*-butyl compounds. The crystals are monoclinic, space group $\text{P2}_1/\text{n}$, $a = 10.1912(6) \text{ \AA}$, $b = 7.0715(4) \text{ \AA}$, $c = 14.9713(8) \text{ \AA}$, $\beta = 108.540(10)^\circ$, $V = 1022.94 \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.934 \text{ Mg.m}^{-3}$, $\mu = 2.46 \text{ mm}^{-1}$ final $R = 2.1\%$ for 1174 significant observed reflections. The complex has a six-coordinate distorted octahedral structure with the methyl groups *trans* to each other, the ligand behaving as a planar tridentate via the imine nitrogen and oxygen atoms from each of the two carboxylate groups. The sixth position in the coordination sphere is taken up by the oxygen atom of a coordinated water molecule. The hydrogen-bonding between the organotin units is also described.

The structure of the dibutyltin complex is believed to be the same as that of the dimethyltin complex.

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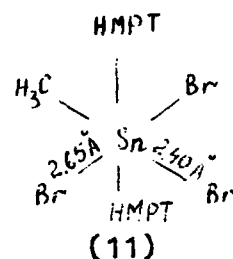
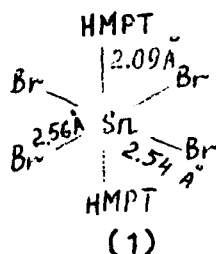
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TRANS-STRENGTHENING EFFECTS IN
THE COORDINATION ORGANOTIN COMPOUNDS

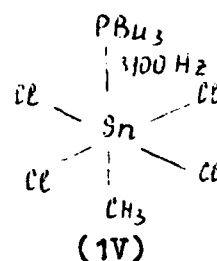
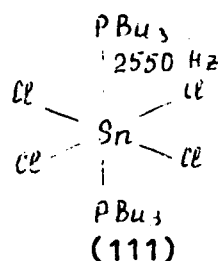
P16

V.S. Petrosyan, O.A. Reutov, Chemistry Department, M.V. Lomonosov University, Moscow 119899 USSR

The systematic studies of crystal structures for $(\text{CH}_3)_n\text{SnHal}_{4-n} \cdot 2\text{D}$, where $n=0-2$; $\text{Hal}=\text{Cl}, \text{Br}$; $\text{D}=\text{HMPT}$ or DMF by X-ray technics have shown(1) that trans-strengthening effects take place in these solid state complexes. For example, substitution of Br in (1) for CH_3 in (11) leads to the cis-weakening of the Sn-Br and Sn-O bonds, but to the trans-strengthening of the Sn-Br bond.



On the other hand the NMR studies of coordination organotin compounds with phosphines have shown(2) that trans-strengthening effects take place in the solution as well. For example, substitution of Bu_3P in (111) for CH_3 in (1V) leads to the trans-strengthening of the Sn-P bond.



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REACTIVE CYCLIC STANNYLENES

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The reaction of 4-nitrocatechol with tin(II) methoxide in tetrahydrofuran gave a bright yellow crystalline product **1** in high yield. By analysis **1** was formulated as a novel tin heterocycle, [para-O₂N-C₆H₃OSnO.THF].

X-ray diffraction shows **1** to be polymeric in the solid state, with intermolecular tin-oxygen bonding giving rise to "stepped" polymeric strands. The tin atom is in an unusual co-ordination environment and provides an extremely rare example of five-coordinate tin(II), and with retention of a stereochemically active lone pair, its geometry can be said to be pseudo six-coordinate distorted octahedral.

In contrast to the majority of catechol tin(II) complexes previously studied, **1** is highly soluble in donor organic solvents and is monomeric in dimethyl sulphoxide solution.

1 reacts with bidentate and tridentate donor molecules, quaternary ammonium salts, and shows "carbene-like" behaviour by undergoing 1,4-cycloaddition reactions. **1** can also act as a "soft" two-electron donor, forming tin-transition metal bonds (M), where M=Mo, Fe, Rh, Pt and Pd.

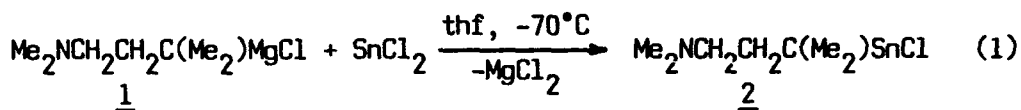
THE REACTION OF 3-DIMETHYLAMINO-(1,1-DIMETHYL)PROPYL
MAGNESIUMCHLORIDE WITH TIN(II)CHLORIDE. STABILIZATION
OF A SnCl^+_{17} CATION IN THE NEW TIN CLUSTER
 $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me}_2)\text{SnCl}]_3 \cdot \text{SnCl}_2$

K. Jurkschat¹, C. Klaus¹, M. Dargatz¹, A. Tzschach¹,
J. Meunier-Piret², B. Mahieu².

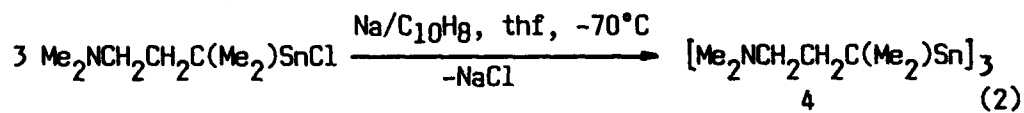
1. Martin Luther University, Halle/S., German Democratic Republic.

2. Université Catholique de Louvain, Louvain-la-Neuve, Belgium.

The functional Grignard reagent $\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me}_2)\text{MgCl}$, 1, reacts with tin(II)chloride under formation of the intramolecular donor-stabilized stannylene $\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me}_2)\text{SnCl}$, 2 (equ. 1).



In solution 2 shows a limited stability and undergoes a disproportionation reaction towards the tin(IV) derivative $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me}_2)]_2\text{SnCl}_2$, 3 and elemental tin. With sodium/naphthalene 3 reacts under formation of the corresponding cyclotrimer 4 (equ. 2).



The structure of the compounds was studied by means of NMR and Mössbauer spectroscopy.

As a byproduct along the reaction according to equ. (1) the new tin cluster $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me}_2)\text{SnCl}]_3 \cdot \text{SnCl}_2$, 5 could be isolated. Formally, it can be interpreted as a SnCl^+_{17} cation being stabilized by three stannylene units ($\text{Sn}1, \text{Sn}2, \text{Sn}3$) in a ψ -trigonal bipyramidal environment.

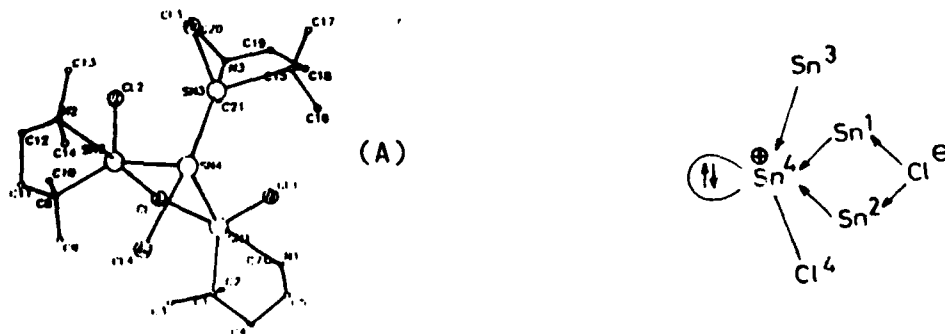
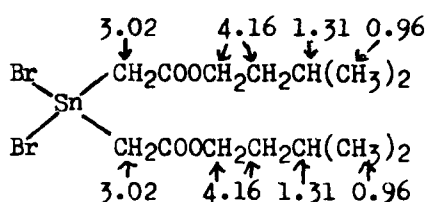


Fig. 1. Molecular structure of $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}(\text{Me}_2)\text{SnCl}]_3 \cdot \text{SnCl}_2$ (A) and schematic presentation of the SnCl^+_{17} cation stabilized by the stannylene units.

INVESTIGATION ON SYNTHESIS AND PROPERTIES
OF DI(α -SUBSTITUTED ALKYLtin)DIBROMIDES AND THEIR COMPLEXES WITH
SOME NITROGEN LIGANDS
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PARTMENT OF CHEMISTRY, NORTHEAST NORMAL UNIVERSITY, CHANGCHUN, P.R.CHINA.

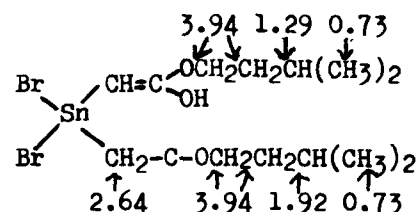
ABSTRACT

Ten di(α -substituted alkyltin)dibromides, $\text{Br}_2\text{Sn}(\text{CH}_2\text{COOR})_2$ (here $\text{R} = \text{Et}, n\text{-Bu}, i\text{-Bu}, \text{Am}, i\text{-Am}, \text{sec-Am}, \text{Ph}, \text{Cyclohexyl}, \text{Benzyl}$ and $n\text{-Heptyl}$) have been synthesized from tin powder and α -bromoacid esters. Their composition, structure and thermal stability have been studied by elemental analysis, chemical properties, molar conductances, MS, IR, UV, ^1H NMR, X-ray diffraction and thermal analysis. It is proposed that the compound shown as below exists as ester-form and enol-form in different solvents. These compounds are non-electrolytic nature in acetone.



ester-form

mp, 136.0-137.10°
C% found 31.28 (calcd. 31.33)
H% found 4.95 (calcd. 4.88)



enol-form

mp, 89.0-91.00°
C% found 31.80 (calcd. 31.33)
H% found 4.96 (calcd. 4.88)

Fifteen complexes of di(α -substituted alkyltin)dibromides with some aromatic nitrogen heterocycles, $\text{Br}_2\text{Sn}(\text{CH}_2\text{COOBu-}n)_2 \cdot \text{L}$, $\text{L} = \text{BPY}, \text{NPH}, \text{PH}, \text{DPPH}$; $\text{Br}_2\text{Sn}(\text{CH}_2\text{COOBu-}i)_2 \cdot \text{L}$, $\text{L} = \text{BPH}, \text{PH}$; $\text{Br}_2\text{Sn}(\text{CH}_2\text{COOR}')_2 \cdot \text{L}$, here $\text{R}' = \text{Am-n}, \text{Am-i}, \text{Am-sec}$, $\text{L} = \text{BPY}, \text{NPH}, \text{PH}$ (where $\text{BPY} = 2,2'$ -dipyridyl, $\text{NPH} = 5$ -nitro, $1,10$ -phenanthroline, $\text{PH} = 1,10$ -phenanthroline, $\text{DPPH} = 4,7$ -diphenyl, $1,10$ -phenanthroline) have also been synthesized in high yields. Elemental analysis, molar conductances, IR, UV, ^1H NMR and X-ray powder diffraction indicate that these complexes might be also existed as ester-form and enol-form in different solvents; all ligands are bidentate ligands; these complexes are non-electrolytic nature in acetone. Octahedral structure for these complexes have been discussed through their thermal analysis.

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SYNTHESIS OF MONO (TRIALKYL STANNYL) PHOSPHONATES FROM DIALKYLPHOSPHONATES.

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Jacques METZGER .

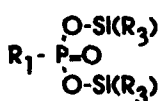
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Implication of phosphonates in introducing catalytic activity into combining sites of antibodies¹ involves the synthesis of phosphonic acid salts from phosphonates under very mild conditions.²

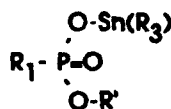
The silylation of dialkyl phosphonates with chlorotrimethylsilane in the presence of sodium iodide in acetonitrile afforded the corresponding bis(trimethylsilyl) phosphonates I in good yields.³

We have synthesized by a very simple reaction several mono (trialkylstannyl) phosphonates II instead of disubstituted esters.

NMR (¹³C, ³¹P and ¹¹⁹Sn) results of these organotin-phosphonates will be presented and discussed.



I



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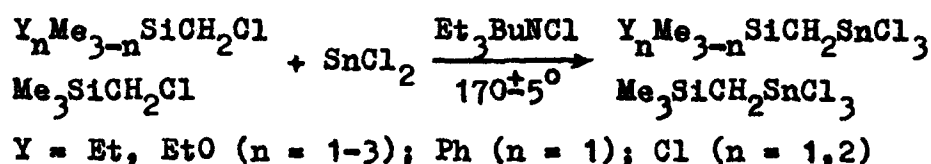
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SOME ASPECTS OF THE MECHANISM OF INSERTION REACTION
OF DICHLOROSTANNYLENES INTO C-Cl BOND OF α -CHLORO-
METHYLSILANES

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Relative rate constants were determined and dependence of k_1/k_0 on silicon substituents Taft constants (σ^*) sum was found for the reaction of SnCl_2 with a number of substituted α -chloromethylsilanes.



The molar ratio of the products in the competing reactions was determined by comparison of signal areas of methylene and methyl protons of SiCH_2 and SiCH_3 groups in the $^1\text{H-NMR}$ spectra. Dependence of $\lg k_1/k_0$ on $\sum \sigma^*$ for methyl, ethyl and phenyl substituents is described by the correlation equation $\lg k_1/k_0 = (-0,03 \pm 0,06) + (0,86 \pm 0,09) \sigma^*$ (correlation coefficient $r = 0,973$). The same dependence for chlorine atoms and ethoxy substituents is described by the equation $\lg k_1/k_0 = (0,05 \pm 0,03) - (0,06 \pm 0,01) \sigma^*$ (correlation coefficient $r = 0,947$).

Positive value of the reaction constant ($\rho = 0,86$) for aliphatic and aromatic substituents at silicon atom gives evidence about the sufficient charge decoupling in the intermediate state and the nucleophilic mechanism of the reaction.

The negative value of the reaction constant ($\rho = -0,06$) in the case of n-donor substituents at silicon atom gives evidence about electrophilic attack of SnCl_2 on C-Cl bond, as it takes place in the insertion reactions of GeCl_2 into C-Cl bond of chlorobenzyles. (O.M. Nefedov, S.P. Kolesnikov et al., Academy of science of the USSR Reports, 1973, v. 211, p. 110).

REACTIONS OF STERICALLY HINDERED ORGANOTINS

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The synthesis of sterically hindered organotin halides cannot always be accommodated by the usual Kocheshkov disproportionation route due to the difficulty of preparing the highly hindered tetraorganotin. We have explored (a) halogen cleavage reactions of $\text{Ph}_n\text{SnR}_{4-n}$ (R = sterically demanding hydrocarbon) and (b) controlled stoichiometric reaction of hindered carbanions with tin halides as routes to these desirable synthons. The hindered nature of the precursor leads to the former route yielding products arising from interactions between the halogen and either C_6H_5 or R as well as cleavage of the Sn-Ph bond. The latter series of reactions lead, in addition to the desired hindered organotin halide, to tetraorganodihalostannanes which in turn can be used in the synthesis of novel, mixed chalcogen ring systems.

The use of sterically hindered organotins in reactions with boronate anions will also be presented, and the possibility of incorporating organotins into B-O rings and cages discussed.

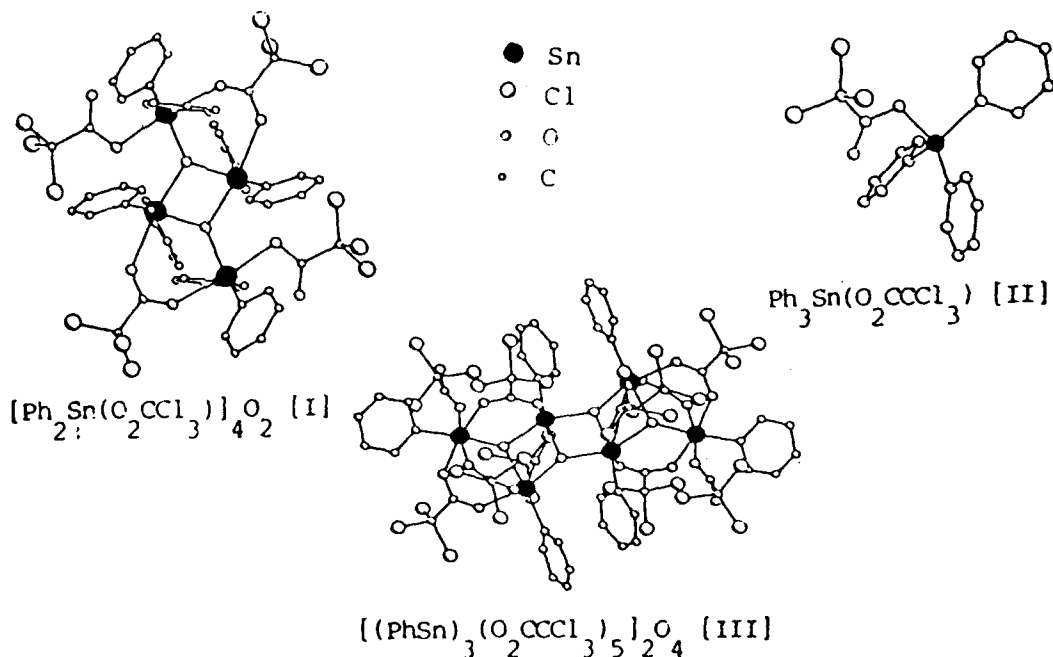
S.M.Roe and N.W. Alcock

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An unexpected dearylation reaction of Ph_3SnOH and Cl_3CCOOH during recrystallization from $\text{CCl}_4/\text{hexane}$ leads to the tetrameric μ -oxo bridged species $[\text{Ph}_2\text{Sn}(\text{O}_2\text{CCl}_3)]_4\text{O}$ [I] rather than the monomer $\text{Ph}_3\text{Sn}(\text{O}_2\text{CCl}_3)$ [II] which is the original product of reaction in methanol.

Carrying out the preparation in refluxing benzene leads to a double dearylation giving the mono-aryl tin hexamer $[(\text{PhSn})(\text{O}_2\text{CCl}_3)]_6\text{O}$ [III].

[I], [II], and [III] have been characterised by X-ray crystallography and spectroscopic techniques. The conditions of formation and interconversion for these compounds have been investigated. Similar μ -oxo complexes to [I] and [III] have been synthesised by Holmes et al.¹ but by reactions not involving dearylation or dealkylation.



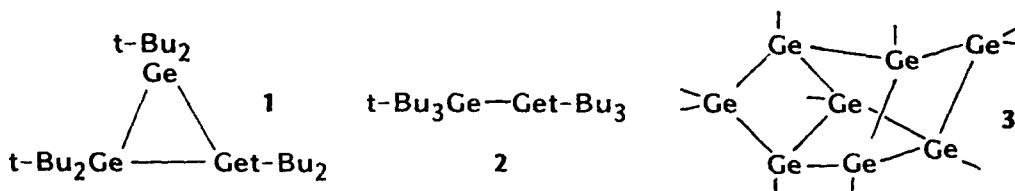
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GERMANIUM AND TIN COMPOUNDS: ARYL-ALKYL REARRANGEMENTS AND FORMATION OF METAL-METAL BONDS

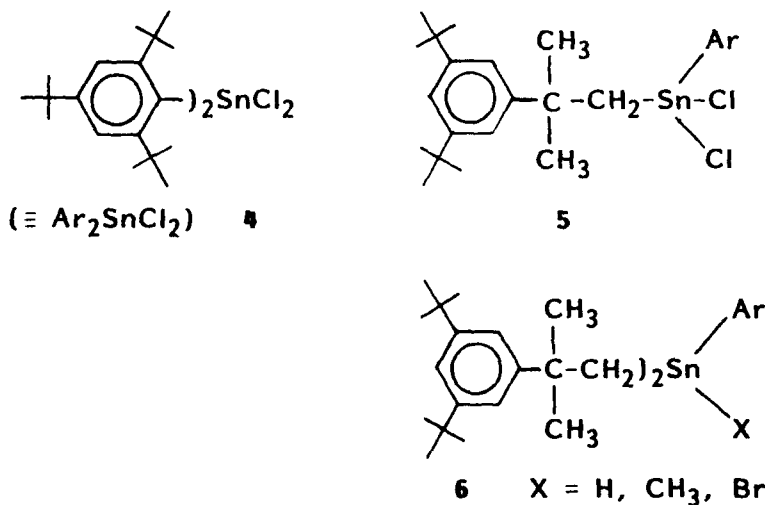
Manfred Weidenbruch, Fred-Thomas Grimm, and Karen Schäfers

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Reductive halogen elimination from several tert-butyl substituted mono- and digermanes leads to linear, cyclic or polycyclic oligogermanes which were characterized by X-ray structure analyses.



The attempted synthesis of sterically congested stannanes by reaction of tin tetrahalides with 2,4,6-tri-tert-butylphenyllithium (ArLi) by an unprecedented aryl-alkyl isomerization gives the rearranged compounds 5 and 6. Under special reaction conditions small amounts of the expected transarylation product 4 are also accessible.



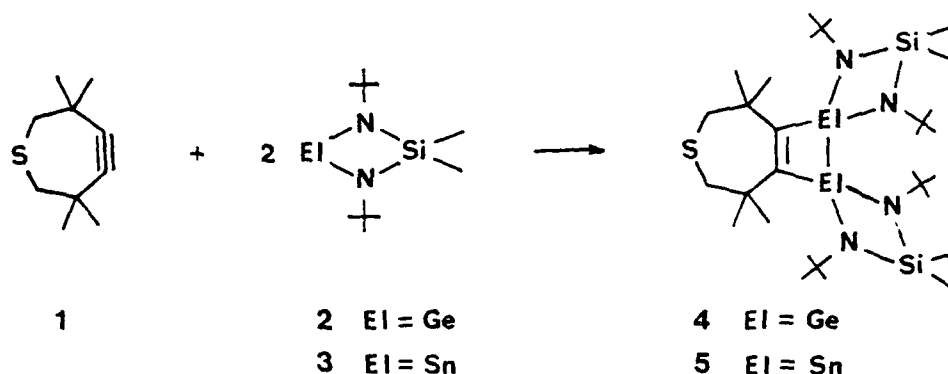
Adolf Krebs, Andrea Jacobsen-Bauer

Institut für Organische Chemie, Universität Hamburg
Martin-Luther-King-Platz 6, D - 2000 Hamburg 13

Michael Veith, Volker Huch, Institut für Anorganische
Chemie der Universität des Saarlandes, Im Stadtwald,
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The first germacyclopropenes ¹⁾ and digermacyclobutenes ²⁾ were prepared by addition of germylenes to the angle strained cycloalkyne 1 which combines high reactivity of the triple bond with steric protection of the resulting adducts.

The stabilized germylene 2 and stannylene 3 yielded with 1 the corresponding 1:2 adducts 4 and 5, resp.. 5 represents the first distannacyclobutene system.



In solution a rapid equilibrium exists between 5 and the educts 1 and 3 with the equilibrium shifted towards the educts on dilution; this equilibrium leads to line broadening in the ¹H- and ¹³C-nmr spectra at room temperature.

The structure of 3 and 4 was proven by an X-ray crystal structure analysis. Whereas the bond lengths and angles of 4 are in the normal range, the C=C-bonds in 5 are significantly shorter and the Sn-C-bonds longer than expected.

1) A. Krebs, J. Berndt, Tetrahedron Lett. 24 (1983) 4083.

2) S.P. Kolesnikov, A. Krebs, O.M. Nefedov, Izv.Akad.Nauk SSSR, Ser.Chim. 1983, 2173.

MOLECULAR STRUCTURE OF PENTA- AND HEXACOORDINATE
GERMANIUM COMPOUNDS

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Research Institute of Chemistry and Technology of
Organoelement Compounds, Moscow, 111123, USSR

Comprehensive results obtained by X-ray and electron diffraction data for coordinated germanium compounds ranging from weak van der Waals through medium to strong interactions in a variety of ionic complexes have been discussed. A meaningful set of structural principles that will aid in the understanding of the penta- and hexa-coordinate germanium formation has been discussed. The existence of germanium extra-coordinate compounds is determined by a combination of factors: electronegativity of the substituents, the size and number of polydentate ligands (chelate effect), steric interactions between substituents.

The expansion of germanium coordination sphere is accompanied with change in germanium bonds and angles. Attractive interaction viewed as incipient valence shell expansion as the stages of bimolecular nucleophilic displacement reactions. Crystallographic data for the reaction pathways described for complexes $XGe(OCH_2CH_2)_3N$ and $Cl_3Ge-C-Y-C=O$ ($Y = C$ and N). This tendency to increase the germanium coordination number above four is compared to silicon and tin.

MASS SPECTROMETRY OF ORGANOGERMANIUM COMPOUNDS.
MECHANISM OF FRAGMENTATION PROCESSES OF 1-GERMA-
CYCLOHEXANE AND THEIR METHYL DERIVATIVES

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Chemistry, College of Arts and Sciences, The University of
Tokyo, Komaba, Meguro-Ku, Tokyo 153 Japan

We report the mass spectrometric fragmentation caused by electron impact of 1-germacyclohexane, 1,1-dimethyl-1-germacyclohexane, thier methyl and deuterated derivatives and the analysis of the process by the shift techniques of these compounds.

Upon electron impact a Ge-C bond is cleaved to give the molecular ion peak M^+ , which is further degraded by the loss of neutral molecules. The whole fragmentation processes can be explained by the combination of the elimination of ethylene, radicals, or the transfer of hydrogen atom, e.g., McLafferty rearrangement. In the last case a relatively stable five- or six-membered transition state can be inferred.

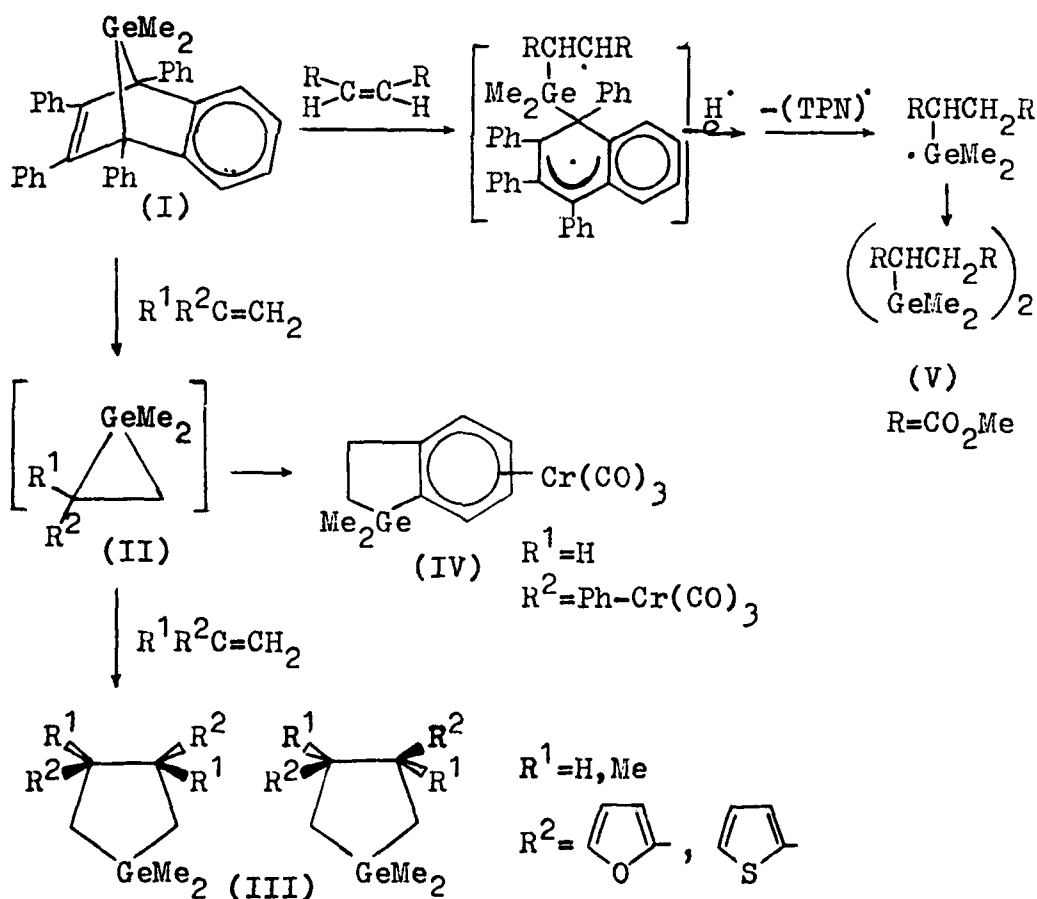
The base peak ion were observed at m/z 74 for 1-germacyclohexane and their methyl derivatives. On the other hand base peak ion were at m/z 89 (hydrogen compounds) or m/z 92 (deuterated compounds) for 1,1-dimethyl-1-germacyclohexane and thier methyl derivatives and furthermore the base peak ions changed, with loss of methyl radical, to germanium cation radical. Fragment ions from hydrocarbons were scarcely detected.

REACTIVITY OF 7-GERMANORBORNADIENE TOWARDS OLEFINES

S.P.Kolesnikov, M.P.Egorov, A.M.Galminas and O.M.Nefedov
N.D.Zelinsky Institute of Organic Chemistry USSR Academy
of Sciences, Moscow, U.S.S.R.

The reactions of various olefines with Me_2Ge produced by thermolysis or photolysis of 7-germanorbornadiene (I) have been studied.

Heteroaryl-substituted terminal olefines react with Me_2Ge regiospecifically to give germacyclopentanes (III) as a mixture of stereoisomers in 50-70% yields. The addition of Me_2Ge to styrenechromotricarbonyl complex results in formation of chromotricarbonyl complex of germaindane (IV) in 70% yield. These reactions proceed through germacyclopropane intermediate (II).



The reaction of (I) with dimethylmaleate unexpectedly leads to digermane (V) in 80% yield. The possible mechanism of the digermane (V) formation will be discussed.

HYDROGERMYLATION OF AROMATICS BY A NEW SUPERACIDIC SYSTEM $\text{HGeHal}_3\text{-AlHal}_3$.

S.P.Kolesnikov, S.L.Povarov, O.M.Nefedov, Institute of Organic Chemistry USSR Academy of Sciences, Moscow, U.S.S.R.

HGeCl_3 is known to possess a high protonating ability. Simultaneously it contains GeCl_3^- anion, which is nucleophilic enough to recombine with the corresponding cation intermediates. So, the reaction of trichlorogermane with alkoxybenzenes leads to long-lived ion pairs containing GeCl_3^- as a counterion or to covalent compounds with GeCl_3^- substituents, depending on the reaction conditions.

However, benzene and methylbenzenes do not react with HGeCl_3 under mild conditions. It does only under drastic conditions (8-14 Kbar, 80-140°C), forming bis(trichlorogermeryl)cyclohexenes.

On the other hand, the protonating ability of Friedel-Crafts superacids $\text{H}^+\text{AlHal}_4^-$ (i.g. conjugated Bronsted-Lewis acids $\text{HHal}+\text{AlHal}_3$) is higher than that of HGeHal_3 . But these superacids do not contain nucleophilic anion, which is able to recombine with generated carbocations.

The complicated system $\text{HGeHal}_3\text{-AlHal}_3$ enables the reaction of hydrogermylation of benzenes under mild conditions (50-70°C, in vacuum sealed tube) with a 70-80% conversion. The reaction is followed by alkylation, which is usual in presence of aluminium halides, and results in compounds of type (I).



REACTIVITY OF BIS (DIMETHYLGGERMYL)ALKANE IRON AND RUTHENIUM
TETRACARBONYLS WITH CARBONYL AND THIOCARBONYL COMPOUNDS

P30

Jacques Barrau, N. Ben Hamida, J. Satgé.

Université Paul Sabatier, U.A. 477, Laboratoire de Chimie des Organominéraux, 118, route de Narbonne, 31062 Toulouse Cedex, France.

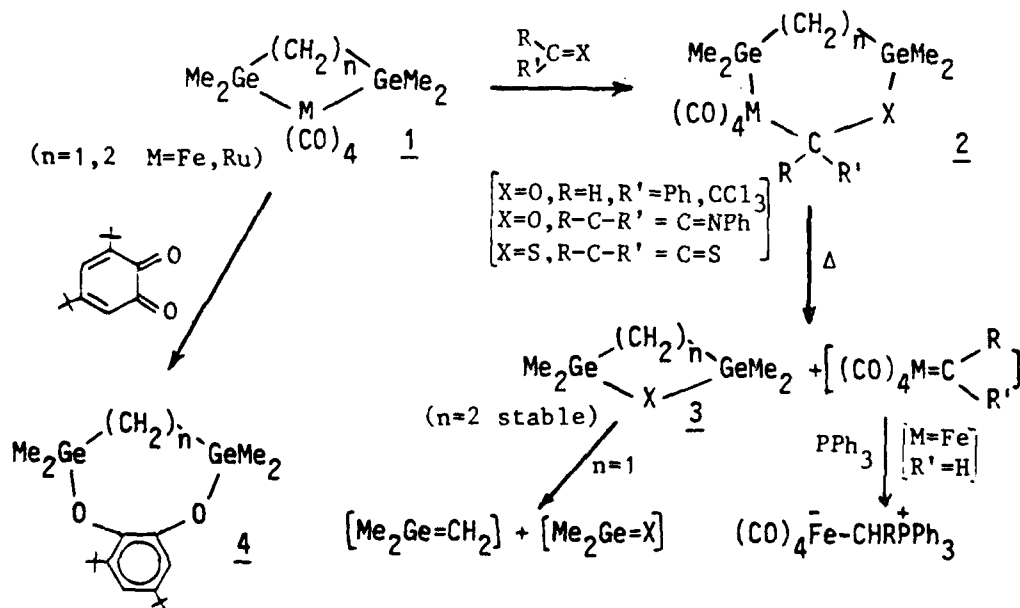
$\text{Me}_2\text{Ge}(\text{CH}_2)_n\text{Ge}(\text{Me}_2)\text{M}(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}$; $n = 1, 2$) 1, the first 4- and 5-ring polymetallic heterocycles having C-M-Ge linkages are obtained by cyclisation of bis(dimethylgermyl)alkanes with $\text{Fe}(\text{CO})_5$ or $\text{Ru}_3(\text{CO})_{12}$ under UV irradiation or thermic effects. These heterocycles 1 have high potential in organometallic syntheses. They can lead to organogermanium heterocycles as well as to polynuclear clusters having M_{14} -M bonds.

With PhCHO , CCl_3CHO , CS_2 and PhNCO , 1 react showing the first insertion reactions of carbonyl compound into germanium-transition metal bond and leading to the heterocycles 2, the stability of which is depending on the size of the heterocycle.

These reactions are faster when carried out upon UV irradiation; without irradiation the rate is depending on nature of transition metal M, on aldehyde, and on solvent.

Thermal decompositions of the expansion reactions adducts 2 produce germylated heterocycles 3 and, with $\text{M} = \text{Fe}$, alkylidenes intermediates $[(\text{CO})_4\text{Fe}=\text{CHR}]$ which were isolated as the ylides $(\text{CO})_4\text{FeCH}(\text{R})\text{P}^+\text{Ph}_3$.

The reaction of 1 with quinones results in the quantitative formation of new digermylated dioxepanes and dioxocanes that are formally the adducts of biradicals $[\text{Me}_2\text{Ge}(\text{CH}_2)_n\text{GeMe}_2]$ ($n = 1, 2$) with quinones.



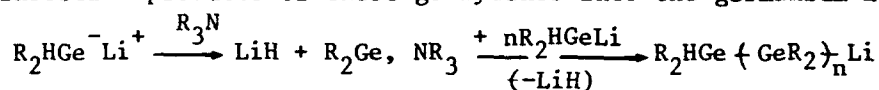
A. Castel, P. Rivière, J. Satgé, Y.H. Ko and D. Desor.

Laboratoire de Chimie des Organominéraux, Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse Cedex, France.


New arylhydrogermyllithiums can be easily prepared from hydrogermylization reactions of tBu-Li. The nature of the germanium-metal bond was deduced from their spectroscopic data (I.R., RMN¹H, ¹³C, ⁷Li).


Transmetallation reactions allowed us to prepare the first arylhydrogermyl Grignard R₂HGeMgBr and -germyl Mercury compounds R₂HGeHgCl. All these compounds were characterized by deuterolysis and alkylation reactions (MeI, SO₄Me₂).

Their nucleophilic α-elimination reactions gave germylenes (R₂Ge) and insertion products of these germylenes into the germanium-Lithium bond.



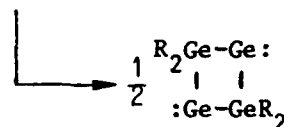
Germylation reactions of organohalogermanes gave hydropolygermanes.

Dihalogermacyclopentenes lead to the formation of the first germylgermacyclopentenes (R₂Ge = Ge ) which dimerise.

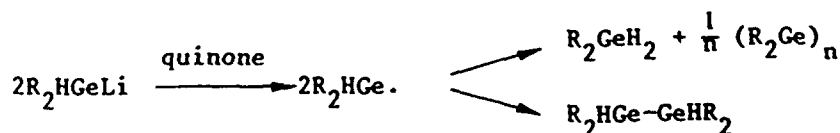
Reaction of arylhydrogermyllithiums with acylchlorides gave new hydrogermylketones H-Ge-CO- and β-germyldiketones  Ge(CO)₂.

Reactions to aldehydes, imines and nitriles were also studied.

Hydrogermylation reactions of dihalogermaylenes X₂Ge : lead to the expected (R₂HGe)₂Ge : and also to the unexpected germylgermylenes R₂Ge=Ge: which dimerise into cyclodigermylenes characterized by Mass spectroscopy and cycloaddition reactions.



In the presence of quinones, disulfides or anthracen (hu) germylmetal compounds produced germanium centered radicals, germylenes and polygermanes through monoelectronic reaction transfers.



NEW ORGANOGERMANIUM CHEMISTRY AT THE SURFACE OF GLASS

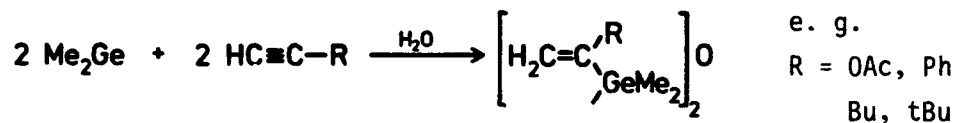
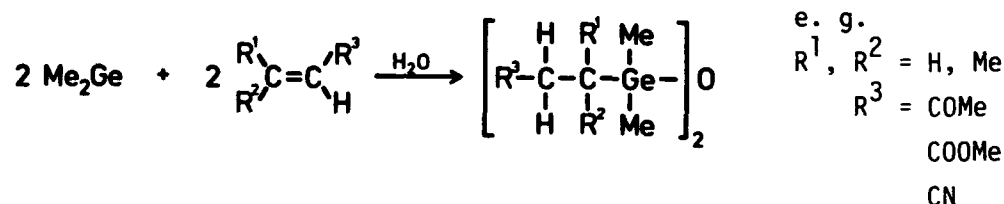
W. P. Neumann, G. Billeb, H. Brauer, J. Köcher, S. Viebahn¹⁾

Lehrstuhl für Organische Chemie I der Universität Dortmund

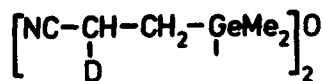
Otto-Hahn-Str. 6, D-4600 Dortmund 50, FRG

Numerous cycloadditions of free singlet germylenes like Me_2Ge to unsaturated systems e. g. of 1,3-dienes, alkynes, vinyl ketones, α -diones have been found in this laboratory.²⁾

In contrast, certain olefins and alkynes opened now a novel route to functionalized germoxanes via the reaction with thermally generated free Me_2Ge . A number of new products have been obtained in good or excellent yields:



Whereas resolved water is inert, surprisingly water bound to surfaces of glass or silica gel gives high yields in this new reaction. For example, the reaction of acrylonitril with Me_2Ge in the presence of glass powder treated with D_2O in order to



give a $\text{H}_2\text{O}/\text{D}_2\text{O}$ -exchange yields the deuterated product nearly quantitatively. Without manipulating the

glass surface, practically no deuterated product was found with a D_2O -saturated solvent.

The mechanisms will be discussed, preparative applications will be given.

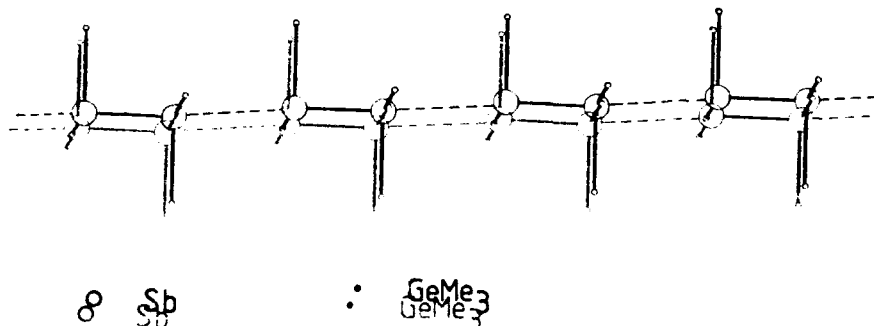
- 1) J. Köcher, Dr. rer. nat. Thesis, Univ. of Dortmund, 1985. S. Viebahn, G. Billeb, H. Brauer, Diploma Theses, Univ. of Dortmund, 1986, 1987, 1988.
- 2) W. P. Neumann, M. Schriewer, *Tetrahedron Lett.* **21**, 3273 (1980); *J. Am. Chem. Soc.* **105**, 897 (1983); W. P. Neumann, E. Michels, J. Köcher, *Tetrahedron Lett.* **28**, 3783 (1987); G. Billeb, W. P. Neumann, G. Steinhoff, *ibid.* **29**, 5245 (1988). Further references are given there.

CRYSTAL STRUCTURE AND COLOUR CHANGES OF (Me₃Ge)₄Sb₂

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Universität Bremen, FB 02, Postfach 330440, D-2800 Bremen,
F.R.Germany

Stefan Roller, Martin Dräger, Institut für Anorganische
und Analytische Chemie der Johannes Gutenberg-Universität,
D-6500 Mainz, F.R.Germany

Air oxidation of (Me₃Ge)₃Sb yields red crystals of
(Me₃Ge)₄Sb₂, which exhibit a colour change to yellow on
solving. The UV/VIS spectra show a bathochromic shift of
ca 120 nm from a saturated solution in C₆H₁₂ to the
solid.
The crystal structure is reported as linear chains of
distibane molecules in trans conformation with Sb...Sb
contacts of 385 pm.



The spectral changes are interpreted in terms of
conjugation along the distibane chains.
Similar phenomena have been observed in the case of
(Me₃Sn)₄Sb₂.

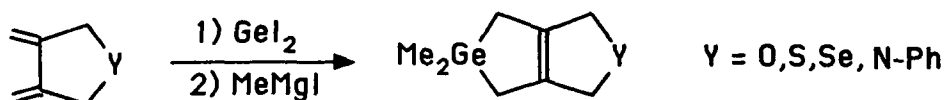
1). S. Roller, M. Dräger, H. J. Breunig, M. Ates, S.
Gülec, J. Organometal. Chem., 329 (1987) 319.

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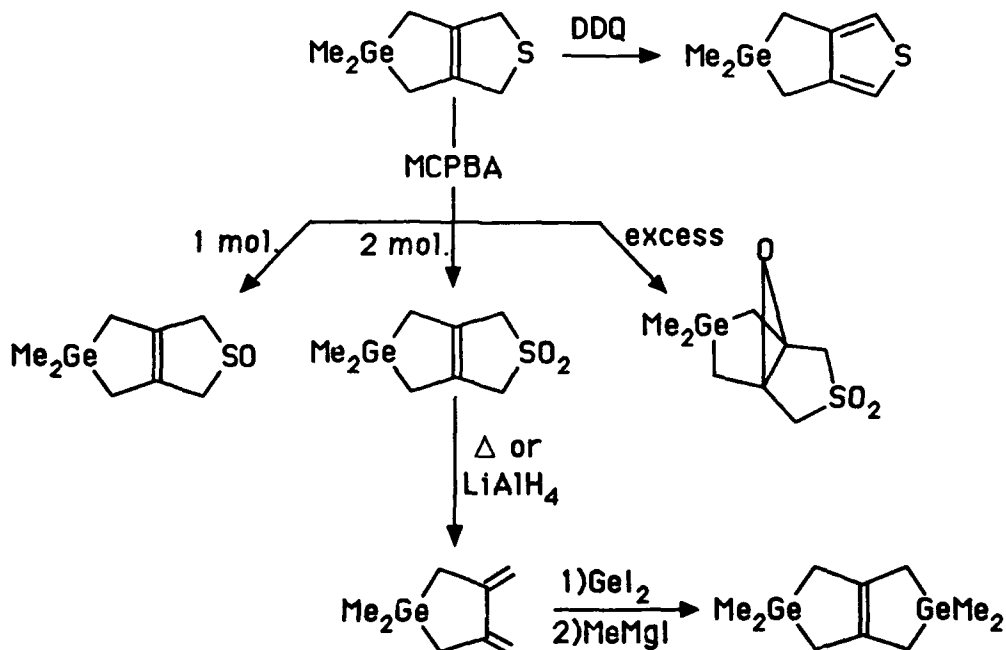
SYNTHESIS AND REACTIVITY OF 3-THIA-7,7-DIMETHYL-7-GERMABI-CYCLO[3.3.0]OCT-1(5)ENE

Pierre Mazerolles, Christian Laurent and Alfréd. er, Laboratoire des Organométalliques, U.A. 477, Université Paul Sabatier, 118, route de Narbonne 31062-Toulouse-Cedex, France.

Germanium diiodide reacts easily with bis(methylene)-oxolane, thiolane, selenolane and phenylazolidine to yield functional bicyclic organogermanium derivatives :



Especially, the sulfur compound (Y = S) is an interesting precursor in cyclic organogermanium chemistry :



SYNTHESIS AND THERMOLYSIS OF ORGANOMETALLIC PRECURSORS OF AMORPHOUS THIN LAYERS OF GERMANIUM-SILICON ALLOYS

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Pierre Mazerolles and Christine Dufor, Laboratoire des Organométalliques U.A. 477, Université Paul-Sabatier, 118, route de Narbonne, 31062-Toulouse-Cedex, France.

David Ajo, Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Corso Stati Uniti 4, 35020-Padova, Italia.

In order to obtain amorphous thin layers of Germanium-silicon alloys by chemical vapour deposition, the following compounds were synthesized :

- | | | |
|-------|---|-----------------------------------|
| (I) | $\text{Me}_3\text{GeCH}_2\text{SiMe}_3$ | (b.p. 63°C/52 mm ; 53 % yield) |
| (II) | $\text{Et}_3\text{Ge-C}\equiv\text{C-SiMe}_3$ | (b.p. 84-5°C/9 mm ; 88 % yield) |
| (III) | $\text{Et}_3\text{Ge-C}\equiv\text{C-SiH}_3$ | (b.p. 61-2°C/10 mm ; 86 % yield) |
| (IV) | $\text{H}_3\text{Ge-CH}_2\text{CH}_2\text{-SiH}_3$ | (b.p. 66°C/760 mm ; 67 % yield) |
| (V) | $\text{H}_3\text{Ge-CH}_2\text{CH}_2\text{CH}_2\text{-SiH}_3$ | (b.p. 97-8°C/760 mm ; 55 % yield) |

and their controlled thermolysis was carried out in helium or hydrogen at atmospheric pressure.

The thermal decomposition of (I)(II) and (III) depends on the relative stability of the Ge-C and Si-C bonds, according to their chemical surrounding ; in (I) all Ge-C and Si-C are broken, while in (II) and (III) the Si-C bond in α - position to the triple bond is preferentially cleaved. The coatings obtained are usually powdered and non adherent to the substrate.

Hydrides (IV) and (V), less thermally stable, decompose above 400°C. Temp °C, % dec : (IV) 425, 45 ; 450, 65 ; 475, 72 . (V) 425, 27 ; 450, 37 ; 475, 52 . The gas phase is a mixture of ethylene and acetylene for (IV) and propene for (V). The homogeneous and clean layers obtained contain germanium and silicon ; the silicon percentage increases with the temperature of thermolysis (EDAX). The presence of carbon was not detected by ESCA.

APPROACH TO LOW COORDINATED GERMANIUM COMPOUNDS
WITH Ge-Se BONDS

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Universität Oldenburg, P.O. Box 25 03, D-2900 Oldenburg,
F.R. Germany

Bis(2,4,6-tri-*t*-butylphenyl)germylene **1** reacts with sulfur to give a germa-indanethiol derivative [1], but a comparable reaction with selenium to give a germaindaneselenol via a transient species with Ge=Se double bond was not observed.

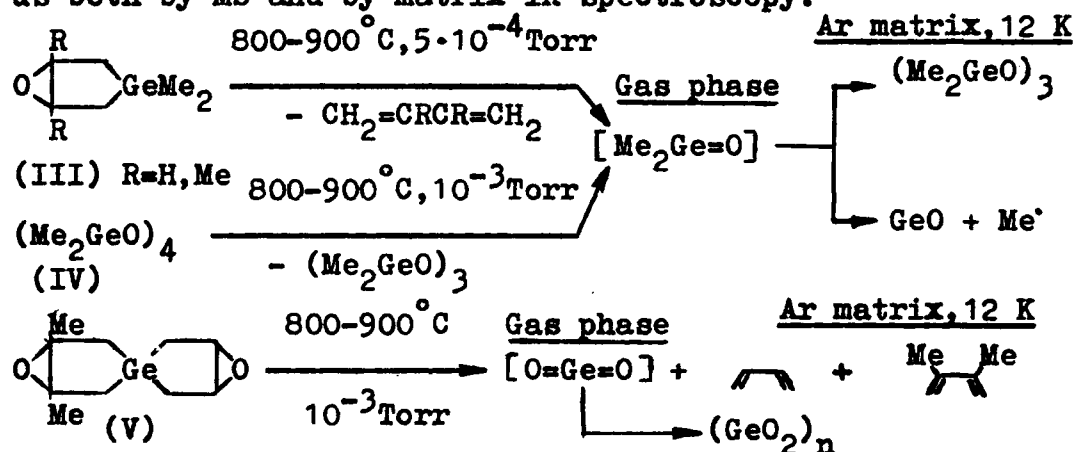
Bis(2,4,6-tri-*t*-butylphenylseleno)germylene **2**, formed in situ by reaction of lithium 2,4,6-tri-*t*-butylphenylselenide with the germanium dichloride dioxane complex, was trapped as monomeric pentacarbonyl-[bis(2,4,6-tri-*t*-butylphenylseleno)germylene]tungsten(0) complex **5**. Reaction of bis(2,4,6-tri-*t*-butylphenyl)diselenide **3** with the germanium dichloride dioxane complex provides dichlorobis(2,4,6-tri-*t*-butylphenylseleno)germane **4**. **3** and **4** were isolated as byproducts when preparation and isolation of monomeric **2** was attempted. Crystalline **5** contains trigonal planar germanium with bonds to two non-equivalent selenium atoms. Well resolved ^1H -, ^{13}C - and ^{77}Se -n.m.r. signals for two 2,4,6-tri-*t*-butylphenylseleno groups in **5** indicate hindered rotation around the Ge-Se bonds at room temperature in solution.

[1] L. Lange, B. Meyer, W.-W. du Mont, J. Organomet. Chem. **329**
(1987) C17

INTERMEDIATES WITH DOUBLE-BONDED GERMANIUM: MATRIX IR
AND MASS SPECTROMETRIC STUDIES OF VACUUM PYROLYSIS OF
ORGANOGERMANIUM PRECURSORS

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J.Tamas, A.Gömöry, I.Besenyey, Central Research Institute
for Chemistry, Hungarian Academy of Sciences, P.O.Box 17,
Budapest, H-1525, Hungary

Species with double-bonded germanium $\text{Ge}=\text{X}$ ($\text{X}=\text{C}, \text{N}, \text{O}, \text{S}$) participate as intermediates in different reactions [1]. For direct detection of germanones $\text{Me}_2\text{Ge}=\text{O}$ (I) and $\text{O}=\text{Ge}=\text{O}$ (II) vacuum pyrolysis of precursors (III-V) has been studied by us both by MS and by matrix IR spectroscopy.



It was established that in contrast to corresponding silanones [2], germanones (I, II) are thermally and kinetically unstable under the same conditions. That causes oligomerization and partial decomposition of (I) as well as polymerization of (II) to $(\text{GeO}_2)_n$.

IR data on pyrolysis of precursors of unstable germene, $\text{Me}_2\text{Ge}=\text{CH}_2$, and germathione, $\text{Me}_2\text{Ge}=\text{S}$, are also obtained.

1. J.Satge, Adv.Organometal.Chem., 21(1982)241.
2. V.N.Khabashesku, Z.A.Kerzina, A.K.Maltsev, O.M.Nefedov, Izvestia Akad.Nauk SSSR.Ser.Khim., 5(1986)1215; J.Organometal.Chem., 347(1988)277.

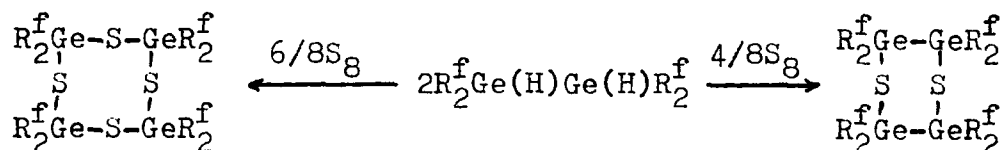
1,1,2,2-TETRAKIS(PENTAFLUOROPHENYL)DIGERMANEDIHYDRIDE
IN THE SYNTHESIS OF POLYNUCLEAR COMPOUNDS

M.N.Bochkarev, L.V.Pankratov, V.I.Nevodshikov, Institute of Organometallic Chemistry of U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

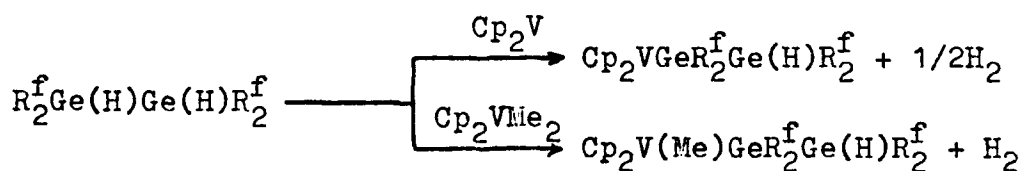
V.N.Latyaeva, A.N.Lineva, I.V.Zhdanovich, Medical Institute, Gorky (U.S.S.R.)

The attempts to use 1,1,2,2-tetrakis(pentafluorophenyl)-digermanedihydride for synthesis of line and cyclic polynuclear organometallics were undertaken.

Six- or eight-membered cycles (depending on the reagent ratio) are formed in reaction of sulfur with $R_2^fGe(H)-Ge(H)R_2^f$ ($R^f = C_6F_5$) in THF (80°C, 10-20 h).



The cyclic dithio- and threethio-germanes are air-stable colourless crystals with m.p. = 175°C and 200°C respectively. Their structures are confirmed by elemental analysis and IR spectroscopy. Interaction of bis(cyclopentadienyl)vanadium and their dimethyl derivative with $R_2^fGe(H)Ge(H)R_2^f$ leads to evolution of hydrogen or methane and formation of polynuclear germylvanadium complexes.

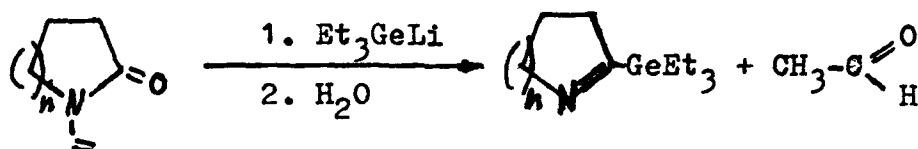


All these products are air sensitive crystals. Their formation is confirmed by elemental analysis, IR and ESR spectroscopy.

ORGANOGERMANIUM CYCLOIMINES

Aleksandr Seleznev, Dmitrii Bravo-Zhivotovskii, Nikolai Vyazankin and M.G. Voronkov, Institute of Organic Chemistry Siberian Branch, Ac.Sci.USSR, 664033 Irkutsk, USSR

A synthesis of organogermanium derivatives of cyclic imines with the trialkylgermyl group attached to the imine carbon, has been carried out for the first time. These compounds were obtained in high yields by the reaction of triethylgermyllithium with the corresponding N-vinyllactam in benzene.



n = 1, yield 76 %

n = 3, yield 83 %

The above reaction with triethylsilyllithium does not lead to the corresponding pyrroline. The reaction of trimethylgermyllithium with N-vinylpyrrolidone gives only 8% α-triethylgermyl-Δ¹-pyrroline.

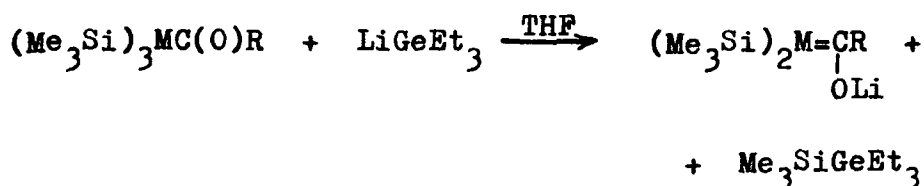
Unlike N-vinyllactams, N-methylpyrrolidone is almost completely metallated with triethylgermyllithium into the - position of the carbonyl group.

THE STRUCTURE AND REACTIONS OF THERMALLY STABLE
SILAENOLATE-ANIONS

P40

Irina Biltueva, Dmitrii Bravo-Zhivotovskii. Inna Kalikhman,
Nikolai Vyazankin and Mikhail Voronkov, Institute of
Organic Chemistry, Siberian Branch, Ac.Sci.USSR, 664033
Irkutsk, USSR

Sila(I,II)- and germa(III)enolate-anions were prepared for
the first time by the reaction of triethylgermyllithium
 Et_3GeLi (IV) with tris(trimethylsilyl)acylsilanes
 $(\text{Me}_3\text{Si})_3\text{SiC(O)R}$ ($\text{R} = \text{CMe}_3$ (V), Ad (VI) and a germanium
analog $(\text{Me}_3\text{Si})_3\text{GeC(O)CMe}_3$ (VII) in THF at 20°:



$\text{M} = \text{Si}$; $\text{R} = \text{CMe}_3$ (I), $\text{R} = \text{Ad}$ (II)
 $\text{M} = \text{Ge}$; $\text{R} = \text{CMe}_3$ (III)

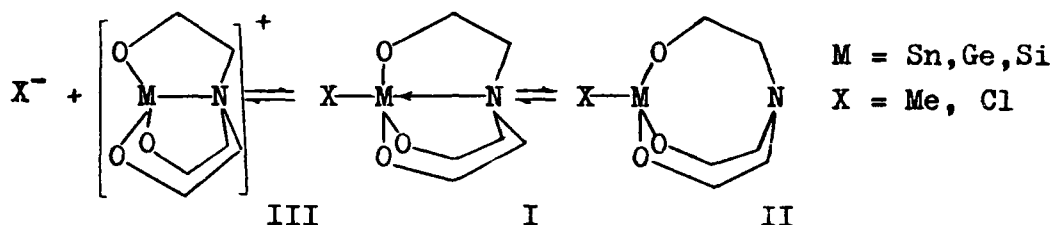
The structure of compounds (I) and (II) is confirmed by
 ^{29}Si NMR. In the spectrum of these compounds the region of
olefinic silicon atom resonance (68.09 and 64.86 ppm for
(I) and (II), respectively) corresponds to the data for the
Brook thermally stable silaolefins. The double bonding of
the central silicon atom is supported by non-equivalence of
the silicon atoms in trimethylsilyl groups (-11.86, -12.2
ppm) for silaenolate (I) and (-11.58, -12.34 ppm) for sila-
enolate (II).

In the reaction of compounds (I), (II) and (III) with AlkI
($\text{Alk} = \text{Me}$, iPr) in THF the products of Si- and Ge-alkyl-
ation, alkylbis(trimethylsilyl)acylsilanes and analogous
acylgermanes, $\text{Alk}(\text{Me}_3\text{Si})_2\text{MC(O)R}$, are formed in nearly 100%
yield.

THEORETICAL ANALYSIS OF HETEROLYTIC CLEAVAGE OF THE X-M-N
HYPERVALENT BOND IN METALLOATRANE MOLECULES $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$
(M = Sn, Ge or Si)

Valerii Sidorkin, Georgii Balakhchi, Vadim Pestunovich and
Mikhail Voronkov, Institute of Organic Chemistry, Siberian
Branch, Ac.Sci. USSR, 664033 Irkutsk, USSR

The potential functions of transitions of metalloatrane
molecules from the really existing *endo*-form (I) to hypo-
thetical *exo*-(II) and ionic (III) forms:



were calculated by MNDO to elucidate the effect of the
central atom (M) and substituent (X) on the relative sta-
bility of these molecules.

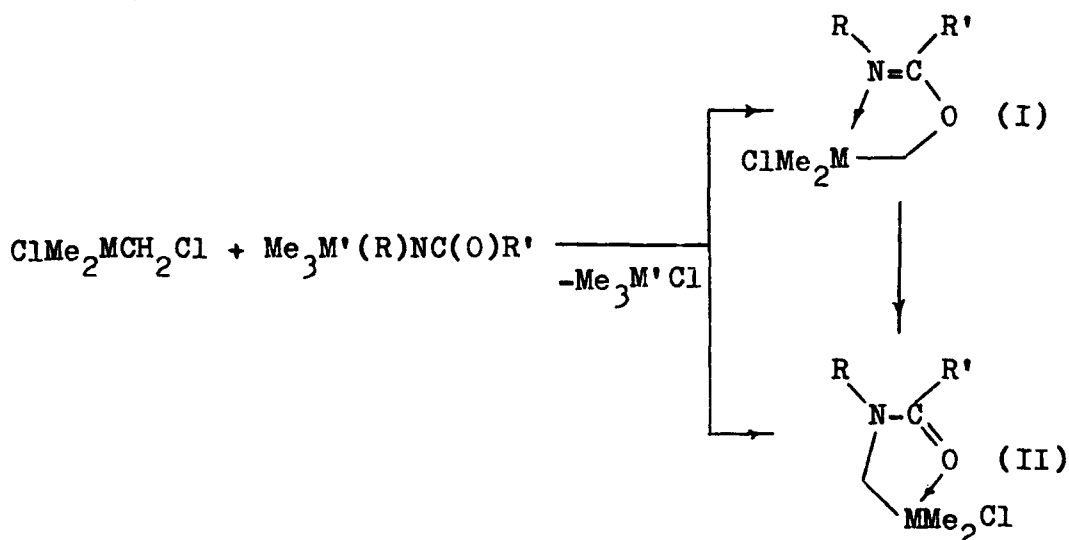
The primary mapping of such transition pathways was per-
formed by the atom-atom potential method with use of the
earlier suggested way of accounting for the influence of
variation in the X-M and M-N bond orders on the force
field and the equilibrium values of the central atom
valence angles.

The main contribution to the *endo*-form stabilization is
made by the formation of a three-centered four-electron
X-M-N bond. This contribution and the degree of charge
transfer from the N atom to the M-X bond increases with
decreasing the ionization potential of the M atom as well
as with increasing the substituent X electronegativity.
Analysis of changes in the orbital structure and the
charge distribution along the reaction coordinate proves
the model of hypervalent bond in pentacoordinate tin,
germanium and silicon derivatives. The character of vari-
ation in the coordination centre geometrical parameters
along the $\text{II} \rightleftharpoons \text{I} \rightleftharpoons \text{III}$ transition pathway demonstrates (in
agreement with the experiment) retention of bond-order
in the X-M-N fragment.

(N-M) AND (O-M) CHELATE $\text{ClMe}_2\text{MCH}_2$ DERIVATIVES ($\text{M} = \text{Ge}, \text{Sn}$)
OF N-METHYLACETAMIDE AND LACTAMS

Vadim Pestunovich, Inna Kalikhman, Yurii Baukov, Olga Bannikova, Lyudmila Belousova, Eugenia Kramarova, Aleksandr Shipov and Mikhail Voronkov, Institute of Organic Chemistry, Siberian Branch, Ac.Sci.USSR, 664033 Irkutsk, USSR

The reaction of dimethyl(chloromethyl)chlorogermane and -stannane with N-trimethylsilyl, -germyl, and -stannyl derivatives of N-methylacetamide, valero- and caprolactam gave two new types of pentacoordinate germanium and tin compounds of (N-M) and (O-M) chelate structure:



$\text{M} = \text{Ge}, \text{Sn}; \text{M}' = \text{Si}, \text{Ge}, \text{Sn};$

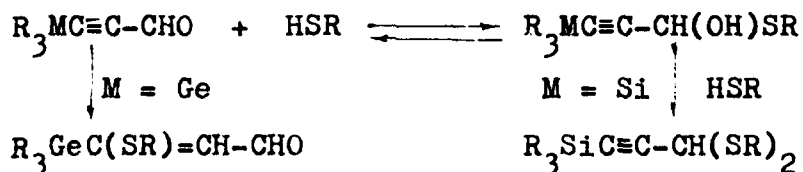
$\text{R} = \text{R}' = \text{Me}$ or $\text{R}, \text{R}' = \text{CH}_2(\text{CH}_2)_n\text{CH}_2$ ($n = 2, 3$)

According to NMR-monitoring data the priority formation of (N-M) chelate compounds (I) occurs at 25°C when $\text{M} = \text{Ge}$ and between 50 and 100°C when $\text{M} = \text{Sn}$, the process being kinetically controlled in both cases. At a higher temperature germanium compounds I completely and tin derivatives I partly rearrange to thermodynamically more stable (O-M)-chelate derivatives II.

THE ROLE OF TRIORGANYLGERMYL(SILYL)PROPYNAL HETEROATOM
IN THE ORIENTATION OF S,N-NUCLEOPHILE ADDITION

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A comparative study of propynals $R_3MC\equiv C-CHO$ ($M = Ge, Si$) in reactions of nucleophilic addition has shown the type of heteroatom to have a substantial effect upon the orientation of nucleophile attack. In the absence of catalyst, thiols form adducts with trimethylsilylpropynal at the $C=O$ bond, which leads to acetylenic hemiacetals and thials. Under the same conditions the behavior of triethylgermylpropynal is quite different, the main reaction course being nucleophilic attack on the $\beta-C_{sp}$ atom to give β,β -triethylgermylthioacroleins.



Participation of the triple bond of triethylgermylpropynal in the nucleophilic addition of thiols is explained by a decrease in the π -acceptor resonance properties of the heteroatom with respect to the triple bond when the silicon atom is replaced by a germanium atom.

Sterically non-hindered amines (morpholine, piperidine) react smoothly with trimethylsilylpropynal to form sila-acetylenic amins. Dialkylamines attack the other electrophilic centre, silicon atom, thus leading to heterolysis of the $Si-C_{sp}$ bond with the formation of β -aminoacroleins in very high yield.

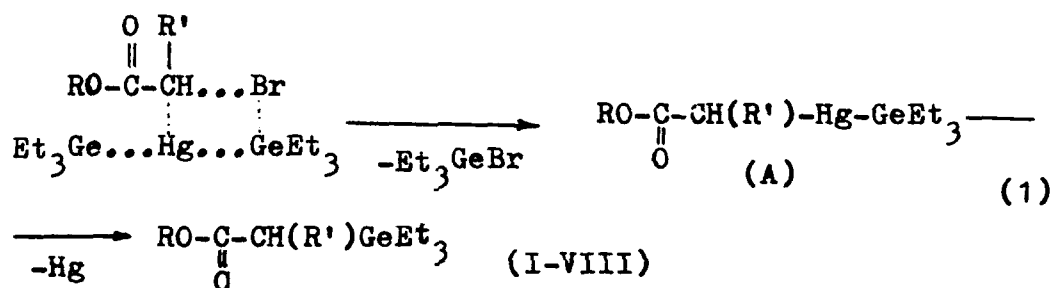
The $Ge-C_{sp}$ bond is stable to the attack by secondary amines. The reaction occurs regioselectively at the carbonyl group to form previously unknown germaacetylenic amins in quantitative yield.

A METHOD FOR PREPARING ESTERS OF α -GERMYLATED CARBOXYLIC ACIDS AND O-SILYLATED KETENE ACETALS

Olga Vyazankina, Dmitrii Gendin and Nikolai Vyazankin

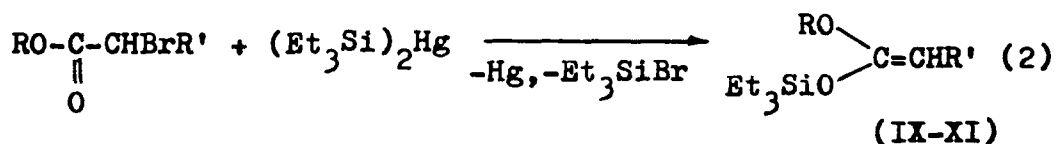
Institute of Organic Chemistry, Siberian Branch, Ac.Sci.
USSR, 664033 Irkutsk, USSR

The reaction of esters of α -bromocarboxylic acids with bis-(triethylgermyl)mercury leads to the formation of the corresponding esters of α -germylated carboxylic acids (I-VIII). The reactions of this type proceed via a four-centered transition state with the formation of intermediates (A) which further undergo demercuration to give compounds (I-VIII).



R = Me, R' = H (I); R = R' = Me (II); R = Me, R' = Et (III);
R = Et, R' = (H) (IV);, R = Et, R' = Me (V); R = i-Pr, R' = Me
(VI); R = t-Bu, R' = Et (VII); R = Et, R' = Cl (VIII).

Besides, a method for preparing O-silylated ketene acetals by the reaction of bis(triethylsilyl)mercury with esters of α -bromocarboxylic acids has been developed.



R = Et, R' = H (IX); R = Et, R' = Me (X); R = Me, R' = Et (XI).

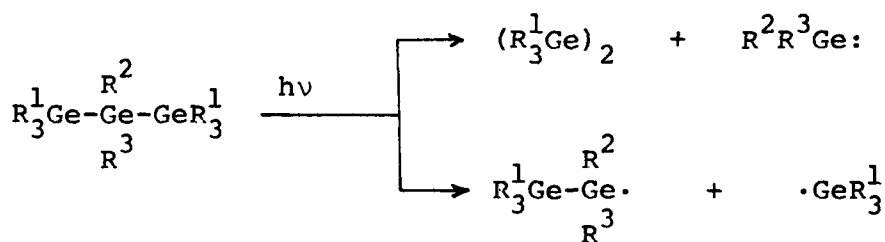
Reaction (2) is accelerated by addition of catalytic amounts of HMPA. The reaction mechanism is discussed.

PHOTOCHEMISTRY OF PHENYL-SUBSTITUTED TRIGERMANES

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The photolysis of phenyl-substituted trigermanes afforded digermanes and germylenes. Trapping experiments, matrix isolation, and laser-photolysis studies indicate that the photoreaction of these compounds involves both the simple extrusion of germylenes and the formation of germlyl radicals.

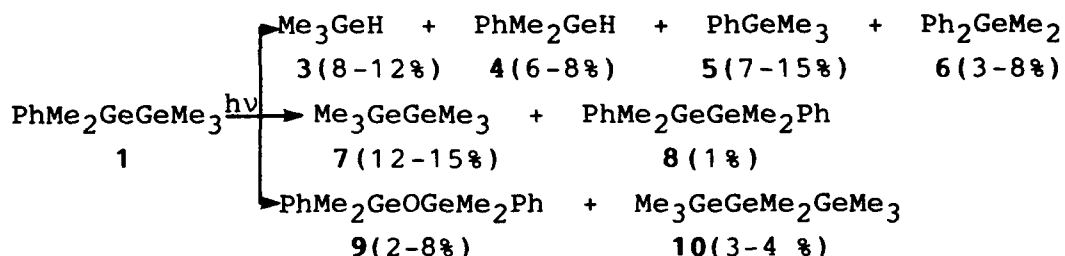


Kunio MOCHIDA, Haruhiko KIKKAWA, and Yasuhiro NAKADAIRA[†]

Department of Chemistry, Faculty of Science,
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Chofu, Tokyo 182

Extensive studies of photochemistry of aryldisilanes have been investigated.¹⁾ We report the photoreaction of the germanium analogue phenylpentamethyldigermene (1). Photolysis of 1 causes germanium-germanium bond homolysis which leads to the formation of germyl radicals and probably germylene.



Irradiation of 1 in cyclohexane gave monogermenes 3-6, and digermenes 7-8 together with germanoxane 9 and interestingly, a trace amount of trigermene 10 as summarized in Scheme. Formation of hydrogermanes 3 and 4 seems indicative of the intermediary of germyl radicals derived from homolytic cleavage of the germanium-germanium bond on irradiation. This accords with the formation of digermenes 7 and 8. Occurrence of germane 5 in the photolysate can be rationalized by the evolution of dimethyl germylene on the photolysis. This is supported by the trapping experiment by means of 2,3-dimethylbutadiene. Unexpected formation of trigermene 10 arises from insertion reaction of the germylene into 7.

1) For examples. (a) M. Ishikawa, T. Fuchikami, T. Sugaya, and M. Kumada, *J. Am. Chem. Soc.*, **97**, 5923 (1975). (b) H. Sakurai, Y. Nakadaira, M. Kira, H. Sugiyama, K. Yoshida, and T. Takiguchi, *J. Organomet. Chem.*, **184**, C36 (1980).

M.B. Taraban, V.I. Maryasova, T.V. Leshina, Institute of Chemical Kinetics and Combustion, Novosibirsk-90, 630090 U.S.S.R.

Recently the method of chemically induced dynamic nuclear polarization (CIDNP) has been widely used for the investigation of the nature of radical stages in the reaction of various organometallic compounds (see, e.g. [1]).

The present report illustrates the application of CIDNP to the investigations of the detailed mechanism of the photolysis of Et_3GeCOPh in the presence of radical traps PhCH_2Cl and PhCH_2Br , methanol, and also in the absence of traps in such nonpolar solvents as cyclo- C_6D_{12} and C_6D_6 .

The analysis of ^1H [1] and ^{13}C CIDNP effects arising in the initial Et_3GeCOPh during its photolysis allow one to determine that the radical photodecomposition of it occurs via Norrish Type I cleavage (Ge-C bond breaking) with the formation of the triplet radical pair of $\text{Et}_3\dot{\text{Ge}}$ and $\text{Ph}\dot{\text{C}}\text{O}$ radicals:



The escaping from the radical cage $\text{Et}_3\dot{\text{Ge}}$ and $\text{Ph}\dot{\text{C}}\text{O}$ enter the reaction with the traps or with the initial Et_3GeCOPh and form the products. These products demonstrate the ^1H [1] and ^{13}C CIDNP effects confirming the abovementioned scheme of the radical decomposition.

This result is of great importance not only from the mechanistic point of view, since element-containing ketones are the model systems for the investigation of the magnetic isotope effects, and the question about the multiplicity of the initial radical pair during their photolyses has the principal character.

- [1] M.B. Taraban, V.I. Maryasova, T.V. Leshina, L.I. Rybin, D.V. Gendin and N.S. Vyazankin, J. Organomet. Chem., 326(3), 347-355 (1987).

SYNTHETIC, STRUCTURAL AND THERMAL STUDIES OF
N-PYRIDINO BENZAMIDE-2-CARBOXYLIC ACID AND ITS
LEAD COMPLEX

P48

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N-pyridino benzamide-2-carboxylic acid is prepared by the reaction of phthalic anhydride and 2-aminopyridine. Its lead complex has been synthesized by condensing lead acetate and sodium salt of the ligand in alcohol medium in 1:2 metal ligand ratio. The structural feature of the ligand and solid complex has been investigated on the basis of elemental analysis, conductivity, molecular weight determination and infrared spectral data. The conductivity data indicate that the complex is non electrolyte in nature. The studies reveal the tridentate nature of the ligand and suggest octahedral structure of metal complex. The thermal properties of metal complex in solid state have been studied under non-isothermal condition in nitrogen atmosphere by simultaneous TG and DTA. TG and DTA curves show that the decomposition took place in single step. Thermodynamic parameters such as activation energy, E_a , frequency factor, Z , entropy of activation, ΔS , and energy of activation, ΔG , have been determined by standard methods.

DISSOLUTION OF TIN AND LEAD
BY AQUEOUS ALKYL HALIDES

P49

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The reaction between tin or lead and aqueous methyl iodide has been investigated primarily for its potential role as a source of methyltin or methyllead compounds in natural waters. This reaction may also be viewed, however, as an approach to dissolving these metals and/or treating their surfaces.

Both tin and lead react slowly with a variety of alkyl halides in the presence of water. The rates of reaction depend on the halide and also on the form of the metal. In all systems tested, the level of dissolved metal increased very markedly in the presence of alkyl halides. Even alloys of these metals, such as solder, behaved in this manner. The surface of metals so treated changed their appearances in ways visible even to the naked eye.

All data are consistent with a mechanism involving attachment of the halide to the metal surface, followed by oxidative addition to a metal atom yielding an organometallic compound which subsequently was released into solution.

Details and implications of these reactions will be discussed, along with some potential applications.

The effects of Sn^{2+} and Pb^{2+} ions on the optical properties of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (1) in aqueous solution have been investigated. Electronic absorption spectroscopy and photoluminescence studies reveal the presence of specific interactions between 1 and each of these ions. The relatively accessible axial sites of 1 facilitate such interactions. For example, Tl^+ and 1 in aqueous solution result in luminescent exciplex formation,¹ presumably involving axial interactions between Tl^+ and 1 in its triplet excited state.

¹ Nagle, J. K.; Brennan, B. A. *J. Am. Chem. Soc.* 1988, 110, 5931.

P51

^{19}F NMR STUDY OF INTRAMOLECULAR COORDINATION IN
ORGANOTIN AND -LEAD DERIVATIVES OF O-SUBSTITUTED
PHENOLS

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The aim of this study was to prove the validity of ^{19}F NMR spectroscopy for comparing intensity of intramolecular coordination in organometallic derivatives of ortho-halophenols containing various halogens and organometallic groups and, besides, for comparing intramolecular coordination intensity with that of intramolecular hydrogen bonds in o-halophenols.

With this aim in view, a number of organomercury, -tin and -lead compounds were synthesized:

$\text{R}_n\text{MOC}_6\text{H}_3\text{X}-2-\text{F}-4$ and $\text{R}_n\text{MOC}_6\text{H}_2\text{X}_2-2,6-\text{F}-4$ ($\text{R}_n = \text{PhHg}, \text{Ph}_3\text{Pb}, \text{Ph}_3\text{Sn}, \text{Et}_3\text{Sn}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$).

Fluorine chemical shifts ($\delta^{19}\text{F}$) were determined in chloroform ($c=0,1$) for the indicated organometallic compounds, as well as for corresponding phenols and anisoles $\text{ROC}_6\text{H}_3\text{X}-2-\text{F}-4$ and $\text{ROC}_6\text{H}_2\text{X}_2-2,6-\text{F}-4$ ($\text{R} = \text{H}, \text{CH}_3$).

For all these derivatives, substituent chemical shifts (^{19}F SCS) for $\text{CH}_3\text{O}-$, $\text{OH}-$ and $\text{R}_n\text{MO}-$ groups have been calculated. Analysis of either ^{19}F SCS changes for organometallic and $\text{HO}-$ groups upon introduction of two o-halosubstituents or differences between these values and those of $\delta^{19}\text{F}$ SCS for $\text{CH}_3\text{O}-$ group indicated by introduction of one o-halogen atom led us to conclude that intramolecular coordination is more intensive in the case of organometallic compounds as compared to intramolecular hydrogen bonds in o-halophenols.

The coordinating ability of both $\text{PhHgO}-$ and $\text{Ph}_3\text{PbO}-$ groups is greater than that of $\text{Ph}_3\text{SnO}-$ group.

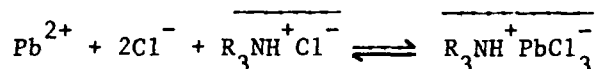
At the same time the data obtained give evidence for approximately equal intramolecular coordination intensity of $\text{PhHgO}-$ and $\text{Ph}_3\text{PbO}-$ groups.

ION PAIR FORMATION BETWEEN LEAD(II) CHLORIDE COMPLEXES
AND TERTIARY AMINES IN XYLENE

P52

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The extraction of lead(II) from an aqueous chloride solution has been investigated as a function of the acidity (1-8M HCl), the concentration and the structure of the extractant. Tertiary amines (TOA, MDOA, TLA) were dissolved in xylene at different concentrations in the range 0.01 to 0.1M at an equal volume phase ratio. Lead(II) does not seem to be particularly well extractable from chloride media with tertiary amines. The distribution curves are similar to that for anion-exchange resins showing a maximum around 1.5M HCl. In HCl solutions lead(II) forms weak chloride complexes predominant at increasing acid concentration. The dependence of distribution coefficient D of lead(II) on amine concentration is regular over the whole range of extractant concentrations investigated. The slope analysis suggests the following extraction reaction:



Many differences in the organic phase interactions affect the formation of ion pair: HCl concentrations, amine structure and concentration. Infrared investigation has emphasized that at high HCl concentration in aqueous solutions dichloride ion HCl_2^- competes strongly with the lead(II) chloride complex PbCl_3^- for ion pairing with the alkylammonium cation, so depressing the extraction of the anionic metal complex into the organic phase.

The aggregation of both the extractant and the trichlorolead(II) complex in the organic phase represents a significant complication. The monomer-micelle equilibrium has resulted to involve several intermediate stages.

The structural effect of the tertiary amine R_3N employed upon aggregation is closely related to the influence of size and symmetry on the dipole moments of the bulky salt. Non symmetrical tertiary alkylammonium cations and small anion, such as PbCl_3^- , exhibits lower aggregation numbers. In addition aggregation has resulted less marked in aromatic diluents (xylene) than in aliphatics of similar low dielectric constant and zero dipole moment.

The ion pairing has resulted to be the driving force for the transfer of lead(II) into the organic phase; its formation is favoured by moderate acid concentration (up to 1.5M HCl), high extractant concentration (0.1M R_3N) and unbranched alkyl chain of the tertiary amine.

TIN EFFECT IN COMPLEX RADICAL
REACTION FORMATION OF Sn-CONTAINING
POLYFUNCTIONAL MACROMOLECULES

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Disposition to coordination tin atom in its functional organic compounds and Sn-containing monomers and macromolecules composes base of these compounds and attaches to them complex specific properties: sensitivity to different aspects of radiation, antifouling, antiviral and stabilized activity.

This report concerns regularity of radical copolymerization of organotin derivatives of methacrylic, monoallylmaleic, N-maleimidacetic acids and their organic analogues with derivatives of maleic acids (anhydride, ester and imid), styrene and substituted allylacetates, specified by structural features of mono- and bifunctional Sn-containing monomers and pentacoordinating condition of tin atom.

Radical copolymerization in donor-acceptor systems with participation bifunctional organotin monomers proceeding on complex mechanism of chain growth reaction with dominant influence of coordinating tin atom and monomeric Charge Transfer Complexes on intramolecular cyclization reaction has been estimated. Complex Radical copolymerization of substituted allylacetates with tributylstannyl methacrylate was realized on mechanism suppression of allyl resonance with coordinating interactions the functional groups of monomeric links in alternating chain growth reactions.

Exposed tin effect allows directly to control composition, structure and properties of polyfunctional Sn-containing copolymers .

HPLC of organotin compounds

P54

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ABSTRACT

Despite the enormous industrial and environmental interest of organotin compounds, good analytical methodology is still lacking. Until now most analytical work was done by gas chromatography. Only a few HPLC methods were developed. Here the research work was mainly focussed on the detection aspect. At this moment however, there is still a lack of good phase systems for this type of analysis and therefore reproducing a published HPLC method is often a very tedious task.

In this study different HPLC phase systems are compared and examined. The best system is based on a cyanopropyl silica gel column eluted in the straight phase mode. Retention, selectivity and efficiency of R_nSnX_{4-n} compounds (R = organo, X = halide, n = 1-4) have been evaluated. Ultra fast reproducible separations of quite complex mixtures can be obtained in less than one minute).

This system can easily be used for fast monitoring of organotin reaction mechanisms, the preparative purification of reaction mixtures and the purity determination of commercially available organotin containing industrial products. Typical examples will be given.

TIN BASED TUNGSTEN CARBONYL PRECURSORS IN THE CATALYSIS OF OLEFIN
METATHESIS

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In the field of olefin metathesis attention recently has focussed on the development of highly active and stereoselective catalytic systems.

$R_nCl_{3-n}SnW(CO)_3Cp$ ($R = Me, Ph; n = 0-3$) precursors activated by $iBuAlCl_2$ in the presence of oxygen in an optimal 1/10/5 ratio show high conversion rates and a good selectivity. The conversion rates for the 2-pentene metathesis follow the sequence $Ph_3Sn- \ll Me_3Sn- < Me_2ClSn- < Cl_3Sn-$. The activation mechanism of the $R_nCl_{3-n}SnW(CO)_3Cp/iBuAlCl_2/O_2$ system has been studied by CGC, HPLC, i.r. and UV-VIS spectroscopy.

A mechanism with donor-acceptor interaction and charge-transfer followed by fragmentation and recombination leading to a Schrock-Type Tungsten Carbene, is proposed.

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Stephen P. Coddington, Department of Chemistry, University of the District of Columbia, Washington, DC 20005

Laura L. Stockton, Department of Chemistry, University of the District of Columbia, Washington, DC 20005

The use of organotin compounds as biocides is well established. Compounds such as triphenyltin hydroxide, triphenyltin chloride and triphenyltin acetate are broad spectrum agricultural fungicides. These chemicals have been found to be effective against a host of plant diseases.¹ In addition to triphenyltin compounds, adducts of triphenyltin chloride have been reported to have a favorable fungicidal to phytocidal activity ratio.²

In the interest of developing a more effective fungicide against Ceratocystis ulmi, the causative agent of Dutch elm disease, our laboratory synthesized and screened several triphenyl- and trimethyltin chloride as well as diphenyl- and dimethyltin dichloride adducts against this fungus using a shake culture method. The ligands employed in this study were dimethyl sulfoxide, triphenyl phosphine oxide, and benzamide. The results of the screening indicate that it is the triphenyltin moiety that is the species responsible for the inhibition of the fungus.

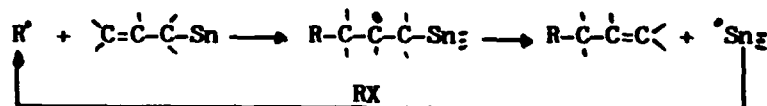
1. A. G. Davies and P. J. Smith, in G. Wilkinson, F. G. A. Stone and E. W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 2, p. 610 and references therein.
2. R. C. Poller, *The Chemistry of Organotin Compounds*, Academic Press, New York, 1970, p. 275 and references therein.

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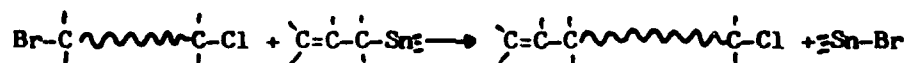
Laboratoire de Chimie Organique et Organométallique, associé
au CNRS (URA 35)

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F - 33405 - Talence-Cedex. France

Under free radical initiation (1), allyltins react with alkyl halides to give alkenes through a chain reaction involving tin radical as carrier :



As kinetic analysis of halogen abstraction by such metallic radicals (2) indicated an excellent selectivity of these reactions : $I > Br \gg Cl$. Whatever is the class of the halide (primary, secondary or tertiary), we decided to investigate the reaction of allyltins with bromochloroalkanes. An easy method to prepare unsaturated chlorides had been developed from this reaction :



Literature

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J. GRIGNON and M. PEREYRE. *J. Organometal. Chem.*, 96, C33. (1976).
(2) K.U. INGOLD, J. LUSZTYK and J.C. SCAIANO, *J. Amer. Chem. Soc.*, 106, 343, (1984).

* Permanent address : Laboratoire de Chimie Organique, Département de Chimie, Faculté des Sciences, Sidi Mohamed Ben Abdellah - FES (Maroc)

SYNTHESIS AND REACTIVITY OF FUNCTIONALLY SUBSTITUTED VINYL TIN

Jean-Baptiste Verlhac, Michel Pereyre

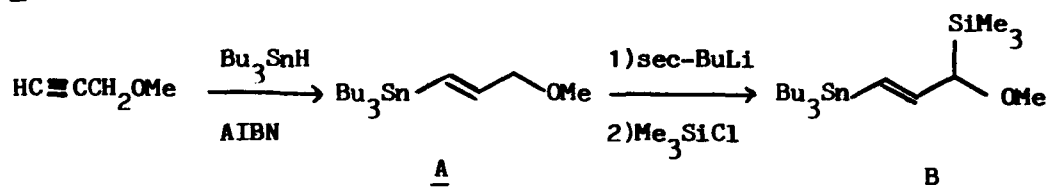
Laboratoire de Chimie Organique et Organométallique, URA 35 CNRS

Université de Bordeaux I, 351, Cours de la Libération

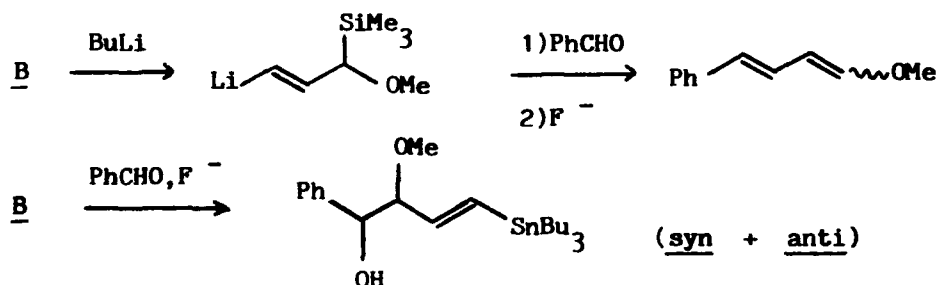
33405 - Talence, France

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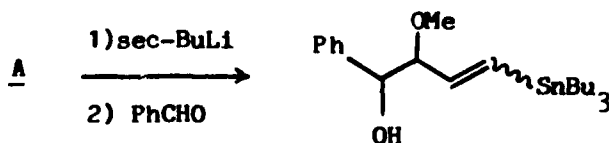
The hydrostannation of methyl propargyl ether yields the vinyltin A which can be easily transformed into the silylated analog B:



Reagents A and B have been already successfully used as organotin homoenolate equivalents in organic synthesis (1). However there are numerous other possibilities from a compound like B which can react either as a vinyltin or an allylsilane. For instance :



The second situation provides highly functionalized compounds which can undergo further transformations at the vinyl-tin bond. However they are more conveniently obtained directly from reagent A :



The use of different Lewis acid catalysts allows a good control of the syn/anti stereochemistry, an important prerequisite for synthetic usefulness.

(1) J.B. Verlhac, J.P. Quintard, M. Pereyre, J. Chem.Soc., Chem. Commun., 503, 1988.

ORGANOALKOXYTIN DIHALIDES AS INTERMEDIATES
IN ORGANIC SYNTHESIS

P59

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In our previous work (1,2), we have shown that 1,5-heptadien-4-ol and various 1,4- and 1,5-glycols are catalitically converted to open-chain and cyclic ethers respectively in the presence of butyltin trichloride. The catalytic efficiency of other organotin chlorides has been tested for the conversion of 1,5-pentanediol to THP: the best results have been obtained with the use of organotin trichlorides.

These dehydration processes are mediated by formation of organoalkoxytin dihalides, RSn(OR')Cl_2 , which work similarly to their parent compounds $\text{R}_3\text{Sn(OR')}$ (3).

Many systems have been analysed using BuSnCl_3 as catalyst precursor in etherification and hydro-hydroxy-elimination processes.

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THE APPLICATION OF INITIATING SYSTEMS BASED ON
ORGANIC COMPOUNDS OF TIN AND LEAD FOR SYNTHESIS
OF BIORESISTANT POLYMERS

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Organotin and -lead compounds such as R_4M ($M = \text{Sn}, \text{Pb}$; $R = \text{Et}, i\text{Pr}, n\text{-Bu}$) initiate greatly a radical polymerization of vinyl monomers (methyl methacrylate, butyl methacrylate, acrylonitrile, methacrylic acid) in the presence of equimolar quantities of SiCl_4 or $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ at temperature $50\text{-}60^\circ \text{C}$. The concentration of a binary initiator is $0.05\text{-}0.06 \text{ mol/l}$.

The polymer formed is bioresistant to the following mold strains:

Aspergillus niger V. Tigehm,
Penicillium funiculosum Thom,
Paecilomyces varioti Bainir,
Trichoderma lignorum Persevr,
Chaetomium globosum Kunze.

The polymer bioresistance to molds is due to the introduction of a binary initiator fragment as end groups into macromolecules in the course of polymerization.

The existence of lines for the corresponding metal and silicon in spectra of polymer samples after their 3-5 fold reprecipitation has been found by the emission spectroscopy. Bioresistance of a reprecipitated polymer is retained.

THE PREPARATION OF BIORESISTANT POLYMERS ON
ORGANOMETALLIC CATALYSTS INCLUDING TIN AND
LEAD COMPOUNDS

P61

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The polymerization of vinyl monomers initiated by binary system of the mixed organometallic compound (R_3MX , $M = Sn, Pb$; $R = \text{alkyl}$; $X = Cl, \text{acyl}$) and boron hydride or tetraphenylborate of sodium has been found to be accompanied with formation of the corresponding polymer of the elevated bioresistance to molds. The estimation of mold resistance has been performed relative to the following mold strains:

Aspergillus niger V. Tigehm,
Penicillium funiculosum Thom,
Paecilomyces varioti Bainir,
Trichoderma lignorum Persevr,
Chaetomium globosum Kunze.

Polymer bioresistance is due to introduction of Sn or Pb atoms into polymer chain as end groups in the initiation stage.

The initiator components were taken in equimolar quantities 0.5 to 1.8 % to monomer weight, polymerization temperature was 50 - 70°C.

By their physico-chemical properties the polymers prepared differ slightly from common ones synthesized on peroxide initiators.

SYNTHESIS AND UTILIZATION OF POLYMER-SUPPORTED ORGANOTIN REAGENTS

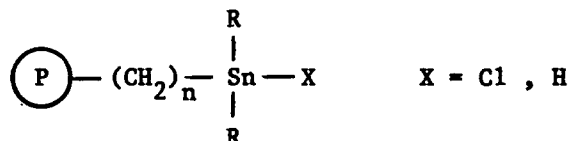
Gilles DUMARTIN , Bernard DELMOND , Michel PEREYRE , Alain RAHM

Laboratoire de Chimie Organique et Organométallique , URA 35 CNRS
Université de Bordeaux I , 351 cours de la Libération
33405 Talence Cédex (France)

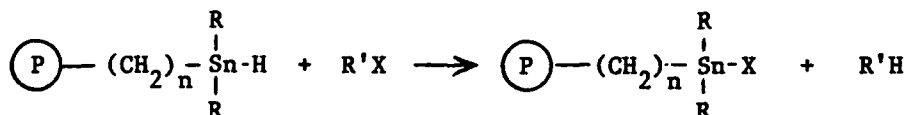
Organotin reagents are very efficient tools for organic synthesis¹. However their utilization in chemical industry is restricted because of the difficulties in product isolation , the toxicity of the residues and the cost of the chemicals .

The use of insoluble polymer-supported organotin reagents is an interesting approach to solve these problems²⁻⁷.

In this work we describe the synthesis of some new polymeric organotins of the following type :



Their use will be described as well . For instance , the reduction of organic halides by means of a polymeric organotin hydride has been successfully achieved :



The insoluble organotin halide has been recovered and recycled satisfactorily .

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- 6 B.L. Miller , J.W. Hersberger , Journal of Polymer Science , Part C Polymers Letters , 25 219-221 (1987) .
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HYDROXYLATION AND OXIDATION OF TERPENIC STRUCTURES
VIA ALLYL- AND BENZYLSTANNANES

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Allyl- and benzylstannanes are versatile reagents and useful precursors for the introduction of a variety of functional groups ¹. Also, we have used these derivatives for the functionalization of terpenic structures ².

The reaction of allylstannanes with *m*-chloroperbenzoic acid has been used to realize hydroxyl group shifts in allylic alcohols ³. We have extended this reaction to terpenic series, using a solution of *p*-nitroperbenzoic acid as oxidant. Without acid hydrolysis at the end of reaction, terpenic allylic and benzylic alcohols were obtained.

The oxidation of allylic tin derivatives has also been reported ⁴. Also when allyl- and benzylstannanes are treated with pyridinium chlorochromate a mixture of terpenic α, β -unsaturated carbonyl compounds was obtained.

We have shown that terpenic allyl and benzylstannanes, readily obtained from terpenes hydrocarbons are versatile intermediates for the synthesis of terpenic derivatives useful in the perfume industry.

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- 4 - W.C. STILL, J.Am.Chem.Soc., (1977), 99, 4186.

PREPARATION AND LEWIS ACID BEHAVIOUR OF ETHYL(ISO-PROPYL)-
TIN DICHLORIDE TOWARDS SOME NITROGEN DONORS

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The wide applications of organotin compounds in agriculture, industries and organic syntheses are well known. In future they may also be used in the treatment of cancer.¹⁻³ Mixed diorganotin dichlorides having different organic groups attached to the same tin atom have received less attention than their simple diorganotin dichloride analogues. Here we report for the first time the preparation of ethyl(iso-propyl)tin dichloride in a very good yield by redistribution reaction between equimolar quantities of diethyldi(iso-propyl)tin and tin tetrachloride at 180-200°C for about two hours. This compound forms solid complexes with bases such as o-toluidine, o-tolidine, 1-naphthyl amine, morpholine, N-ethyl piperidine, quino-line, triethyl amine and 2,2'-bipyridyl. All these complexes except the last one which is equimolar, possess 1:2 (acid:base) stoichiometries. Conductometric titrations of ethyl(iso-propyl)tin dichloride with the above bases in nitrobenzene indicate the formation of ions during these reactions. ¹H NMR spectra of these complexes indicate that all the ligand proton signals shift downfield on complexation due to the flow of electrons from ligand to tin atom. I.R. spectral data also support the same. X-ray powder diffraction data for the pyridine complex consists of 14 reflections with maximum intensity at $2\theta = 19.1^\circ$ and agree well with the orthorhombic symmetry of the crystals to give the lattice constants; $a = 15.9464 \text{ \AA}$, $b = 14.0511 \text{ \AA}$, $c = 10.1354 \text{ \AA}$ and cell volume $V = 2270.932 \text{ \AA}^3$.

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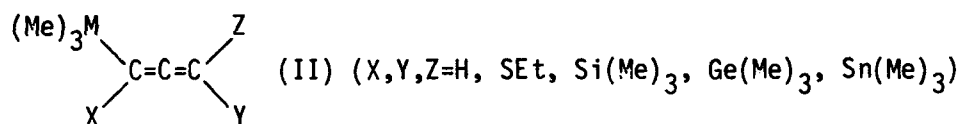
$^{13/12}\text{C}$ ISOTOPE SHIFTS IN ^{119}Sn AND ^{29}Si NMR SPECTRA P65
OF STANNYL- AND SILYLACETYLENES AND -ALLENES

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A systematic study of isotope shifts $^n\Delta(\text{M})(^{13/12}\text{C})$ (IS) in ^{119}Sn and ^{29}Si NMR spectra for approximately 50 acetylenes of the type $\text{R}_{3-n}(\text{t-Bu})_n\text{MC}\equiv\text{CX}$ (I) ($\text{M} = ^{119}\text{Sn}, ^{29}\text{Si}$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$; $\text{X} = \text{H}, \text{Me}, \text{Et}, \text{t-Bu}, \text{Cl}, \text{J}, \text{Si}(\text{Me})_3, \text{Ge}(\text{Me})_3, \text{Sn}(\text{Me})_3, \text{OMe}, \text{Ph}, \text{CF}_3, \text{C}_6\text{F}_5, \text{P}(\text{O})(\text{OMe})_2, \text{CN}, \text{SEt}$; $n=0-3$) and for approximately 30 allenes has been carried out.



Quantitative relationships between $^{13/12}\text{C}$ IS on ^{119}Sn and ^{29}Si nuclei were established. The IS values were used to rationalize changes in the length and stability of M-C bonds under the influence of substituents in molecule.

Linear correlations were demonstrated between the IS values and $^n\text{J}(\text{M}-^{13}\text{C})$ spin-spin coupling constants both for I and II, as well as between I and II. Due to the hyperconjugation of the type $\text{H}-\text{C}^+-\text{M}-\text{C}^-=$, different correlations exist in I both for different n and for substituents carrying a variable number of α -protons in the R radicals. The degree of the hyperconjugation differs for I and II, as reflected by the correlation slope.

The influence of element M nature on the transfer of electronic effects exerted by the substituents along the molecule's backbone will be discussed.

DIORGANOTIN(IV) COMPLEXES OF SOME DIHYDROXAMIC ACIDS

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Hydroxamic acids are of considerable biological importance; so are the organotin compounds. Dihydroxamic acids may be regarded as the synthetic analogues of rhodotorulic acid, a naturally occurring siderophore. Based on the idea of potential enhancement of biological activity in the compounds formed from the combination of organotin and hydroxamic acids, organotin complexes of monohydroxamic acids have attracted considerable attention,^{1,2} but no such complexes of dihydroxamic acids³ have been reported so far. Therefore, a number of diphenyltin and dibutyltin complexes of dihydroxamic acids (H_2L), $(CH_2)_n[CON(R)OH]_2$ ($n = 2, 3, 4, 6, 8$; $R = C_6H_5, 4-CH_3C_6H_4, 4-ClC_6H_4$), have been synthesized. Analytical data conform to the stoichiometry R'_2SnL ($R' = C_6H_5, n-C_4H_9$). For $n \geq 4$ acids, the complexes are monomeric, R'_2SnL , but for $n = 2$ and 3 acids, they are dimeric through bridging of the other ends of the ligands, because of the constraint involved in the formation of an additional intramolecular chelate, as required for the formation of monomeric species. The 1H NMR spectra support the formulations, and the IR spectra confirm the replacement of the NO-H proton and coordination of the carbonyl group to the metal, as indicated by the considerable lowering of the $\nu(C=O)$ in the ligands themselves.

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COORDINATION CHEMISTRY OF
TRIPHENYLTIN ISOTHIOCYANATE

P67

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Triphenyltin isothiocyanate reacts with aminobenzene, 3-methylpyrazole, diphenylamine, 2-[4(2',4'-dichlorophenoxy)-phenoxy]-propionic acid to give 1:1 and 1:2 complexes, and with o- or m-phenylene diamine to give 1:1 complexes.

Measurements of electrical conductivities in acetonic and methanolic solutions (concentration range $c = 10^{-3}$ mole dm^{-3} to $c = 10^{-5}$ mole dm^{-3} , 25°C) were carried out (the compounds triphenyltin chloride and triphenyltin isothiocyanate are included in this series) to estimate the electrolytic dissociation and stability constants (values given).

Time dependent UV absorption behaviour of diluted methanolic solutions of the complexes confirm different stabilities of the species and mechanisms for ligand exchange processes.

Triphenyltin selenocyanate complexes with N-donors are included in this investigations.

**SYNTHESIS AND STRUCTURAL STUDIES OF COORDINATION COMPOUNDS
OF TIN(II) WITH SULPHUR DONOR BENZOTHAZOLINES**

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India

The condensation of Furfuraldehyde, Thiophene-2-aldehyde, Indole-3-carboxylaldehyde, glyoxal and diacetyl with 2-aminobenzenethiol involves the undesirable side reaction resulting in the ring closure with the formation of heterocyclic compound (benzothiazoline). It however appears to be in equilibrium with Schiff base form in solution. On reacting metal alkoxide with the ligand in presence of methanol, the Schiff base form appears to react with alkoxide and the equilibrium is shifted towards the formation of Schiff base complexes of these metals.

The infrared electronic and proton magnetic spectra confirm the coordination of sulphur and nitrogen to the metal atoms. The covalent bonding of sulphur with tin and nitrogen indicate square pyramidal geometry for these derivatives. This is also confirmed by ^{119}Sn Mössbauer spectral studies.

^1H , ^{13}C , ^{15}N AND ^{119}Sn NMR SPECTRA OF SOME ORGANOTIN(IV)
OXINATES AND THIOOXINATES

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The ^1H , ^{13}C , ^{15}N and ^{119}Sn NMR spectra of $\text{R}_3\text{Sn}(\text{oxin})$, $\text{R}_3\text{Sn}(\text{txin})$, $\text{R}_2\text{Sn}(\text{oxin})_2$ and $\text{R}_2\text{Sn}(\text{txin})_2$ (R = 1-butyl, benzyl, phenyl or vinyl, oxinH = 8-hydroxyquinoline, txinH = 8-mercaptoquinoline) have been measured in various solvents. In non-coordinating solvent (deuteriochloroform), all compounds exist as chelate complexes with weak Sn-N bonding. $\text{R}_3\text{Sn}(\text{oxin})$ and $\text{R}_3\text{Sn}(\text{txin})$ form a cis-trigonal bipyramide arrangement while $\text{R}_2\text{Sn}(\text{oxin})_2$ and $\text{R}_2\text{Sn}(\text{txin})_2$ form trapezoidal bipyramide (skew) arrangements, central tin atom being six-coordinate.

Several NMR characteristics have been tested to describe the strength of Sn-N bonding ($\delta(^{119}\text{Sn})$, $\delta(^{15}\text{N})$, $\delta(^{13}\text{C}(4))$, $J(^{119}\text{Sn}, ^{15}\text{N})$, $^2J(^{15}\text{N}, \text{H}(2))$, $^3J(^{119}\text{Sn}, \text{H}(2))$, $^3J(\text{H}(2), \text{H}(3))$, $J(^{119}\text{Sn}, ^{13}\text{C}(2))$ etc.). Most of the above-mentioned characteristics show mutual correlations.

$\text{R}_3\text{Sn}(\text{oxin})$ and $\text{R}_2\text{Sn}(\text{oxin})_2$ interact with molecules of coordinating solvent (pyridine, HMPA) to form $\text{R}_3\text{Sn}(\text{oxin})\cdot\text{S}$ and $\text{R}_2\text{Sn}(\text{oxin})_2\cdot 2\text{S}$ (S = molecule of solvent) in which oxinate groups are monodentate due to the splitting of Sn-N bonding in the starting compounds.

Synthesis & Biological study of Pb^{+2} & Sn^{+2} complexes with some new Schiff-bases.

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1:1 & 1:2 metal-ligand complexes of Pb^{+2} & Sn^{+2} with the schiff-bases derived from 2-hydroxy-1-naphthaldehyde & anthranilic acid, 2-aminothiophenol, 2-amino pyridine & 2-aminothiazole were synthesized. Elemental analysis, Molecular weight determination, IR & UV spectral data, magnetic & conductance measurements were used to deduce the probable structures of the resulting complexes. These complexes have been found of three types viz : $ML(H_2O)_3$, $ML_2(H_2O)_2$ & ML_2 (Where $M=Pb^{+2}$ & Sn^{+2} ; L = different schiff bases) ². Analytical data reveals that all the complexes appear to have an octahedral geometry. Biocidal studies of all the synthesized ligands & their metal complexes were carried out on fungi (A.niger & A.flavus) & bacteria (S.aureus & E.coli). It is noted that the antimicrobial activity of the ligands has several times enhanced in the form of their metal complexes.

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MOLECULAR ADDUCTS AND COMPLEX ANIONS OF PHENYL TIN AND PHENYL LEAD AZIDES

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P73

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Fifteen 1:1 molecular adducts of Ph_3SnN_3 with a variety of oxygen- and nitrogen-donor ligands have been prepared and characterized. They are white solids which melt sharply above 100°C and cannot be recrystallized from non-polar solvents without dissociation. Triphenyltin azide reacts with piperidine, quinuclidine, tetramethylethylenediamine, morpholine and triethylamine to produce crystalline compounds having the unusual composition $\text{Ph}_3\text{Sn}(\text{N}_3)_2\text{L}$, the X-ray crystal structures of which will be described.

Eleven 1:1 molecular adducts of Ph_3PbN_3 with a variety of oxygen- and nitrogen-donor ligands have been prepared and characterized. They are white solids which dissociate and/or decompose without melting, and are slightly soluble in non-polar organic solvents from which they cannot be recrystallized without dissociation.

Attempts to prepare $\text{Ph}_2\text{Sn}(\text{N}_3)_2$ by the reaction of Ph_2SnCl_2 with NaN_3 under a variety of conditions were unsuccessful. However, treatment of $\text{Ph}_2\text{SnCl}_2 \cdot 2\text{HMPA}$ with NaN_3 in acetone gave $\text{Ph}_2\text{Sn}(\text{N}_3)_2 \cdot 2\text{HMPA}$ (44% yield, m.p. 121°C). The diazido salt $[(\text{Ph}_3\text{P})_2\text{N}]^+ [\text{Ph}_3\text{Sn}(\text{N}_3)_2]^-$ (80% yield, m.p. 161°C) was obtained by the reaction of $(\text{Ph}_3\text{P})_2\text{N}^+ \text{N}_3^-$ with Ph_3SnN_3 in ethanol. Reactions of Ph_3SnN_3 , $\text{Ph}_2\text{Sn}(\text{N}_3)_2 \cdot 2\text{HMPA}$ and $[(\text{Ph}_3\text{P})_2\text{N}]^+ [\text{Ph}_3\text{Sn}(\text{N}_3)_2]^-$ with diphos and triphos are being investigated in the hope of obtaining novel cyclic phenyltinphosphinimines. Our latest results will be described together with infrared, Raman and nmr spectra of all new compounds.

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FT-IR STUDY OF THE THERMAL DECOMPOSITION OF DIORGANOTIN
DICARBOXYLATES

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The thermal decomposition of the dialkyltin dicarboxylates, $R_2Sn(O_2CR')_2$, dimethyltin diacetate (DMTDA), dimethyltin ditrifluoroacetate (DMTDTFA), dibutyltin diacetate (DBTDA), and dibutyltin ditrifluoroacetate (DBTDTFA), have has been investigated by FT-IR in both in the presence and absence of oxygen. In the presence of oxygen the major reaction products are the corresponding alkyl esters, RO_2CR' , resulting from reductive-elimination. Without oxygen the major products are the carboxylic acid, $R'CO_2H$, and methane ($R = CH_3$) or butene ($R = C_4H_9$). At higher temperatures the carbonyl-containing products decompose further, and the ultimate product mixture contains alkane or alkene, carbon dioxide, a small amount of carbon monoxide, and trifluoromethane. Mechanistically, the reactions take place via chemisorption and subsequent surface-mediated processes.

KINETICS AND MECHANISM IN THE THERMOLYSIS OF
TRIMETHYLSTANNANE

P75

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The thermal decomposition of trimethyltin hydride has been studied by FT-IR methods in both the presence and absence of oxygen. In the temperature range 378-503K in the absence of oxygen, decomposition proceeds to form methane, tetramethyltin and hexamethylditin together with very small amounts of ethane, and the reaction is found to be 1/2 order with respect to Me_3SnH . The activation energy for the reaction is 45.0 kJ mol^{-1} . Deuteration studies employing Me_3SnD give an identical value for the activation energy, and further show that only CH_3D and no CH_4 is formed.

In the presence of oxygen the thermolysis reaction proceeds differently. Temperatures for decomposition are higher than those without oxygen, and products observed in the temperature range 438-518K include methane, methanol and trimethyltin hydroxide. The order with respect to Me_3SnH is observed to be unity with an activation energy for the reaction of 110 kJ mol^{-1} . Nitric oxide has an even greater inhibiting effect upon the thermolysis.

The data are interpreted mechanistically in terms of surface and/or radical processes.

VISUALIZATION OF INTRACELLULAR DISTRIBUTION
OF DIBUTYLTIN COMPOUND

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395 Yada, Shizuoka-shi, Shizuoka 422, Japan

Intracellular distribution of dibutyltin in intact cells
was examined using a fluorescence technique with Morin (Y.
Arakawa et al, Anal. Chem. 55, 1901-1904, 1983).

Cultured normal human skin fibroblasts incubated with
dibutyltin were further treated with Morin reagent and were
observed using a fluorescence microscope.

Golgi apparatus was strongly fluorescent. Cells
incubated with Morin alone or dibutyltin alone did not give
any fluorescence. These results suggests that dibutyltin has
a strong affinity for the Golgi apparatus.

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THERMAL DECOMPOSITION OF ORGANOTIN COMPOUNDS

Paul Harston and James L. Wardell, Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland

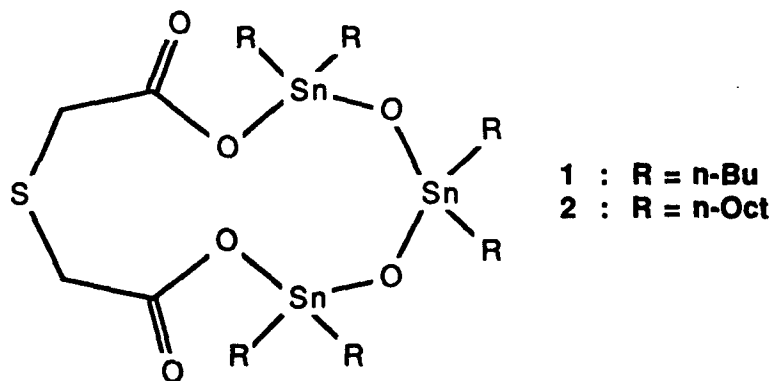
Thermolysis of series of tri- and tetra-organotin compounds have been studied using thermal analysis (DTA, DTG, TGA) and by product analysis.

Diorganotin(IV) Derivatives of Thiodiglycolic Acid: Synthesis, Spectroscopic Characterization, and *in vivo* Antitumour Activity

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Di-n-butyl- and di-n-octyltin(IV) oxides react with thiodiglycolic acid in a very different way than for instance unsubstituted or N-substituted iminodiacetic acids: they react in a 3:1 molar ratio, yielding $R_2Sn(O-SnR_2-OCOCH_2)_2S$ when the preparation is carried out in acetone/chloroform or ethanol/chloroform, leaving unreacted thiodiglycolic acid if a smaller molar ratio is used.



If the same reaction is carried out in dimethylformamide/chloroform, the same stoichiometry is found as in the case of iminodiacetic acid and $R_2Sn(OCOCH_2)_2S$ complexed with DMF is obtained. The prepared compounds have been fully characterized by 1H , ^{13}C and ^{119}Sn NMR, Mössbauer and mass spectrometry. They were tested *in vivo* against P388 leukemia and were found to be not active.

Diorganotin(IV) Derivatives of Substituted Iminodiacetic Acids: Synthesis, Spectroscopic Characterization, X-Ray Structure Analysis, *in vitro* and *in vivo* Antitumour Activity

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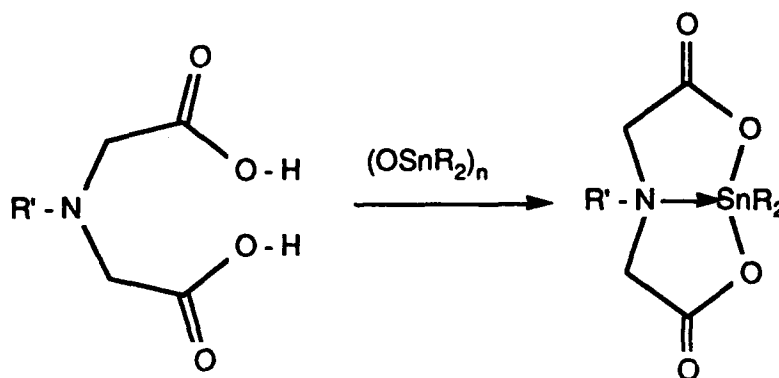
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Diorganotin(IV) derivatives of iminodiacetic acid, and of N-methyl-, (2-hydroxyethyl)- and N-carbamoylmethyl-iminodiacetic acid have been prepared, characterized by ¹H, ¹³C and ¹¹⁹Sn NMR, Mössbauer and mass spectrometry.



with R, R' being respectively H, n-Bu (compounds 1); H, n-Oct (2); H, PhCH₂ (3); Me, n-Bu (4); Me, n-Oct (5); Me, PhCH₂ (6); HO-CH₂CH₂, n-Bu (7); HO-CH₂CH₂, n-Oct (8) and H₂N-CO-CH₂, n-Bu (9).

The structure of compound 7 has been determined by X-ray diffraction and exhibits a severely distorted octahedral environment, the OH group of the N-hydroxyethyl side chain co-ordinating to the central metal atom.

In vitro and *in vivo* tests against P388 and L1210 leukemia have been performed and will be discussed.

***In vitro* and *in vivo* Antitumour Activity of
Diorganotin(IV) Derivatives of the Type
 $\text{Bu}_2\text{Sn}(\text{O}-\text{XY}-\text{O})$**

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We have prepared and characterized by ^1H and ^{13}C NMR, Mössbauer and mass spectrometry a series of diorganotin(IV) derivatives of the type $\text{Bu}_2\text{Sn}(\text{O}-\text{XY}-\text{O})$, with XY respectively equal to $\text{O}=\text{C}-\text{CRR}'-\text{C}=\text{O}$ ($\text{R}, \text{R}' = \text{H}, \text{Me}; \text{H}, \text{Et}; \text{Me}, \text{Me}; \text{Et}, \text{Et}; \text{CH}_2\text{CH}_2\text{CH}_2$), to $\text{O}=\text{C}-\text{C}(\text{Ph})\text{H}$ [D(-) and dl], to $\text{O}=\text{C}-\text{o}-\text{C}_6\text{H}_4$, and to $\text{CH}_2-\text{o}-\text{C}_6\text{H}_4$.

Their *in vitro* and *in vivo* antitumour activity against P388 and L1210 leukemia has been determined. They exhibit a rather important *in vitro* activity, but almost no *in vivo*.

Their LD_{50} values have been determined and compared with values obtained recently for several other organotin compounds.

**SYNTHESIS AND CHARACTERIZATION OF A
SERIES OF DIORGANOTIN(IV) COMPOUNDS OF
THE TYPE**



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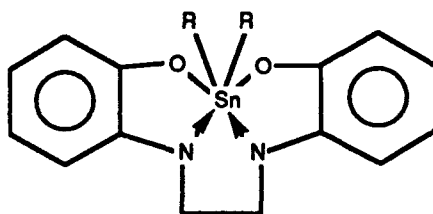
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Four diorganotin(IV) derivatives of $\text{HO}-\text{C}_6\text{H}_4-\text{o}-\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}-\text{C}_6\text{H}_4-\text{o}-\text{OH}$ have been prepared:



with R = Me, n-Bu, t-Bu and Ph.

The Mössbauer parameters obtained for these compounds are compatible with a cis-octahedral structure.

They have been fully characterized by 1D and 2D ^1H and ^{13}C NMR, and by IR and mass spectroscopy.

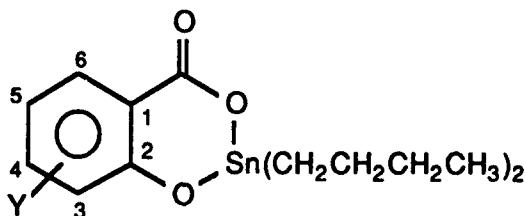
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**SYNTHESIS AND CHARACTERIZATION OF A
SERIES OF SUBSTITUTED
2,2-DI-n-BUTYL-4-OXO-BENZO-
1,3,2-DIOXASTANNINES**

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The characterization by ¹H and ¹³C NMR, Mössbauer and mass spectrometry of a series of di-n-butyltin derivatives of substituted salicylic acids of the type



with Y = 3-Me (1), 4-Me (2), 4-MeO (3), 5-MeO (4), 3,5-I₂ (5) and 4-NH₂ (6) will be described.

and its Reactions

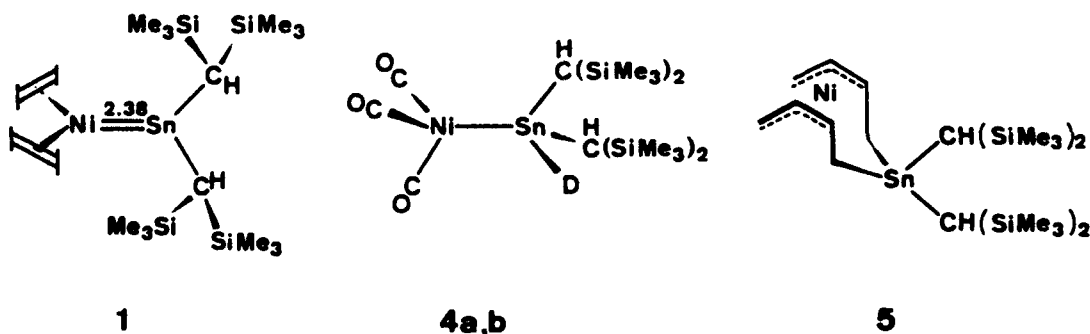
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We have included diorgano stannylenes in our studies on the interaction of nickel(0) alkene complexes with main group metal alkyls¹ and hydrides².

Bis{bis(trimethylsilyl)methyl}tin(II) reacts with tris(ethene)nickel(0) (pentane, -10°C) to yield thermolabile, air sensitive red crystals (70 %) of $(C_2H_4)_2NiSn\{CH(SiMe_3)_2\}_2$ (1). 1 exhibits in the crystal a short Ni-Sn bond of 2.38 Å (sum of covalent radii: 2.56 Å) with the C,C,C,C,Ni,Sn and Sn,C,C planes twisted about 74° to each other. With NH_3 and pyridine, 1 forms the yellow adducts $(C_2H_4)_2NiSn\{CH(SiMe_3)_2\}_2$ (Donor) (2a,b). Reaction of 1 with CO yields the orange carbonyl derivative $(CO)_3NiSn\{CH(SiMe_3)_2\}_2$ (3), which forms NH_3 and pyridine adducts $(CO)_3NiSn\{CH(SiMe_3)_2\}_2$ (Donor) (4a,b). According to the 1H and ^{13}C NMR spectra, the bulky $CH(SiMe_3)_2$ -substituents in 2a,b and 4a,b are non-equivalent at low temperature, presumably due to steric effects. Butadiene reacts with 1 to cleave the Sn-Ni bond and a light-yellow compound 5 forms, which appears to be a $\mu-\eta^3,\eta^1$ -butendiyl-Ni(II)-Sn(IV) complex (anti-isomer). 5 produces with PMe_3 an orange adduct 6 (syn-isomer).



1 Chem. Ber. 118 (1985) 275; 121 (1988) 1913; 121 (1988) 1921.

2 J. Organomet. Chem. 349 (1988) 257; 358 (1988) 519; and ref. therein.

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CO-ORDINATION CHEMISTRY OF FUNCTIONAL SUBSTITUTED
ORGANOTIN COMPOUNDS

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Aspects of the co-ordination chemistry of organotin compounds of the
type $\text{XR}_2\text{Sn}-(\overset{\text{I}}{\underset{\text{n}}{\text{C}}})-\text{Y(I)}$ (e.g. X = halide, Y = O, S or Se donor group) in
both the solid state and in solution will be presented. The effect
of Y and n on the strength of the intramolecular co-ordination in (I)
will be discussed. Brief mention will also be made of the nucleo-
philic assistance provided by Y groups in Ph-Sn cleavage reactions of
 $\text{Ph}_3\text{Sn}(\text{CH}_2)_n\text{Y}$.

CHLOROSTANNATION OF CARBONYL ACTIVATED
DOUBLE BONDS IN AROMATIC SYSTEMS.

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Recently methods have developed¹ to prepare estertin compounds by reacting tin (ii) chloride (or tin powder) and HCl with carbonyl activated double bonds (e.g. $\text{CH}_3\text{O}-\text{CO}-\text{CH}=\text{CH}_2$) in aliphatic systems. Similar type of reactions have been carried out by reacting HSnCl_3 with chalcone, benzal acetone etc. Reaction with chalcone, under suitable conditions, yields $\text{Ph}.\text{CH}(\text{SnCl}_3)\text{CH}_2.\text{CO}.\text{Ph}$. Elemental analyses, I.R., N.M.R. (^1H , ^{13}C and ^{119}Sn) spectra showed pentacoordination around the tin atom, involving the CO group. Benzalacetone also give a similar compound. These compounds exhibit strong acidic character even in non-polar solvents. Unlike² $(\text{CH}_3\text{O}.\text{CO}.\text{CH}_2\text{CH}_2)_2\text{SnCl}_2$, these compounds react with bases like pyridine, quinoline, bipyridyl etc to give chalcone, tin(ii) chloride and base- hydrochloride. But with ligands like 8-hydroxyquinoline, dithizone, chelate complexes have been prepared³.

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