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13. ABSTRACT *(Maximum 200 words)*

Low-coordination phosphorus compounds of various types (RO-PO_2, R-PO_2, RO-P(S)O, R-P=CH_2) were generated in the presence of suspended solids known to contain surface OH groups (silica gel, alumina, Zeolites, titanium dioxide). In all cases, the phosphorus atom became covalently attached to the O atom on the surface. CP-MAS ^{31}P NMR was used extensively to prove the presence of the bonded group. Valuable HPLC characteristics were found for phosphorylated silica gel.

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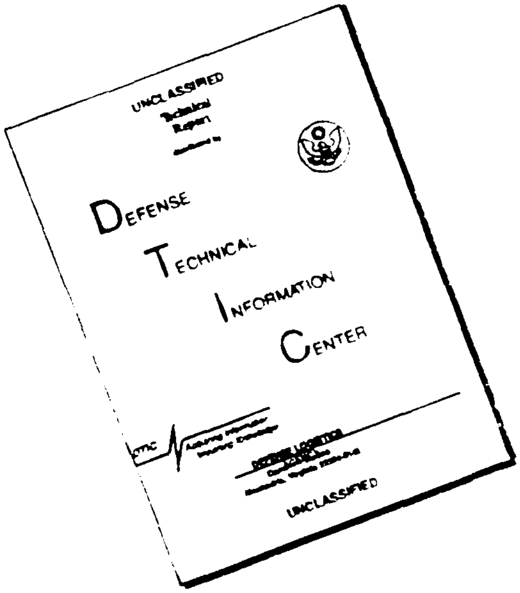

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Technical Report

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APPLICATIONS OF LOW-COORDINATION PHOSPHORUS CHEMISTRY IN THE CHEMICAL MODIFICATION OF SURFACES.

FINAL REPORT

LOUIS D. QUIN

November 13, 1992

U. S. Army Research Office

DAAL03-89-K-0101

Department of Chemistry
University of Massachusetts
Amherst, MA 01003

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I. PURPOSE OF THE RESEARCH PROGRAM

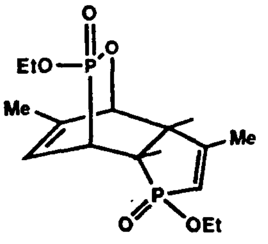
This project was a consequence of a several-year period of research into the synthesis of phosphorus heterocyclic systems that can be fragmented into low-coordinated forms of phosphorus by retrocycloaddition reactions. Such species were found to be extraordinarily reactive as electrophiles, and this led to the suggestion that even OH groups on solid surfaces could act as nucleophiles toward them, thus becoming converted to surface-bonded phosphorus functions.

It was considered that useful properties might reside in the solids after this change in their surface groups. Solids to be considered included (especially) silica gel, alumina, and Zeolites. As will be seen in this report, considerable progress has been made in the application of low-coordinated phosphorus species for surface modification. The concept is indeed a practical one, and at least for the silica gel products, some valuable modifications in properties have been observed. It was also anticipated that new syntheses and chemical properties of the heterocyclic precursors would be discovered, and this has proved to be the case. As an outgrowth of these studies, a new and very practical method for the generation of metaphosphates from non-heterocyclic precursors (phosphoramidic acids) was discovered.

II. MAJOR ACCOMPLISHMENTS

A. Preparation and Properties of Phosphorylated Silica Gel.

It has been conclusively established that monophosphate groups can be covalently bonded to the surface of silica gel by generating alkyl metaphosphates in the presence of the solid held in suspension. This is an observation of considerable importance; as will be seen, it has opened the door to some major application possibilities, and the technique can be extended to the phosphorylation of other surfaces as well. In some earlier exploratory work,[1] we had employed metaphosphate precursors of structure **1** for this purpose, but the resulting product appeared to have a pyrophosphate group on the surface. This was indicated by a high phosphorus content, and by the presence of two equal-intensity ^{31}P NMR signals (δ -12 and -15, with $CaHPO_4$ as reference) seen on the spectrum of the solid when obtained by the cross polarization-magic angle spinning (CP-MAS) method. When a different precursor (**2**) was employed in the new work,[2] the ^{31}P NMR spectrum was quite different, and consisted of a single signal at δ -9.9. Usually a small signal at δ +1 accompanied the major signal; this has been found to be due to adsorbed, non-bonded ethyl phosphate, since it can be selectively removed from the solid by washing with 2-propanol. Furthermore, intentional adsorption of a typical phosphate $(EtO)_2PO_2H$, on silica gel gave a CP-MAS signal at δ +1. The nature of the phosphorylated silica gel produced is represented by **3**, although at this time there is no direct evidence that an OH group is present on phosphorus.



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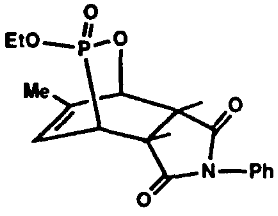

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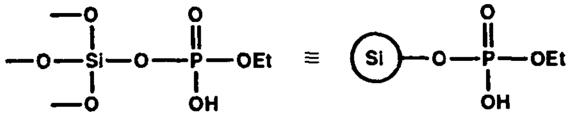


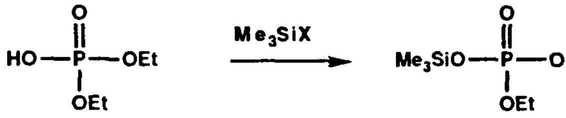
$\mathrm{(-O)_3Si-O-P(=O)(OH)-OEt \equiv (Si)-O-P(=O)(OH)-OEt}$

3

In these experiments, the silica gel must be thoroughly dried (195°C, 0.1 mm; 96 hr) and the OH content on the surface determined so that the proper amount of metaphosphate precursor can be employed. Using the calcium nitrate method,[3] the OH content of two silicas used in our work was determined: (a) Aldrich, 70-230 mesh, 60Å, B.E.T. surface area ca. 500 $m^2\ g^{-1}$, pore volume 0.75 $cm^3\ g^{-1}$: 0.69 ± 0.14 meq OH per g; (b) Exmere Exsil 100, HPLC grade, 5 μm, 100Å pore diameter, B.E.T. surface area 200 $m^2\ g^{-1}$, pore volume 0.5 cm^{-3}: 0.26 ± 0.12 meq OH per g.

In the phosphorylations, a small excess of precursor (10-15%) is employed, and the reaction carried out in toluene at 110° for 6-8 hours. The solid is washed with various solvents, including toluene at 80°, chloroform ethyl acetate at reflux, and 2-propanol at 25°. The phosphorus content, when desired, can be determined by the inductively coupled plasma (ICP) method, which utilizes the specific emission spectrum for phosphorus (213.618 nm); attempts to use the conventional calorimetric analysis for phosphorus were not satisfactory since silica interfered with the method. A Plasma II Emission Spectrometer was used for this determination.

Solid-state CP-MAS ^{31}P NMR has been used to characterize the treated silica. A typical spectrum for Aldrich silica gel, before the final 2-propanol washing, is shown in Fig. 1. Such spectra have been obtained reproducibly in our work. The chemical shift of δ -10 is quite indicative of the presence of a siloxy group on phosphorus; in simple model phosphates (e.g., those shown below), it is seen that upfield shifting in the range of 8-10 ppm is quite common on silylation, and since solid and solution spectra give virtually the same chemical shifts for a given compound, it is safe to attribute the signal we have observed to structure 3 (with uncertainty about the presence of OH).



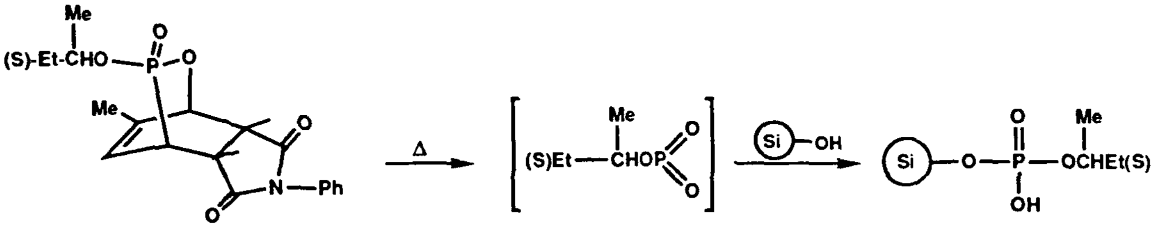
$$HO-\overset{O}{\overset{\|}{\underset{OEt}{\underset{|}{P}}}}-OEt \xrightarrow{Me_3SiX} Me_3SiO-\overset{O}{\overset{\|}{\underset{OEt}{\underset{|}{P}}}}-OEt$$

$\delta\ ^{31}P\ (CDCl_3)\ +1$ $\delta\ ^{31}P\ (CDCl_3)\ -9.1$

Very similar results were obtained on O-ethyl phosphorylation of the HPLC grade of silica obtained from Exmere. This silica has only about 40% of the OH content of the Aldrich silica, but is especially useful in OH silanization reactions, and picked up enough phosphate to give a strong ^{31}P NMR signal. It was more difficult to dehydrate this silica, which led to a larger adsorbed phosphate signal at +1 (Fig. 2). However, as for the Aldrich material, the adsorbed phosphate was easily removed by washing with 2-propanol without affecting the bonded group (Fig. 2). A typical analysis by the ICP method showed a P content of 0.093 meq per g, or a coverage of 35.8% of the surface OH groups. This is an excellent extent of coverage; silanization of surface OH groups typically provides 15-20% coverage.

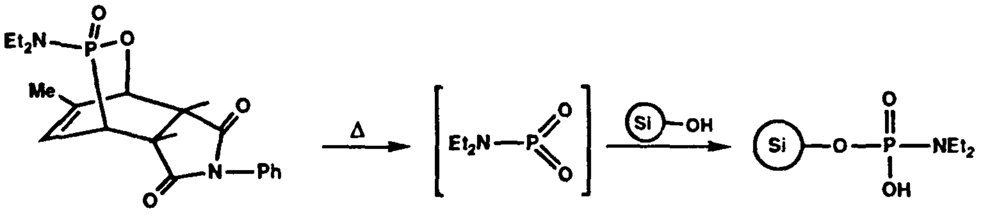
Convincing proof that the phosphate group has been attached directly to the surface through a covalent bond was obtained by the use of CP-MAS Si-29 NMR spectroscopy. As stated in the literature,[4] silica gel (Aldrich) was found to give two signals of nearly equal intensity at δ -104 for silicon bearing one OH group, and at δ -114 for silicon bearing no OH. After the phosphorylation, the signal at δ -104 was absent or greatly diminished, indicating that the surface no longer contained free OH groups. The signal at δ -114 increased in intensity, and it appears that it is overlapping with the new signal for Si bearing the phosphate group. This was confirmed by measuring the relaxation times for the δ -114 signal before (76.2 ms) and after (49.6 ms) the phosphorylation. That a change has occurred indicates the lack of homogeneity of the new δ -114 signal. An upfield shift of Si on phosphorylation is expected; the model compound Me_2t-BuSiOH is to be reacted with ethyl metaphosphate to confirm this expectation.

Most of the work was conducted with **2** as a precursor of ethyl metaphosphate. It has also been established that compound **4** releases the optically active (S)-sec.-butyl metaphosphate (5), and this reacts with both types of silica to give a product (6) with δ ^{31}P NMR δ -9.6.



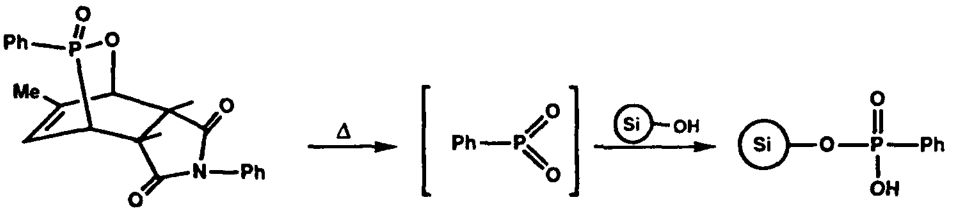
4 **5** **6**

We have also employed compound 7 as a proposed precursor of a metaphosphoramidate (8) in this process. The ^{31}P NMR spectrum revealed that phosphorylation did occur, but two strong upfield signals (δ -8, -20) were present, rather than the single peak expected for **9** at about δ 0 (an upfield shift of about 10 ppm from the phosphoramidate). A similar result was obtained when the Me_2N analog of 7 was used. The more complex nature of these products will require additional study for structure elucidation; surface phosphorylation has occurred, but perhaps with loss of the amino group (see Section I. H).

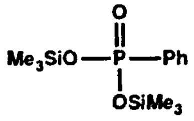


7 **8** **9**

A meta-anhydride of a phosphonic acid (**11**) has been shown to react with Aldrich silica gel. Compound **10** was decomposed at 110° in toluene solution in the presence of silica gel, and gave a solid with CP-MAS ^{31}P NMR +10 (?), which is reasonable for phosphonate **12**. A model disilyl phosphonate (**13**) has a shift of 0.0,[5] which illustrates the upfield shifting effect (*cf.* to δ +17 for the free acid[3a]).



10 **11** **12**



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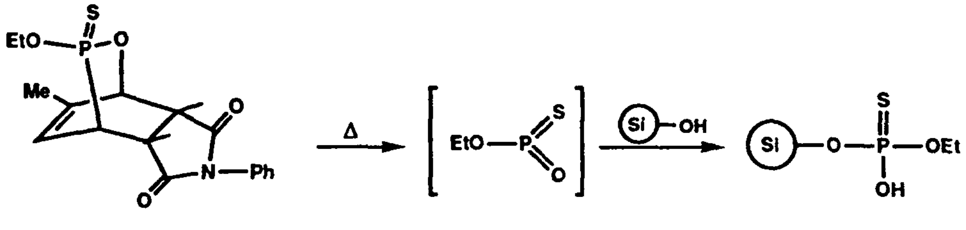
The result definitely proves that the phosphonate group can be bonded covalently to silica, and opens up new possibilities for the structural type that can be placed on the surface.

A precursor (**14**) of ethyl metathiophosphate (**15**) has been synthesized in sufficient quantity to allow the initiation of studies on its reaction with silica gel, and the comparison of the product with the oxygen analog. Since replacement of oxygen by sulfur reduces the acidity of phosphates, there could be significant changes in the chromatographic behavior of this new type of silica (**16**). The product formed in the reaction with Exsil 100 had a CP-MAS ^{31}P NMR signal at δ 52, which is the expected position for a surface thionophosphate (*cf.* to δ 64.0 for $(EtO)_2P(S)OH$, with upfield shifting due to the silyl effect). HPLC experiments will soon be conducted with this new packing.



14 **15** **16**

B. Use of Phosphorylated Silica in Chromatographic Separations.

To demonstrate that there can be practical applications for a surface-phosphorylated silica, we have proceeded to employ the O-ethyl phosphorylated Exmere Exsil 100 as an HPLC packing. Two types of columns have been packed, using commercial apparatus designed for pressure packing of HPLC solids. A short column (3 by 0.46 cm, holding 0.7 g of the packing) was prepared first to show the feasibility of using the new form of silica as a chromatographic packing. Such columns, in fact, have practical value as they can exhibit relatively brief retention of substrates, yet give sharp peaks and good resolution. They can be used for rapid sample analyses. We have also packed a longer column (25 by 0.46 cm) for more demanding separations. In Table 1, the conditions and retention times for elution of a wide variety of (mostly) aromatic organic compounds from both the 3 cm and the 25 cm columns are given. It will be noticed from these studies that particular classes of compounds tended to be eluted in blocks of time that differed from one class to the other. The compounds were specially selected to serve as models for those found in petroleum (and its distillates), shale oil, liquefied coal, etc., since there is a definite need for a practical method of compound class fractionation of such complex mixtures.[6] An initial class separation by HPLC is desired to simplify the subsequent use of gas chromatography for analysis of such complex mixtures. This application of HPLC has been studied in the past in the laboratory of Professor Peter Uden, a collaborator on this project; it has been discussed extensively in ref. 6. In fact, no packing of any durability has ever been found for this application. We have proceeded to use the 25 cm column for a separation of a pentane-soluble (de-asphalted) fraction of a crude petroleum. The conditions and the resulting chromatogram are shown as Fig. 3. It is clear that a good separation of this complex mixture has been achieved. It is now planned to perform some GC-MS analyses on several fractions to show that the desired class separation has been achieved.

Included in the compounds of Table 1 are some primary aromatic amines. It was noted that excellent peak shape, with little tailing, was obtained, and this suggested another practical value for the phosphorylated silica. With commercial untreated silica, amines frequently give broad, unsymmetrical peaks and poor mixture separation. Chemists must resort to reversed-phase packings to obtain useful separations of amines. This prompted a more extensive examination of the behavior of amines on the new columns, and in Table 2 are summarized some results of retention time measurements on some common aromatic amines. All compounds gave nearly symmetrical peaks. One of these amines (2,4-dimethylaniline) was also run on untreated Exsil 100, and gave a broad, tailing peak of no value. To demonstrate the value of the new packing for direct HPLC analysis of amines, some mixtures of these amines were prepared and chromatographed. Conditions and the chromatogram from one such separation are presented as Fig. 4, where it is seen that good separation has been achieved.

The data in Table 1 suggest that many families of compounds will respond well on the new packings, and other valuable separations can be achieved. Thus, we have proceeded to demonstrate that a mixture of some ketones can be processed with the new packing (Fig. 5), and many other possibilities can be visualized. We plan to show that organophosphorus compounds can be processed, since the rapid analysis provided by the 3 cm column might have practical value in compound detection.

Also in progress at present are experiments designed to explore the possibility that silica bearing optically active alkyl groups on the phosphate function can be used for the resolution of racemic mixtures. We have prepared several grams of the precursor (4) of optically active (S)-sec.-butyl metaphosphate (5) so that a large batch of optically active phosphorylated Exsil 100 can be prepared. Many applications are possible if it can be shown that the optically active surface phosphate groups do lead to efficient discrimination among the two enantiomers of a racemic mixture. We have, in fact, created a silica gel with a chiral phosphate group by another phosphorylation technique that we are studying. This is discussed in Section I. H. There are some preliminary indications that resolutions are being achieved.

C. The Phosphorylation of Other Surfaces.

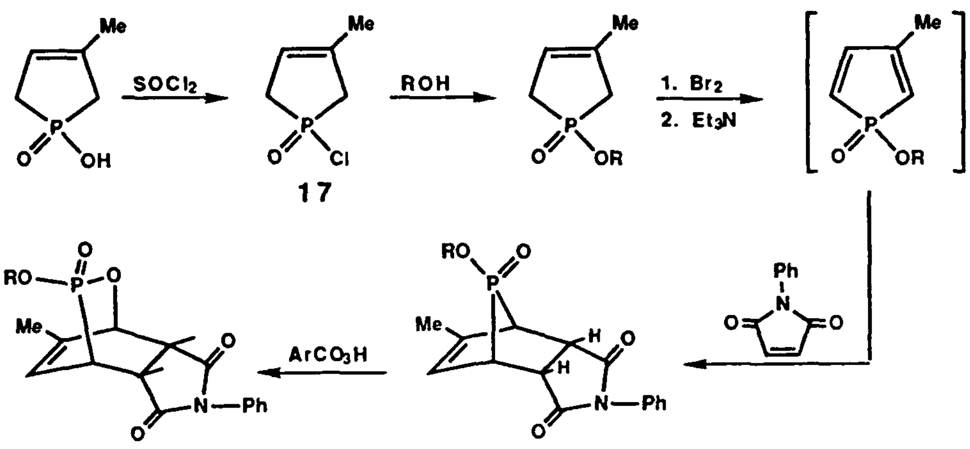
Some exploratory attempts to place phosphate groups on other surfaces known to possess OH groups have been made. Zeolites, which are crystalline alumino-silicates of both natural and synthetic origin, and which have enormous importance as industrial catalysts, are suitable OH-bearing substrates for the phosphorylation. A sample of ZeoliteY, a large-cage form known to contain OH groups,[7] was used in the first experiment, and subjected to the same reaction conditions as used in the O-ethyl phosphorylation of the silica samples. We were extremely gratified to find that the material gave a very strong CP-MAS ^{31}P NMR signal with δ -12.7 (Fig. 6), not unlike that found for the silicas (Fig. 7). We have also phosphorylated Zeolite ZSM-5; the ^{31}P spectrum shows that the desired reaction has occurred. Detailed study of the properties of the phosphorylated Zeolites and their application will be performed in the future. Similarly, we have subjected alumina to the phosphorylation, and found the product to have a strong CP-MAS ^{31}P NMR signal at δ -8.8 (Fig. 8). Alumina impregnated with phosphoric acid is employed as an industrial catalyst, suggesting that in the future a test of our phosphorylated alumina should be performed. Our treated alumina is clearly different from the commercial material; a recent report[8] indicated CP-MAS ^{31}P signals in quite different regions (as far upfield as δ -32) from ours. Titanium dioxide gave complex signals from δ 0 to -20. Cellulose represents another type of OH-bearing solid, and the attachment of covalently bonded phosphate groups would open up the possibility that metaphosphate chemistry might find an application in flame-proofing, since phosphorus compounds are among the most important of the commercial flame-proofing agents.[9] We have performed one experiment on the reaction of cellulose powder (Aldrich 20 micron) and obtained a strong signal at δ +1.4, as expected for a dialkyl phosphate.

D. Synthesis of Metaphosphate Precursors.

A major part of the time spent on this project had to be devoted to the development of synthetic methods for the heterocyclic precursors of the various types of metaphosphates. Since much of this work has been or is being published, it will only be summarized briefly in this report.

The basic synthetic method is shown as Scheme 1. The reactions involved have been in use in our Laboratory for a number of years; the novelty in our recent work comes from the selection of new O-substituents on the phosphorus function. The various substituents that have been used successfully are indicated in Scheme 1. Not all substituents respond well in the final step of O-insertion into the C-P bond; the bulky adamantyl group makes this step quite slow, requiring 6 days rather than the usual 1-2 days, and neither mesityl nor 2,4,6-tri-t-butylphenyl gave any O-insertion product, even after prolonged reaction periods.

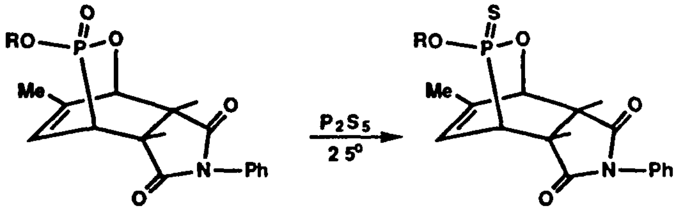
Scheme 1



18, R = Et, (S)-sec.-Bu, Me_3CCH_2, $PhCH_2$, 1-adamantyl

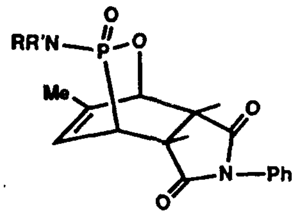
Precursors of alkyl metathiophosphates have been prepared by replacement of phosphoryl oxygen with sulfur as shown in Scheme 2.

Scheme 2



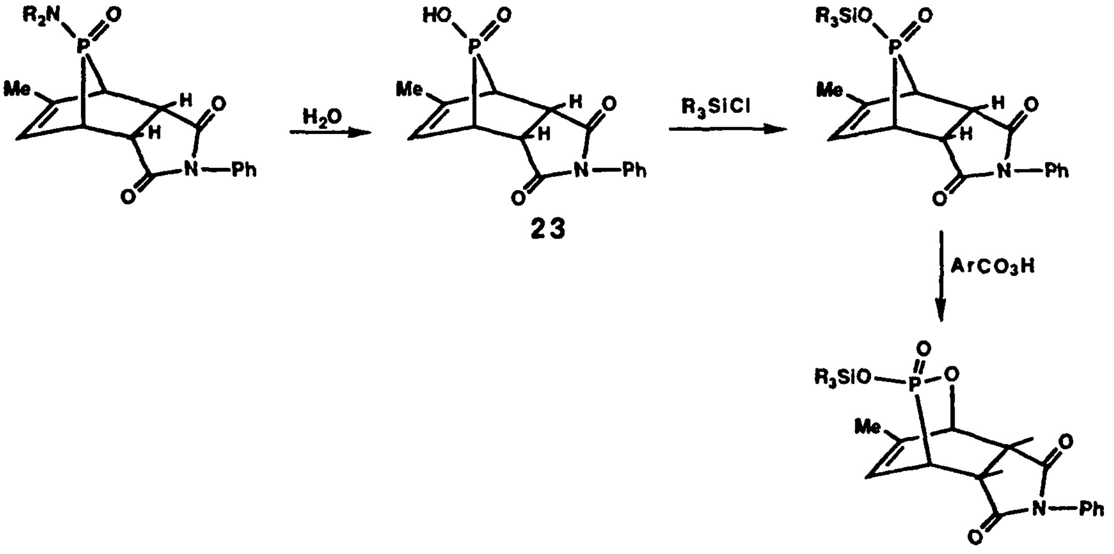
R = Et, (S)-sec.-Bu

The synthesis of precursors of metaphosphoramidates proceeds in the same way as established for the ester precursors; the amine group is placed on phosphorus by reaction with the phosphinic chloride **18**, and can then be carried through all of the steps of Scheme 1 with no difficulty. During this project, compounds **19** and **20** were synthesized; compounds **21** and **22** were made available from another project being conducted in this Laboratory.



19, R = R' = Me
20, R = R' = Et
21, R = mesityl, R' = H
22, R = t-butyl, R' = H

A difficulty sometimes encountered in the above synthetic approach has been turned to advantage and allows the synthesis of other novel metaphosphates, and of metaphosphoric acid itself. Alkoxy and especially amino substituents at the 7-norbornene position are easily displaced, and if care is not exerted to prevent their contact with water, the grouping can be lost during work-up procedures. Intentional hydrolysis is, therefore, a source of the acid 23. This compound is a precursor of metaphosphoric acid, although we have not yet had an occasion to generate this species. The crystalline acid 23 has been characterized by X-ray diffraction and shown to have the configuration at phosphorus with OH *syn* to the ring double bond.[10] The acid was found to be easily silylated, thus giving the novel compounds 24 and 25. Oxygen insertion then gave precursors of silyl metaphosphates. Silyl metaphosphates were indeed released from these precursors when the photochemical generation method (see Section A.5) was applied to them.

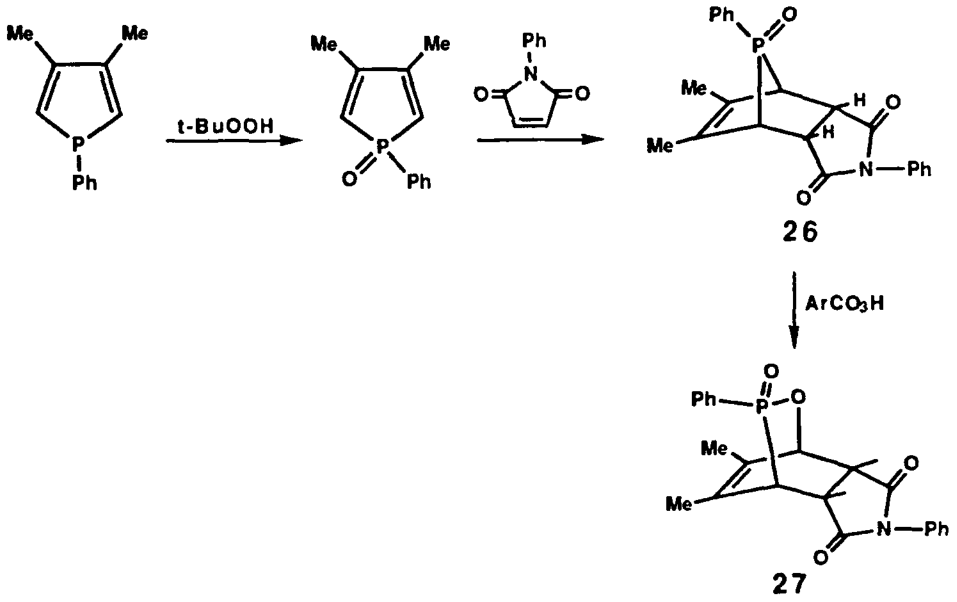


23

24, R_3Si = Me_3Si
25, R_3Si = Me_2-t-BuSi

Related to the metaphosphoric acid family are the anhydrides of phosphonic acids. We have previously shown that they too can be generated by thermolysis of appropriate bridged heterocycles.[11] We have perfected a new synthetic approach to give easy access to a practical precursor (27) of Ph-PO_2. This approach is shown in Scheme 3. Full details of this process, and of some novel properties discovered for the intermediate 27, have been published.[12]

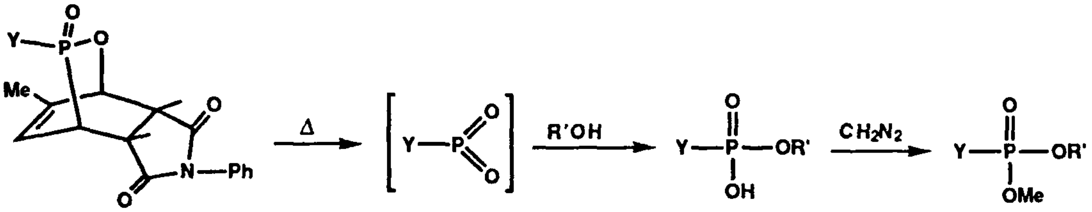
Scheme 3



All of the intermediate compounds and final products included in the schemes above have been fully characterized. Either elemental analysis or mass spectrometry has confirmed their compositions, and details of their structure and stereochemistry have been provided by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy.

E. Techniques for the Generation and Trapping of the Low-Coordinate Species.

To confirm that a new bridged heterocyclic system can function as a generator of a low-coordination species, the compound is thermolyzed in the presence of simple alcohols, which serve as efficient trapping agents for the released species. Techniques have been perfected for the characterization of these trapping products; this is accomplished by first determining the ^{31}P NMR spectrum of the product, and then by methylating the free OH group on phosphorus with diazomethane. This gives stabilization of the product, and also provides a more volatile derivative (29) that is easily characterized by GC-MS.

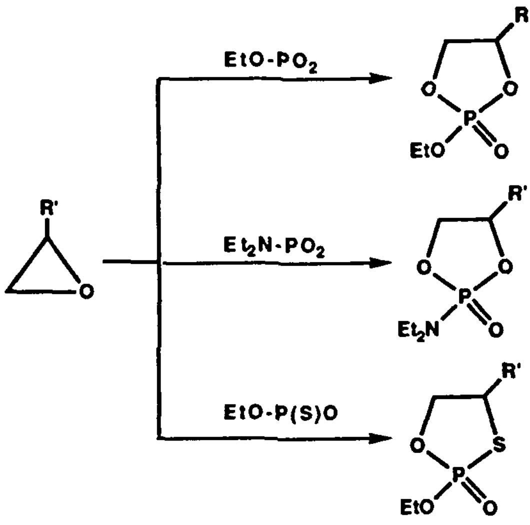


28 29

The initial reaction products (28) are especially unstable when Y is an amino substituent. We have deduced that the cause of this instability is a strong tendency for fragmentation with loss of the amino group, providing an alkyl metaphosphate. This is an extremely important observation, for the reaction can be used to advantage in the synthesis of metaphosphates. This possibility is discussed in Section II.H.

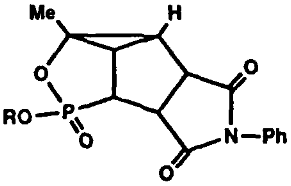
The fragmentation of the heterocyclic compounds can also be effected photochemically, and we have developed considerable information on this useful alternative to thermolysis.[13] We have not yet applied this method in the phosphorylation of silica samples, however.

Trapping of the metaphosphate intermediates has also been accomplished with epoxides. This constitutes a new reaction of metaphosphates. It is useful in showing that a truly free species is being released in the fragmentation; it is most unlikely that a combination of the bridged heterocycle and an epoxide would take place *before* the fragmentation reaction. The products are 1,3,2-dioxaphospholane oxides, and are easily recognized from their unique, significantly downfield-shifted ^{31}P NMR signals. Three derivatives of this type have been prepared and characterized. Full details have been published.[14]



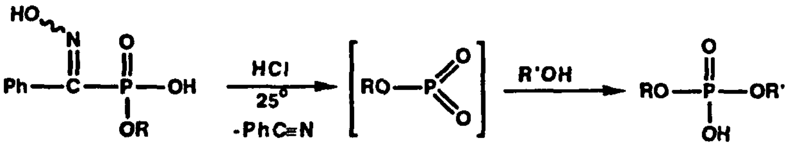
Another approach to confirm that the low-coordinate species is a discrete intermediate is based on kinetics measurements. It has been found that all of the compounds undergo fragmentation with first-order kinetics in various solvents. There is relatively little influence of the solvent on the rate, even though the solvents ranged from the non-polar toluene to the highly-polar dimethyl sulfoxide. The entropy of activation for the process was small and negative, and hardly affected by increased solvent polarity. These facts are consistent with a retro-cycloaddition process that has only weak polarity developing in the transition state. Furthermore, the reactions were found to remain first-order when alcohols were present as trapping agents, and the identity of the alcohol exerted no effect on the observed rate. We therefore can eliminate the possibility that an association of the heterocycle and the trapping alcohol precedes the fragmentation, and the concept of demonstrating the existence of the metaphosphate as a discrete species by trapping reactions is validated. The photochemical process was also studied, through the measurement of quantum yields. It was found that the quantum yields were independent of the concentration or identity of the trapping alcohol, implying that the photochemical excited state is achieved without involvement of the alcohol and then collapses to the reactive metaphosphate. These mechanistic studies have been published.[15]

We have attempted to employ the photochemical method for the generation of metaphosphates at -75°C, where they might have sufficient lifetime to be directly observed. The sterically demanding 1-adamantyl and neopentyl groups were placed on oxygen to decrease the tendency for polymerization to polyphosphates. However, an unexpected skeletal rearrangement *occurred during these conditions, and there was no indication of the formation of a stabilized monomeric* metaphosphate. This new product of rearrangement was a crystalline solid, and its structure was confirmed by X-ray diffraction analysis. This work has been published.[16]

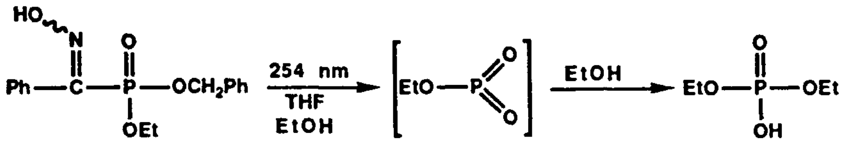


F. Exploration of the Oxyiminophosphonate Route to Metaphosphates.

Through an Israel-United States Binational Science Foundation Grant, we have been collaborating with the laboratory of Professor Eli Breuer, School of Pharmacy, Hebrew University, Jerusalem, in their studies of the formation of metaphosphates by fragmentation of α-oxyiminophosphonates.[17]

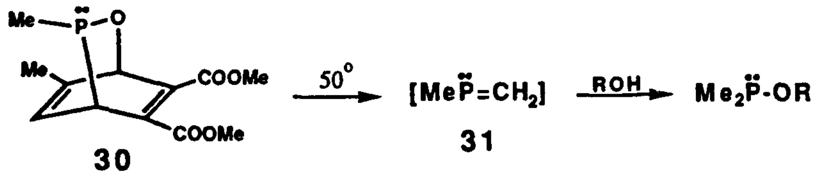


A student visitor (M. Mahajna) from the Jerusalem laboratory worked in Amherst for several months, and was successful in showing that the Breuer method can be conducted in toluene as solvent rather than in an alcohol as usually practiced.[17] This allowed the application of the method for the phosphorylation of silica gel.[2] The metaphosphate was generated by adding dry HCl to a toluene solution of the phosphonate containing suspended Aldrich silica gel. The product was washed in the usual way; its CP-MAS ^{31}P NMR signal was found to be δ -10, just as had been previously observed for the silica gel after phosphorylation by the heterocycle fragmentation method. This result confirms that a free metaphosphate intermediate is released in the Breuer method. In another study,[18] a photochemical technique for release of the metaphosphate was devised. By placing a photolabile benzyloxy group on phosphorus, it was possible to initiate the fragmentation without the use of the strong acid HCl. The metaphosphate was as usual detected by trapping it with an alcohol included in the medium. This could prove to be a synthetically useful way of generating metaphosphates for phosphorylation of delicate alcoholic compounds.

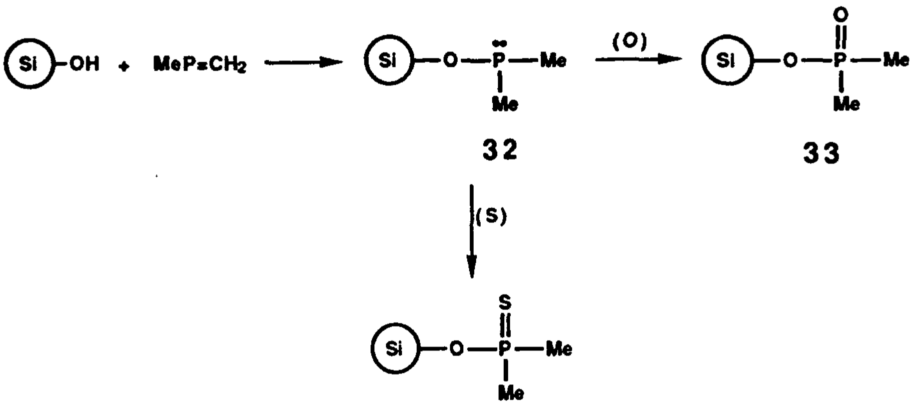


G. Generation and Silica Gel Trapping of 2-Phosphapropene.

In the report for the last grant period, we announced a thermal fragmentation method for the generation of unstabilized phosphaalkenes (such as 31). This work was subsequently published.[19,20] One of the properties noted for these highly reactive species was the rapid reaction with alcohols, which gave phosphinites as products.



It has now been shown that the OH groups on the surface of silica gel are reactive to 2-phosphapropene (31), thereby leading to the establishment of phosphinite groups on the surface, as in 32. We have had difficulty in obtaining a ^{31}P NMR signal for the initial product (32), however; by analogy to simple

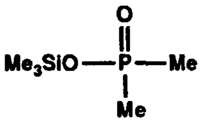


32

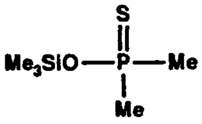
33

34

phosphinites,[20] a value of about δ 100 might be expected, but a strong signal is obtained at about δ 33 (also a weaker signal at δ 54). This is in the expected region for the oxidation product 33, a phosphinate. The model compound 35 has a shift of δ +41.8.[21]


$\mathrm{Me_3SiO{-}\underset{Me}{\overset{\overset{O}{\|}}{P}}{-}Me}$

35

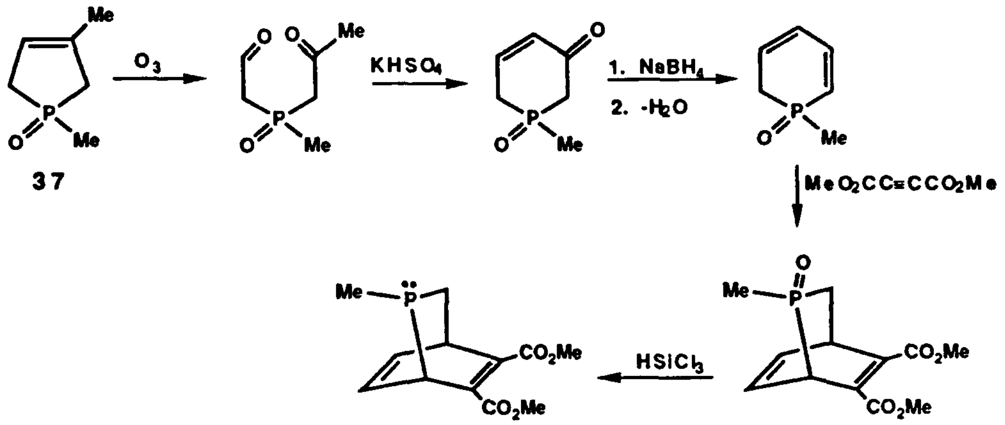

$\mathrm{Me_3SiO{-}\underset{Me}{\overset{\overset{S}{\|}}{P}}{-}Me}$

36

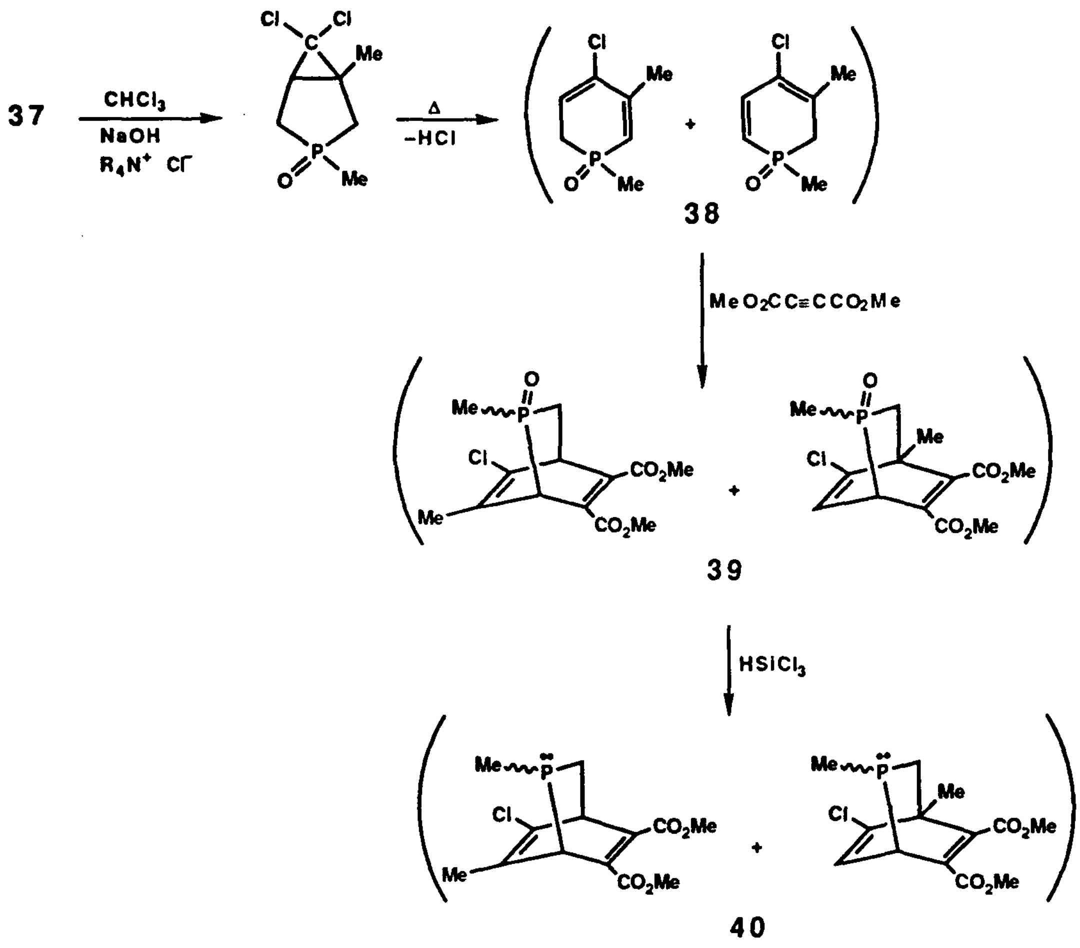
To prove that the 3-coordinate phosphinite 32 was an intermediate that then underwent very rapid oxidation, sulfur dissolved in benzene was added to the reaction mixture immediately after completion. The product should give a unique chemical shift, quite different from that of an oxidation product. Indeed, the ^{31}P NMR signal appeared at δ 86, which was expected for 34 based on a value of δ 79.9 for a model silyl thiophosphinate (compound 36).[22] Having established that a phosphinite group can be placed on the surface, albeit one of great oxidizability, it should now be possible to perform other chemistry on this function, such as metal coordination which would be of interest in the area of catalysis.

The 2-phosphapropene precursor used in this study has a new C-substitution pattern compared to the precursor 30 that we have described previously.[19,20] In our earlier work outlined in Scheme 4, we achieved a yield of the precursor 30 of only 5.0% from a monocyclic starting compound (37). A different route has now been investigated for the construction of a bridged phosphine capable of ready fragmentation. The new synthesis is presented in Scheme 5; it has recently been published in complete detail.[23] The step of dichlorocarbene addition to 37 requires phase-transfer conditions[24]; ring expansion to the dihydrophosphinines 38 occurs on heating for only a few minutes at 135°. Both were developed[24] by Dr. G. Keglevich, Technical University of Budapest (Dr. Keglevich was a former postdoctoral associate in this Laboratory, and continues to collaborate on heterocyclic chemistry). From the Keglevich dihydrophosphinines, we formed the Diels-Alder adduct 39 as a mixture of two positional isomers, each as two configurational isomers. The mixture is used as such for the reduction step, since all of the four resulting phosphines (40) provide 2-phosphapropene on fragmentation. The overall yield in this new procedure is 31%, and therefore the process represents a considerable improvement over the original synthesis[19] of a 2-phosphapropene precursor.

Scheme 4



Scheme 5



H. Generation of Metaphosphates by Thermolysis of Phosphoramidic Acids.

As already noted, we observed that O-alkyl N,N-dialkylphosphoramidic acids were unstable on heating and appeared to release metaphosphates. We have performed some preliminary experiments that confirm this reaction, and reveal that this is a potentially very valuable and practical route to metaphosphates. As shown below, the reaction is a unimolecular process when conducted in the presence of an alcohol as a trapping agent; the first order rate constant is not affected by the concentration or structure of the alcohol. The only product is the expected dialkyl phosphate.

When a trapping agent is omitted, the released metaphosphate reacts with the OH group of some of the starting phosphoramidic acid to form a pyrophosphate. This structure is easily recognized from the ^{31}P NMR spectrum. An example is provided below.

The phosphoramidic acids are easily prepared from $POCl_3$ by successive replacements (one mole each) with an alcohol, an amine, and water (as aq. NaOH). When they are thermally decomposed in the presence of suspended silica gel, the released metaphosphate efficiently phosphorylates the surface; the ^{31}P spectrum and HPLC behavior are exactly the same as found for silica gel phosphorylated by metaphosphates generated from the bicyclic precursors. This technique for generating metaphosphates is the major subject of a new project to be performed under support from Army Research Office. It has great potential especially for the synthesis of optically active metaphosphates. We have recently generated (+)-menthyl metaphosphate by this method and reacted it with silica gel. In an HPLC column, this chiral silica has given indications of racemate resolution. Thus a sample of racemic benzoin, which gives a single peak on elution with methylene chloride-cyclohexane, gave a partially resolved double peak with pure methylene chloride, suggesting that some resolution has been effected. The eluted material would of course need to be studied to determine if optical activity is present.

I. Direct Observation of a Phosphenite.

We have been successful in the direct observation of a novel 2-coordinate phosphoryl compound, a phosphenite. This is the first demonstration of the existence of this structural type, which has long been postulated as an intermediate in reactions. We have generated the species by two thermolytic processes, outlined below. In each case the phosphenite is eliminated in monomeric form and trapped from the gas phase either in liquid nitrogen (Method 1), or in the case of Method 2 (based on a literature report[25] on the probable formation of the monomer) on spectral windows chilled at liquid helium temperatures (around 12K). Using a KBr window, it was possible to record the infrared spectrum at 12K; this as its most significant feature a strong signal at 1230 cm^{-1} for P=O stretching. As the sample was allowed to warm, the signal diminished and was absent at room temperature.

Simultaneously, a new signal for P-O-P bending at 920 cm^{-1} appeared as the highly reactive monomer condensed to form dimer or trimer. Similarly, the ultraviolet spectrum at 12K consisted of two equal-intensity peaks at 270 and 275 nm which disappeared as the sample was warmed. The ^{31}P NMR spectrum was recorded on a sample collected in a liquid nitrogen trap and dissolved in ethylene dichloride; since the temperature was probably around 0° by the time the spectrum was recorded, only a weak signal for the monomer was observed; the spectrum was primarily that of the dimer and trimer. The signal for the monomer appeared at 238, which is a reasonable position for a low-coordinated form of phosphorus such as this. We were also able to trap the monomer from the gas phase on the surface of silica gel, giving an H-phosphonate with CP-MAS ^{31}P NMR, -4. As expected, this value is about 8 ppm upfield of the value for an O-ethyl model. Full details of this work have been submitted for publication.

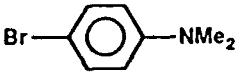
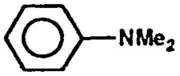
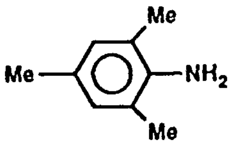
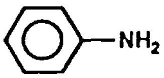
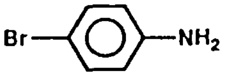
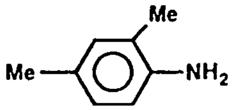
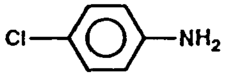
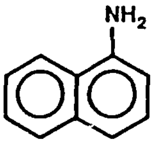
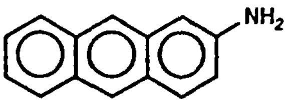
Table 1. Chromatography of Model Fuel Compounds

	3 cm[a]	25 cm[b]
Hexane	0.1	0.1
Hexadecane	0.1	0.1
Naphthalene	0.6	1.8
Phenanthrene	0.8	2.9
Anthracene	0.8	2.1
Dibenzothiophene	0.4	1.8
Thianthrene	0.4	2.0
9-Nitroanthracene	1.0	5.8
1-Nitronaphthalene	2.5	5.1
1-Cyanonaphthalene	2.4	8.6
4-Isopropylphenol	9.6	11.7
p-Dodecylphenol	4.8	10.2
2,4-Dimethylphenol	5.0	9.2
9-Fluorenone	3.6	10.3
Anthraquinone	10.4	9.6
2-Methylindole	2.5	7.7
Carbazole	2.2	5.1
1-Naphthol	5.6	11.8
2-Naphthol	9.7	12.7
3-Aminofluoranthene	19.8	17.8
2-Aminoanthracene	12.3	14.6
Quinoline	22.0	15.7
Quinaldine	19.6	14.4
7,8-Benzoquinoline	20.2	19.6

a. 100% cyclohexane for 15 min, ramp to 90% cyclohexane - 10% 2-propanol in 15 min, 2 mL per min.

b. 100% cyclohexane for 10 min, 1 mL per min; ramp to 40% cyclohexane-60% CH_2Cl_2 at 2 mL per min in 20 min.

Table 2. HPLC of Aromatic Amines[a]

	4.3 min.
	6.2
	5.4
	7.8
	8.4
	8.6
	9.0
	6.8
	6.8

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a. On a 250 x 4.6 mm column; 90% cyclohexane - 10% 2-propanol, 0.75 mL per min.

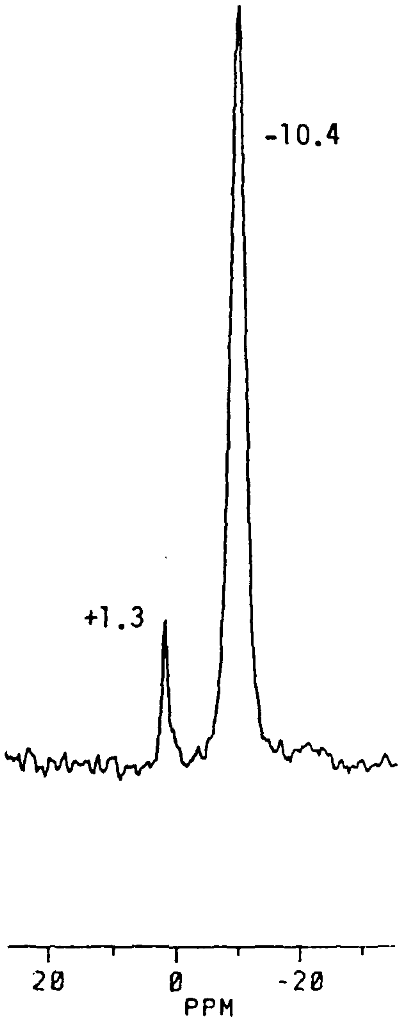
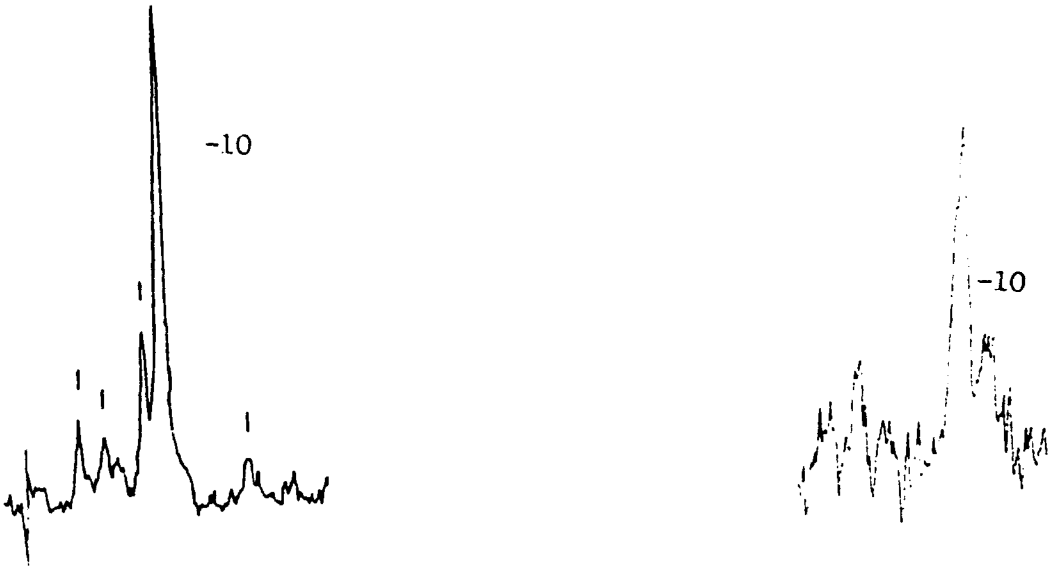


Figure 1. CP-MAS ^{31}P NMR of Phosphorylated Aldrich Silica Gel.



(before 2-propanol wash)

(after 2-propanol wash)

Figure 2. CP-MAS ^{31}P NMR of Phosphorylated Exsil 100.

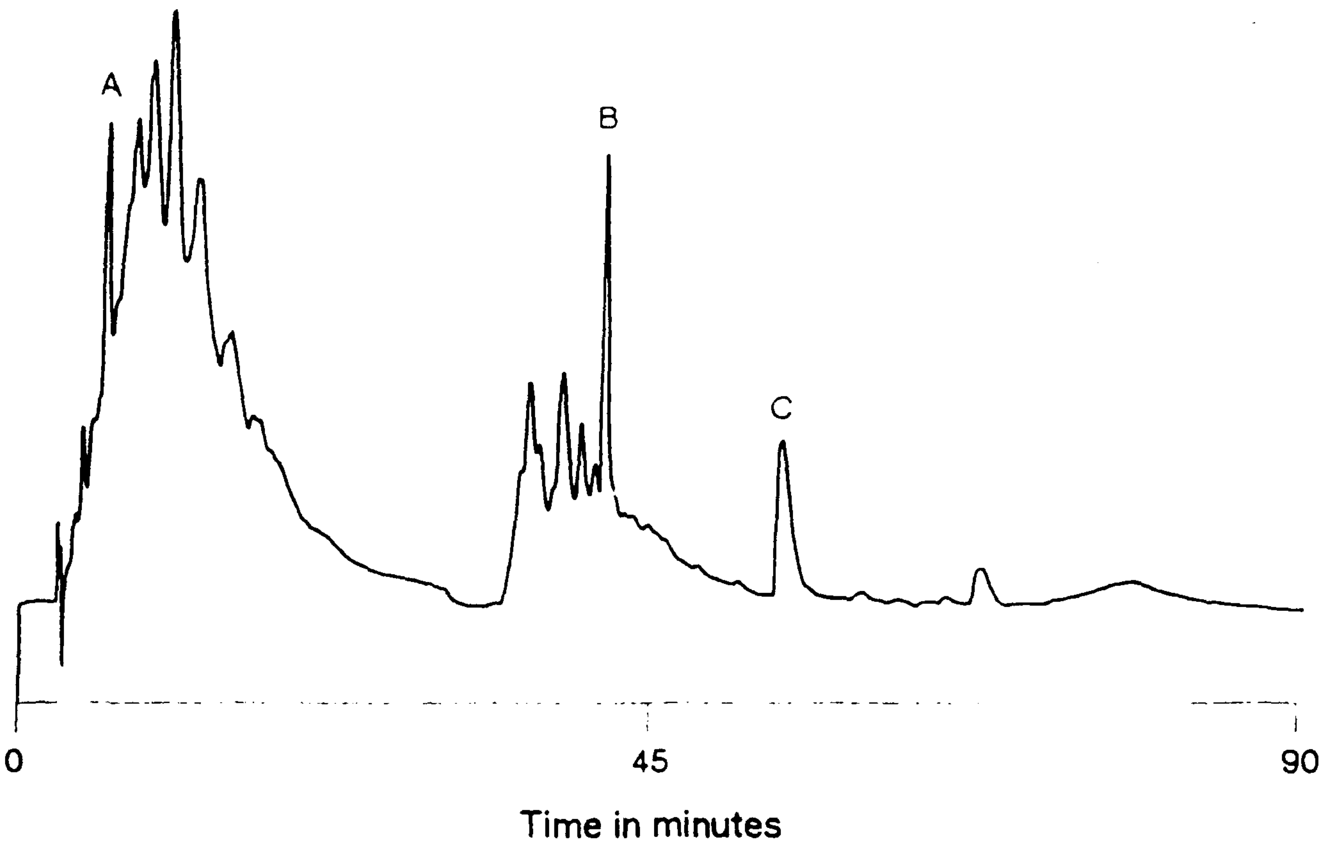


Figure 3. Normal-phase liquid chromatographic class fractionation of OLMECA crude oil spiked with naphthalene, carbazole, and 3-aminofluoranthene. Peaks: A = naphthalene; B = carbazole; C = 3-aminofluoranthene. Column: 250 x 4.6 mm phosphorylated silica; mobile phase: 100% cyclohexane from 0 min to 30 min, ramp to 40% cyclohexane/60% methylene chloride from 30 min to 60 min; flow rate: 1 mL/min from 0 min to 30 min, 2 mL/min from 30 min to 60 min; detection: UV @ 254 nm.

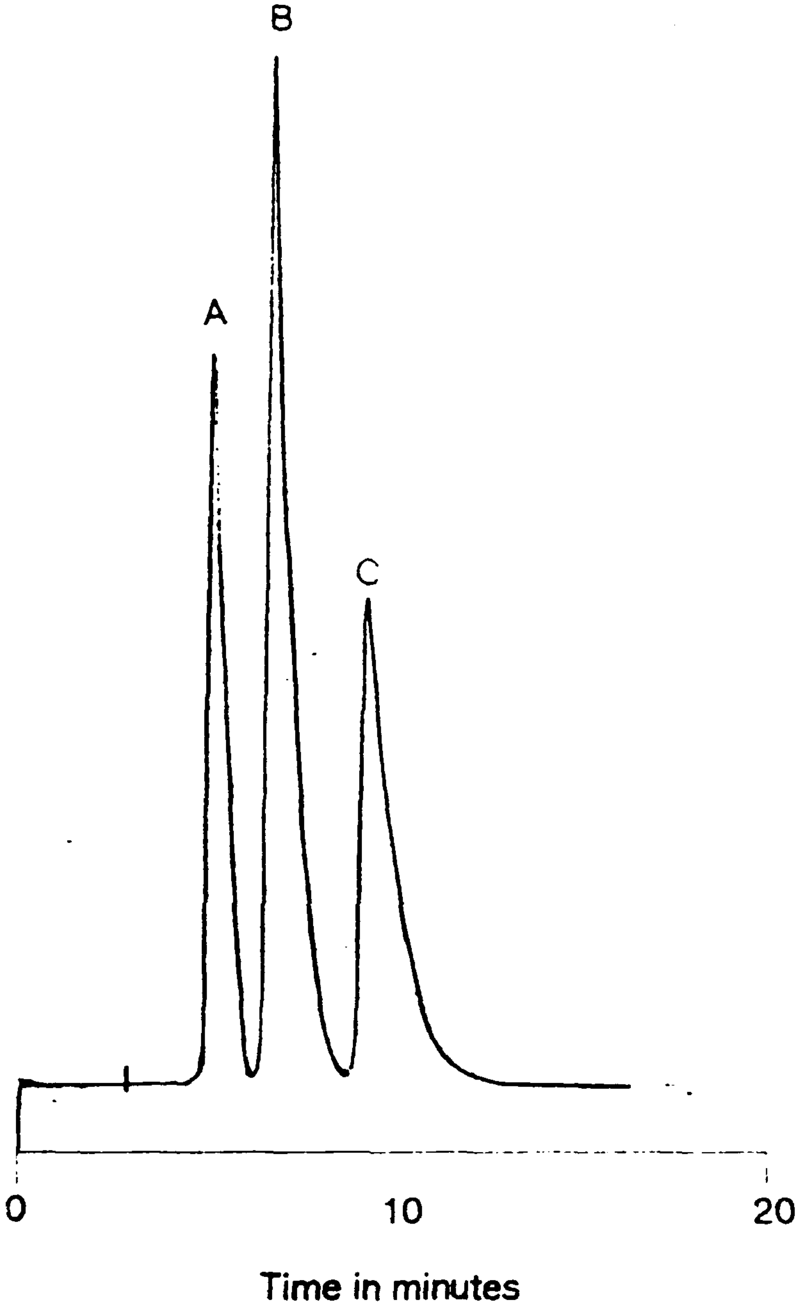


Figure 4. Normal-phase liquid chromatographic separation of basic compounds. Peaks: A = 2,4,6-trimethylaniline; B = 1-aminonaphthalene; C = 2-aminoanthracene. Column: 250 x 4.6 mm phosphorylated silica; mobile phase: 97% cyclohexane/3% 2-propanol; flow rate: 1 mL/min; detection: UV @ 254 nm.

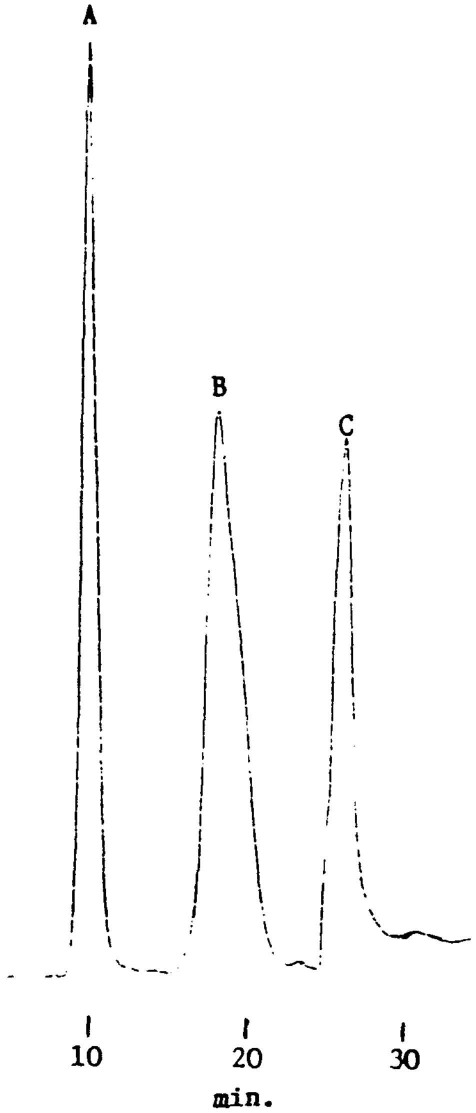


Figure 5. Separation of acetophenone (A), benzophenone (B), and acetone (C) on 250 x 4.6 mm phosphorylated silica; mobile phase cyclohexane 10 min, then up to 4% 2-propanol in 20 min, 0.75 mL/min.

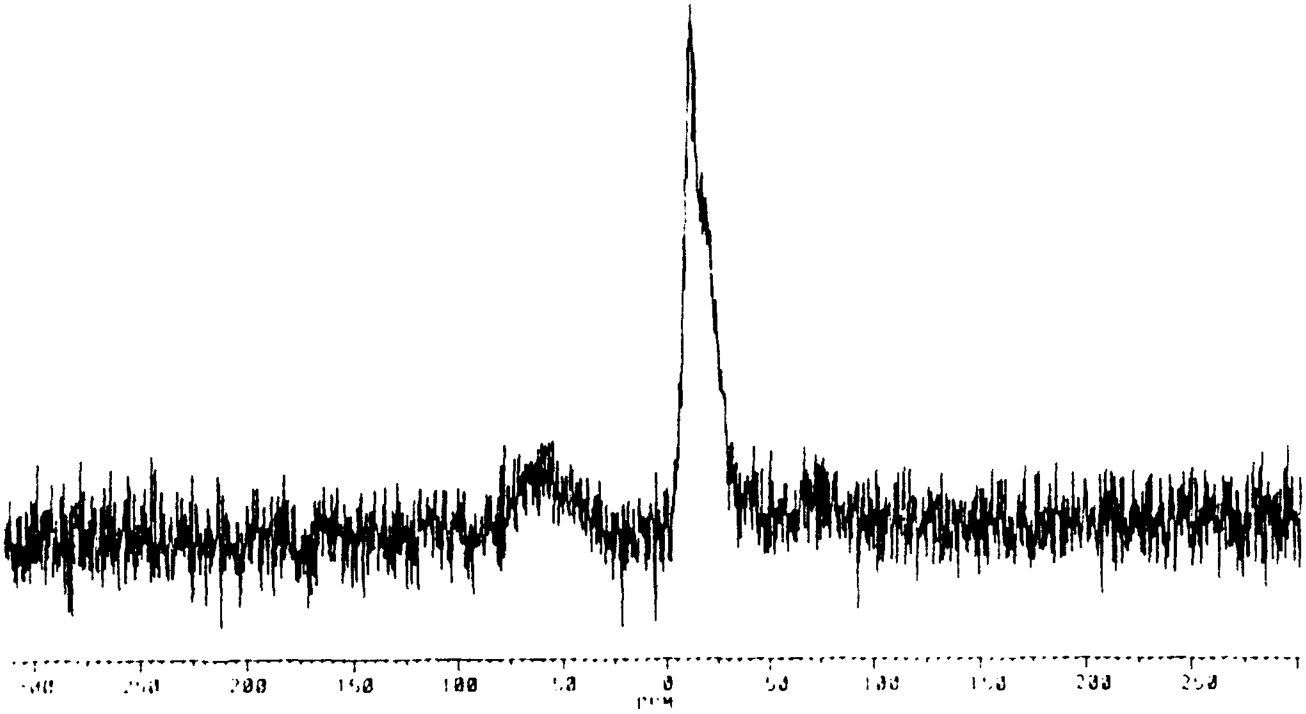


Figure 6. CP-MAS ^{31}P NMR of Phosphorylated Zeolite Y.

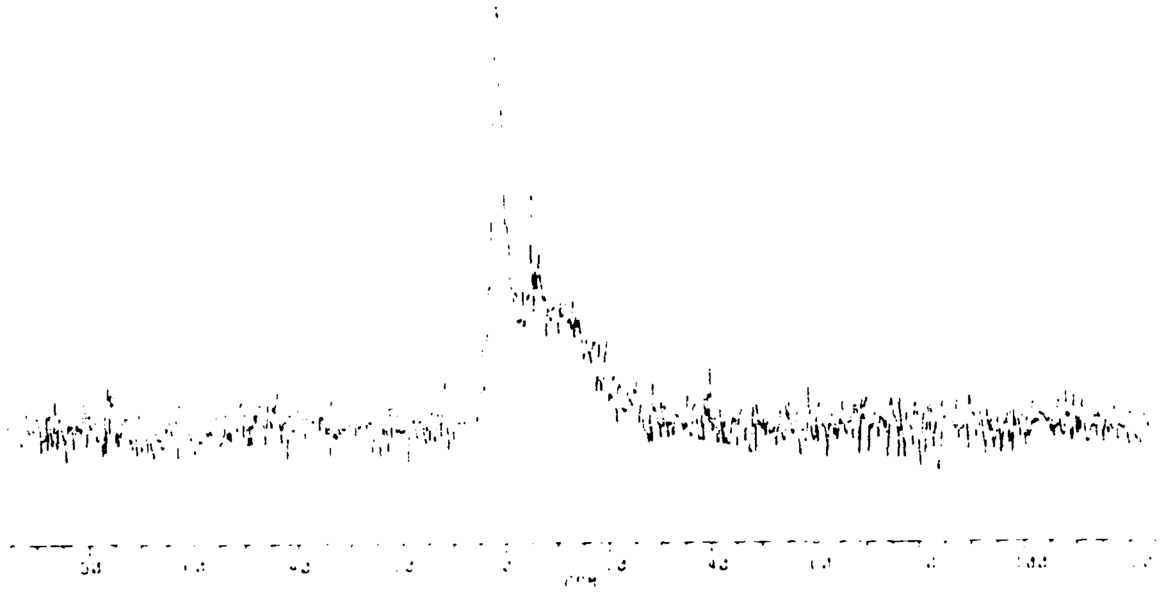


Figure 7. CP-MAS ^{31}P NMR of Phosphorylated Zeolite ZSM-5.

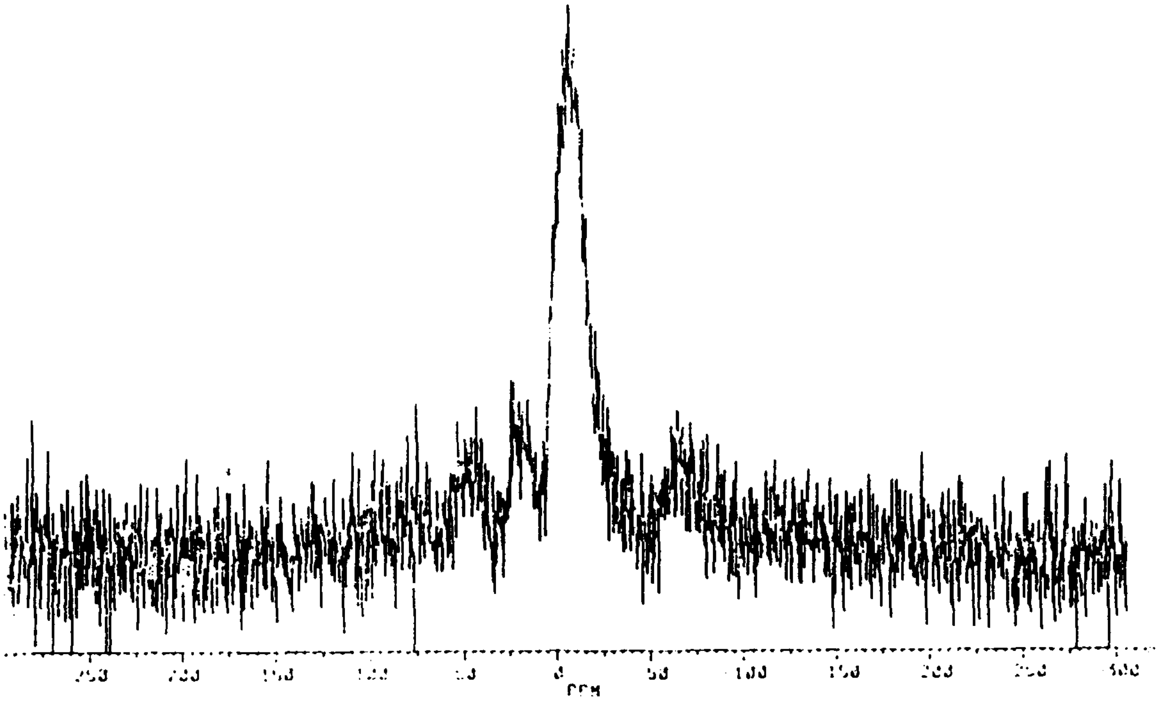


Figure 8. CP-MAS ^{31}P NMR of Phosphorylated Alumina.

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IV. PUBLICATIONS RESULTING FROM THIS GRANT

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Ryszard Bodalski, Postdoctoral Research Associate

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Ivan Lukes, Postdoctoral Research Associate

Narayan D. Sadanani, Postdoctoral Research Associate

Xiao-Ping Wu, Graduate Research Assistant and Postdoctoral Research Associate

Mark Kizirian, Graduate Research Assistant