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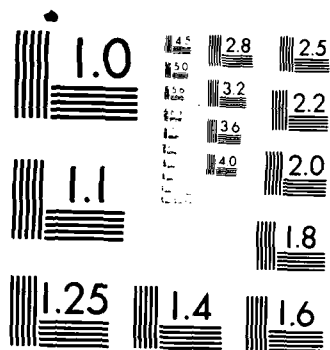
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The 5,6-oxaphosphabicyclo[2.2.2]octene ring system was created by O-insertion into a strained C-P bond of 7-phosphanorbornene derivatives, and then used for the generation of metaphosphoric and metaphosphonic acid derivatives by retrocycloaddition. Synthetic methods were developed for creating 2-phosphabicyclo[2.2.2]-octene derivatives as potential generators of phosphalkenes. The new fragments $Me_2N-P=S$ and $Cl_3CH_2OP=S$ were generated from retrocycloaddition of 7-phosphanorbornene derivatives.		

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GENERATION OF PHOSPHORUS ESTER, PHOSPHORUS AMIDE,
AND PHOSPHINE DERIVATIVES OF LOW COORDINATION NUMBER

FINAL REPORT

LOUIS D. QUIN

OCTOBER 10, 1985

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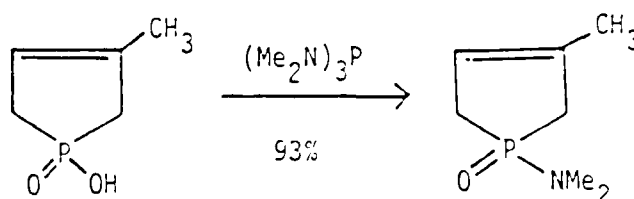
I. Purpose of the Research Program

The 7-phosphanorbornene system is synthetically readily approached, and because of the considerable strain involved in the bridged structure, along with a mechanism provided by the double bond for a retro-cycloaddition process, this system was considered as a potential precursor of a variety of phosphorus species with low coordination numbers. The ring strain is known to permit the insertion of oxygen into a C-P bond, thus creating another ring system potentially capable of undergoing a retro[4+2] cycloaddition to release a phosphoryl compound of low coordination. A further extension of this concept could result in the synthesis of species with C-P double bonds, from the phosphabicyclo[2.2.2]octene system. To explore these possibilities, syntheses of suitable precursors are required. This report summarizes work both on the precursor syntheses, as well as on the successful generation of several low-coordination species. The original concept behind the project has been amply demonstrated experimentally.

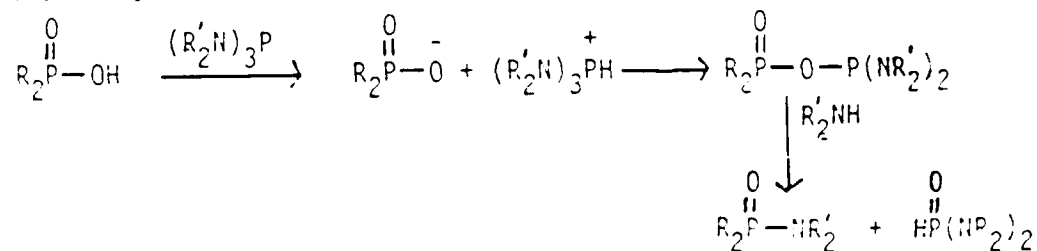
II. Major Accomplishments

A. New Synthetic Methods in Phosphorus Chemistry

1. Direct Synthesis of Phosphinamides from Acids. A one-step method has been developed for the conversion of certain phosphinic acids to phosphinamides. It consists of the transamination of the acids with tris(dialkylamino)phosphines, as in the example below.

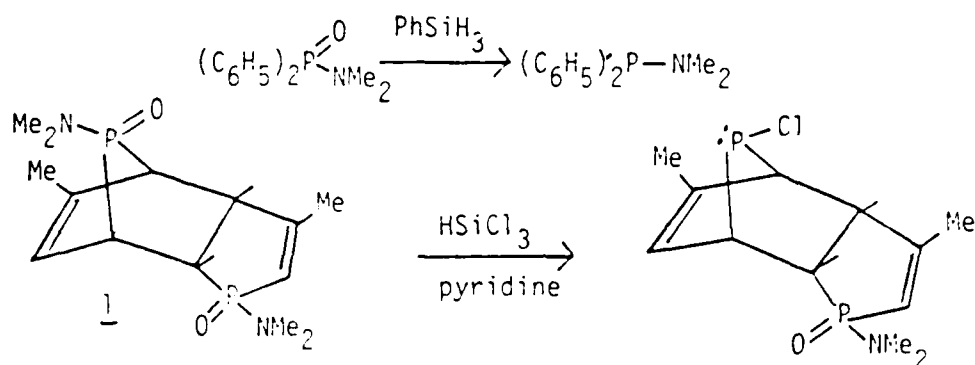
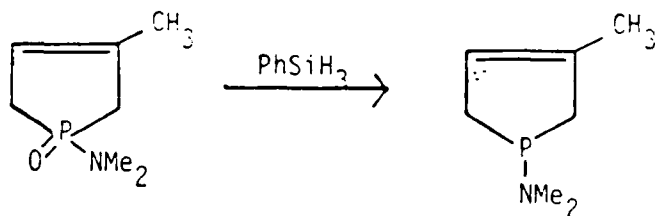


Several cyclic amides were prepared by this method and the mechanism was studied by examining intermediates with ^{31}P NMR. The reaction appears to proceed by the following pathway:

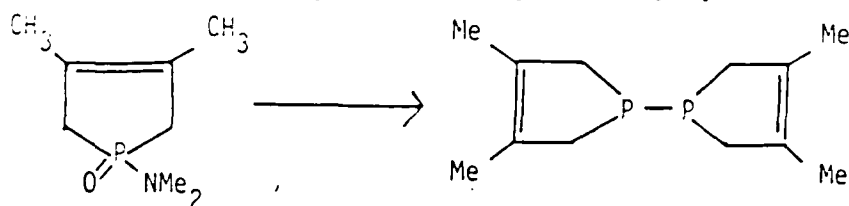


The bis(dialkylamino) derivative can also deliver the remaining R_2N groups to the acid. The method is of limited scope; so far it has only proved useful with 5-membered cyclic phosphinic acids. However, these are of great importance in this research program, and the direct amide-forming process has been quite valuable. It would be of considerable practical value if the method were applicable to phosphoric acid derivatives, and indeed a low conversion (30%) of $(\text{EtO})_2\text{PO}(\text{OH})$ to its amide was achieved. With further development, the scope of the method might well be broadened. Full experimental details on the work so far completed have been published¹.

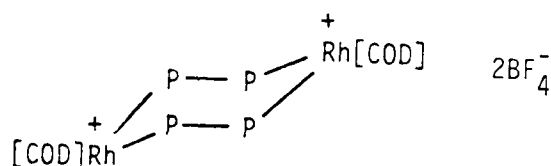
2. Reduction of Phosphorus Amides and Esters. Silanes were introduced over two decades ago for the deoxygenation of phosphine oxides to phosphines, and this has become a standard synthetic method of phosphorus chemistry. We have developed methods that permit the conversion of phosphinamides to aminophosphines (with phenylsilane) or to chlorophosphines (with trichlorosilane-pyridine). The methods have so far been found useful for cyclic phosphinamides, diarylphosphinamides, and phosphinamides based on the 7-phosphanorbornene system, but probably have much wider scope. Some examples are shown below; full experimental details have been published².



With both reagents, other reduction conditions can lead to P-P bond formation, and indeed this has been exploited for synthetic purposes.



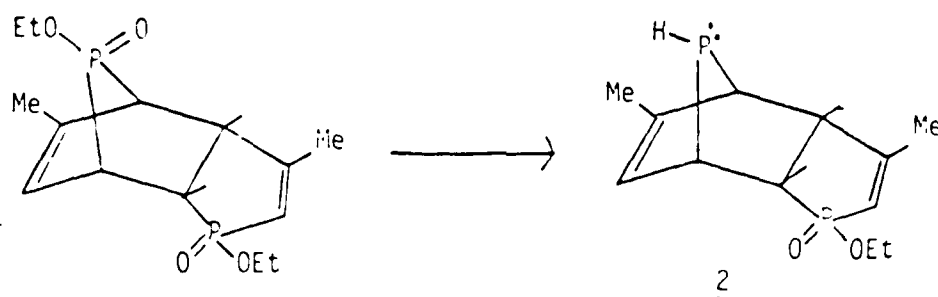
This unusual diphosphine has proved to be of interest as a ligand in coordination chemistry; for example it forms a novel cyclic complex with a Rh(I) derivative, shown in abbreviated form below (each P is incorporated in the phospholene ring; COD is cyclooctadiene).



The X-ray analysis proves the presence of the chair conformation. A manuscript describing this work is to be published³.

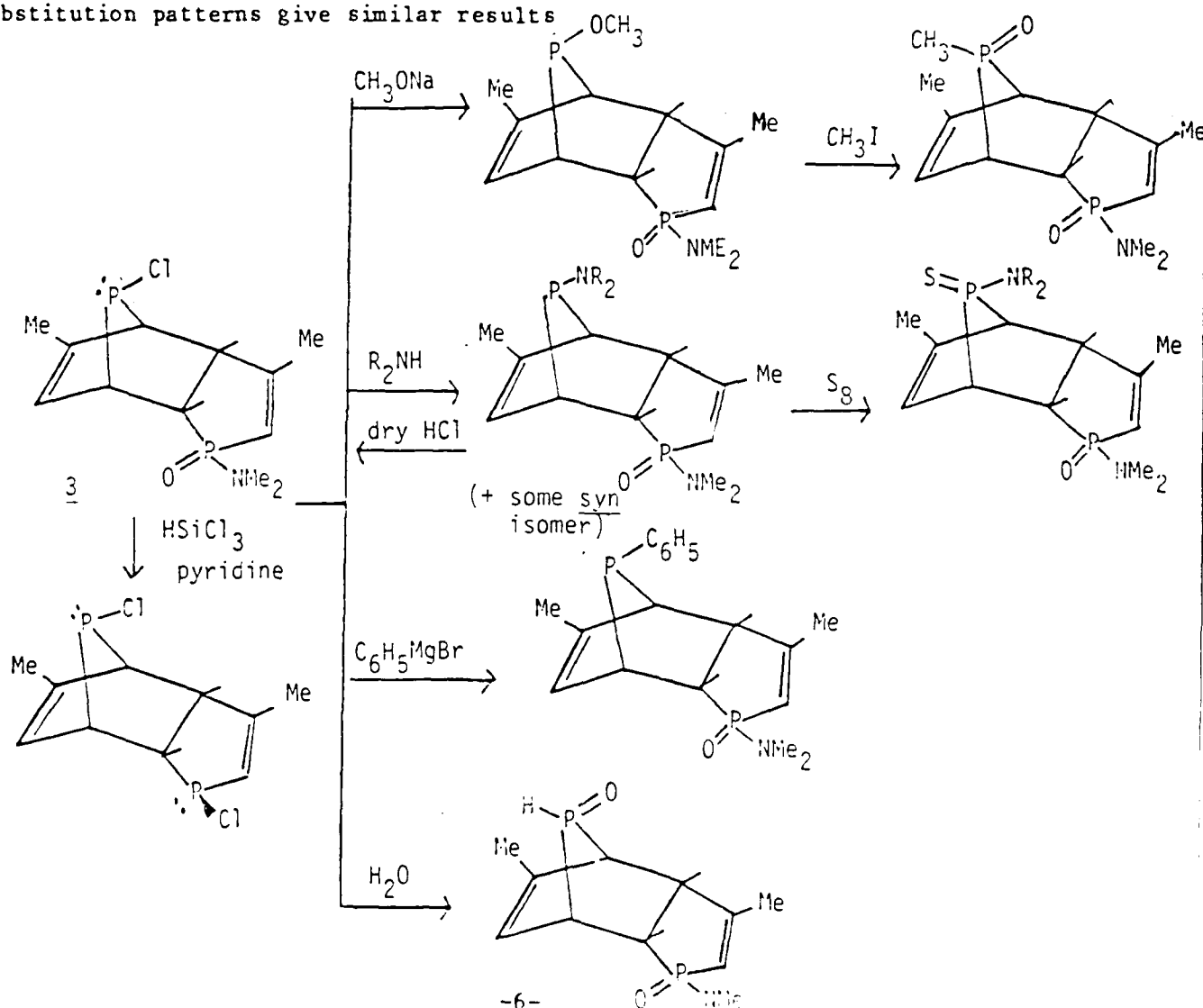
We have also studied the deoxygenation of esters with silanes, but so far have not been able to stop the reduction at the desired stage; secondary phosphines are known⁴ to form from phosphinates with PhSiH_3 and this is the result we normally observe. One feature of interest is that the

7-phosphanorbornene position in phosphole oxide dimers is the more readily reduced function, and we have prepared the unusual mixed phosphine-phosphinate 2.



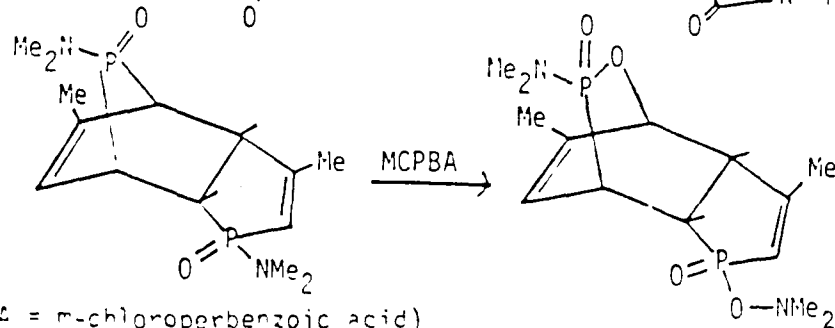
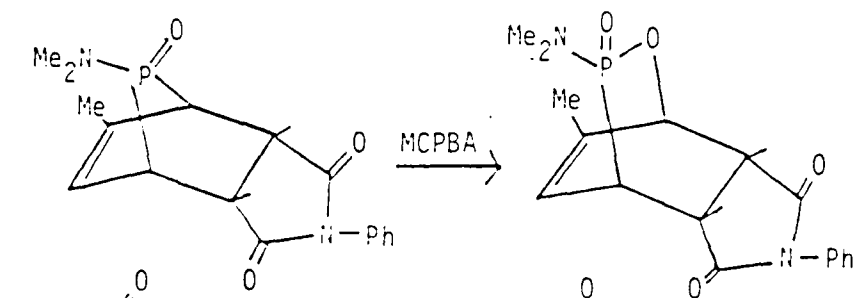
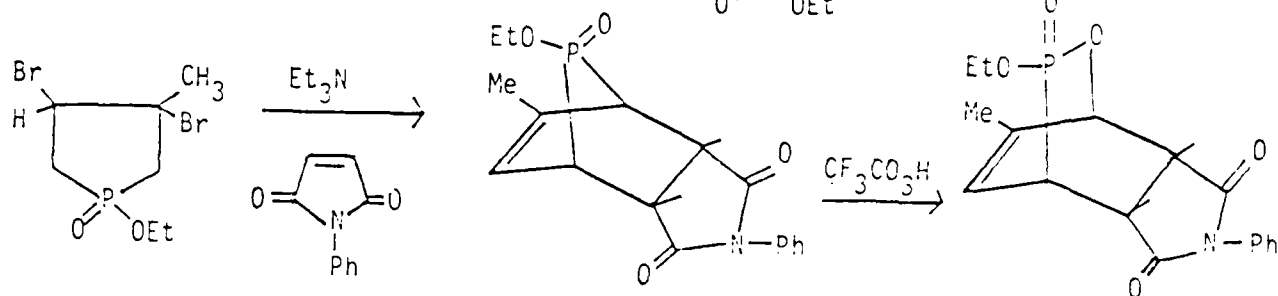
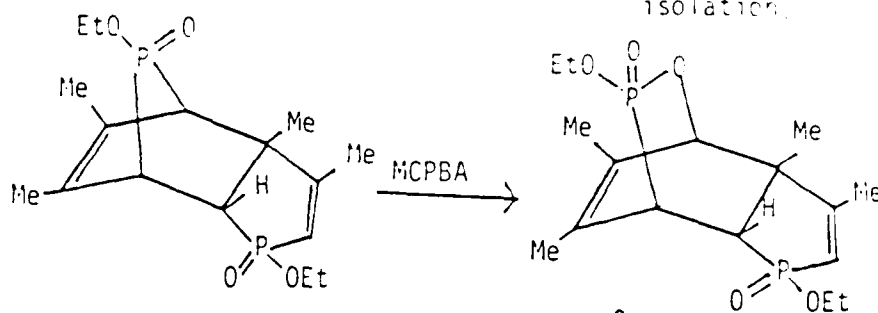
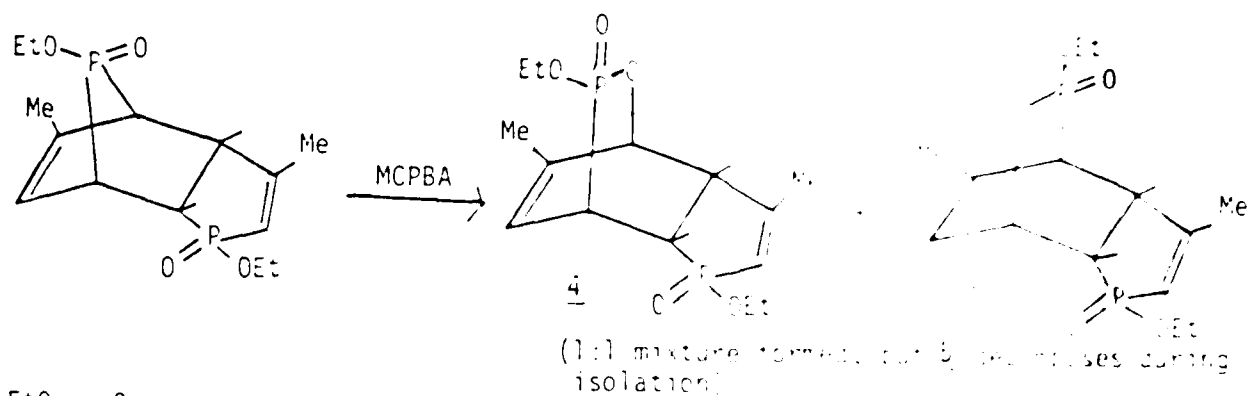
Attempts to engage the phosphine in conventional reactions (anion formation, additions to carbonyls or double bonds) have not yet been fruitful.

Of special significance to the present research program is the high-yield formation of phosphinous chlorides in the 7-phosphanorbornene series⁵. The availability of compound 3 has led to a number of other mixed-function P derivatives that could not have been synthesized by other known methods. Some results are summarized below. Phosphole oxide dimers with other substitution patterns give similar results



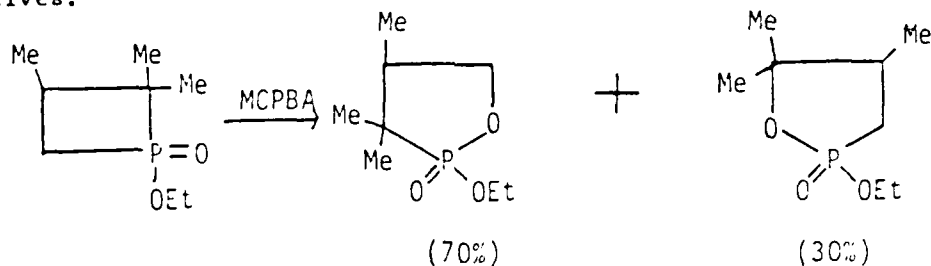
Stereochemical retention, which is observed consistently in these reactions, is notable, since inversion is the result expected from studies with less unusual phosphinous chlorides⁶. This result is of mechanistic importance; it implies that a phosphoramide ion adduct is formed that prefers to keep the highly strained ring in apical-equatorial positions of the trigonal bipyramid. This requires a pseudorotation (hence retention) before expulsion of chloride from an apical position can occur. All structures have been assigned from ^{31}P shift and $^3\text{J}_{\text{PP}}$ properties, as well as by stereospecific ^{31}P - ^{13}C couplings, and are not in doubt. An X-ray analysis of the dimer 1 was also performed to put all assignments on a firm basis.

3. O-Insertions in C-P Bonds of Strained Phosphinates and Phosphinamides. We recently demonstrated⁷ a variety of strained phosphine oxides to be quite receptive to O-insertion into a C-P bond by peroxy acids. We have now succeeded in demonstrating that strained esters and amides also undergo this reaction, which has never before been observed. The reactions below have been accomplished.



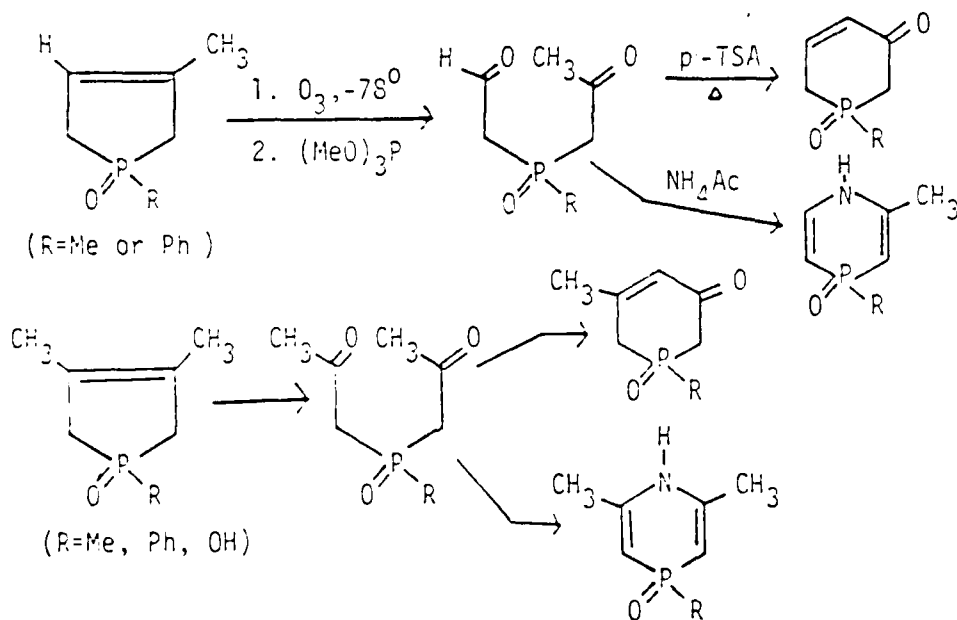
(MCPBA = m-chloroperoxybenzoic acid)

In the final reaction shown, spectroscopic properties indicate insertion of O also into a P-N bond, a reaction recently observed by others⁸ and attributed to a rearrangement of an N-oxide intermediate. Some preliminary experiments indicate that O-insertion into the readily-obtained phosphetane ring also occurs, possibly constituting a useful new synthesis of 1,2-oxaphospholane derivatives.



A brief account of these discoveries has been published⁹

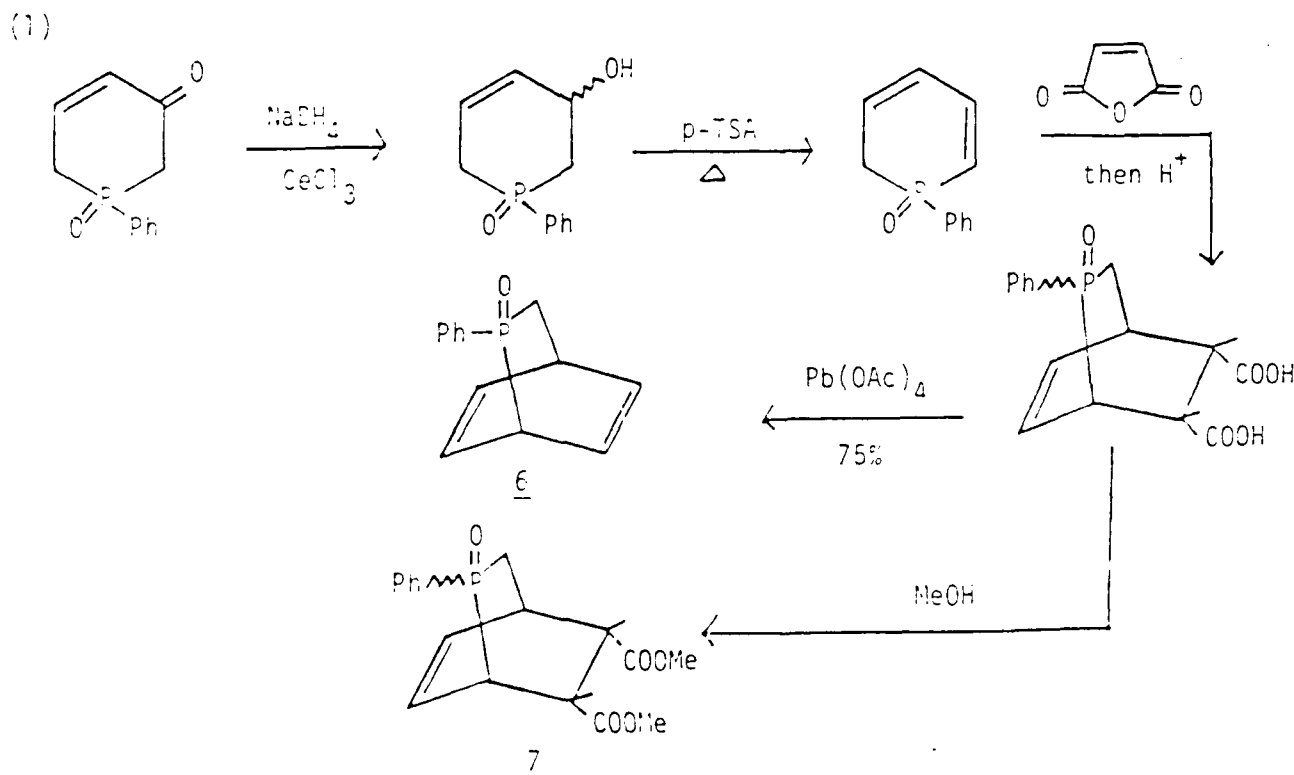
4. Two-Step Conversions of 3-Phospholene Oxides to 3-Phosphorinones or to 1,4-Azaphosphorins. We have perfected the synthetic schemes outlined below, which are simple in concept, yet are quite valuable in using readily accessible 3-phospholene derivatives as precursors of 6-membered rings. Numerous compounds of these types have been prepared, usually in good overall yields.

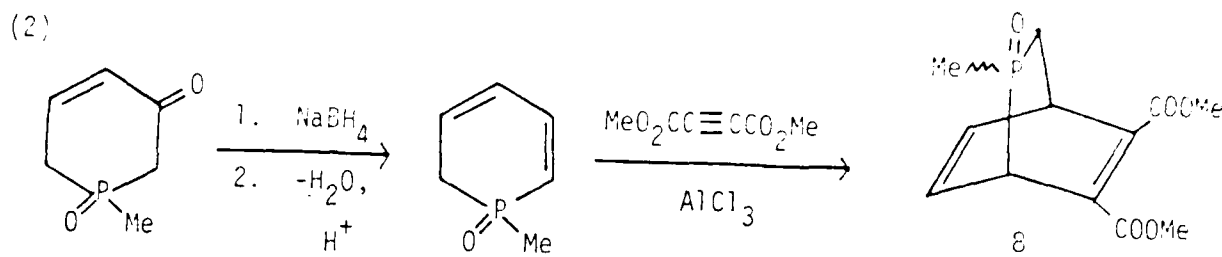


Papers providing full details on the 3-phosphorinone¹⁰ and 1,4-azaphosphorin syntheses¹¹ have been published. Utilization of the 3-phosphorinones as precursors of the 2-phosphabicyclo[2.2.2]octene system is discussed below.

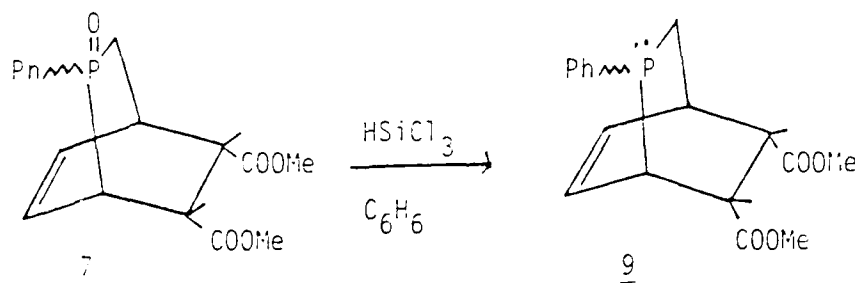
B. Synthesis and Retrocycloaddition of Unsaturated Derivatives of the 2-Phosphabicyclo[2.2.2]octane System.

One of the major goals set forth in the original research proposal was to explore the possibility of using a retro-cycloaddition approach for the generation of phospho-alkenes ($RP=CH_2$). It was for the synthesis of appropriate precursors of the 2-phosphabicyclo[2.2.2]octene system that the 3-phosphorinone synthesis described above was developed. These compounds have indeed been found to be useful for this purpose. Two syntheses of phosphine oxides have been completed, and the intermediates (all new) fully characterized.





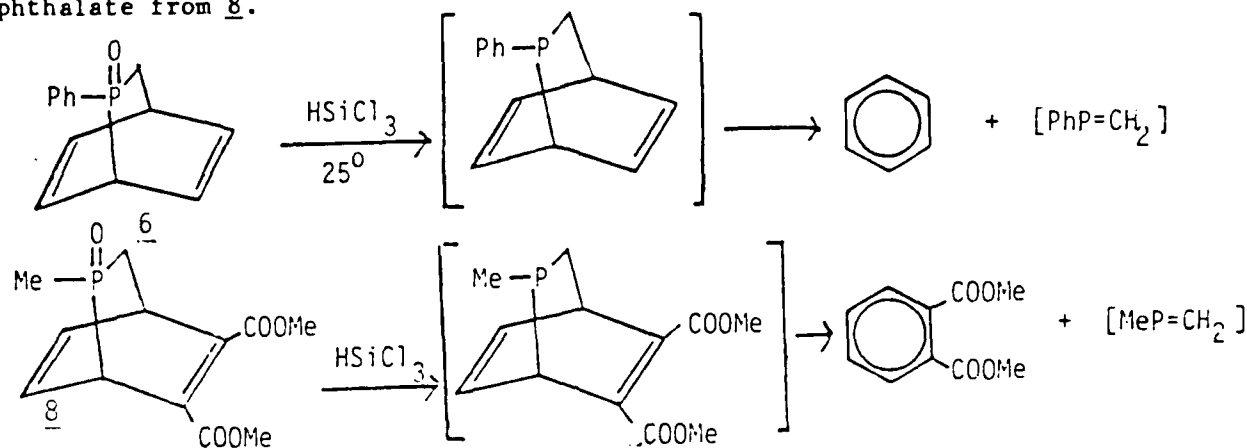
It has also been established that deoxygenation with silanes of the 2-phosphabicyclo[2.2.2]octene derivative 7 occurs in high yield (retention) with none of the complications (loss of P bridge) found for the bicyclo[2.2.1]heptene system¹². The ³¹P NMR spectrum (δ -31) of the phosphine (9) was quite normal for a tertiary phosphine, whereas the shift for the [2.2.1] system is found far downfield (δ +100 or more).



Phosphine 9 proved to be stable on heating in solution up to about 150°. However, under conditions of flash vacuum pyrolysis (450°, 0.01mm) it was destroyed and the expected "diene", dimethyl dihydrophthalate, was identified in the pyrolysate. The phosphorus fragment reacted to form several species, none of which have yet been identified. The experiment was successful, however, in showing that the retro-cycloaddition did indeed occur. In future work, trapping

agents will be present to react with the $\text{PhP}=\text{CH}_2$ presumably released.

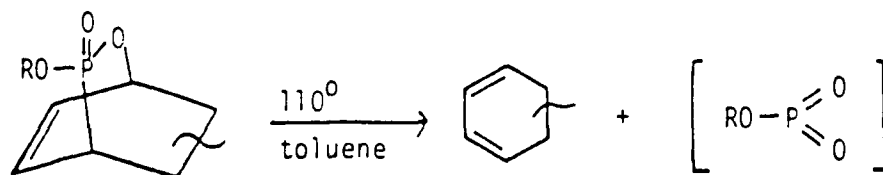
The deoxygenation of the dienes 6 and 10 has also been attempted. Each compound reacted with HSiCl_3 at room temperature, but the resulting tertiary phosphines were unstable and underwent the desired retro-cycloaddition reaction. This was evident from the detection by ^{13}C NMR of benzene from 6 and dimethyl phthalate from 8.



NMR analysis of the reaction mixtures also indicated that the P fragment appeared as PhPHCH_3 from 6 and $\text{Me}_2\text{PSiCl}_3$ (tentative) from 8. These results clearly indicate that the desired retro-cycloaddition accompanies the formation of the phosphine from the oxide, and that the highly reactive P fragment reacts with other compounds in the reduction medium. Further work on the use of this phospho-alkene generating system and on the chemistry of this reactive species are clearly called for.

C. Retrocycloaddition of the 5,6-Oxaphosphabicyclo[2.2.2]octene System

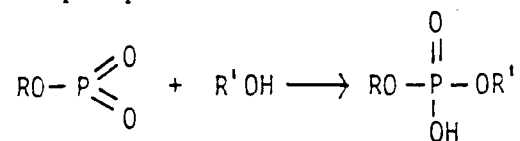
The bicyclic phosphonates described in Section II A.3 also have been found to undergo the retrocycloaddition process, as indicated in general form below.



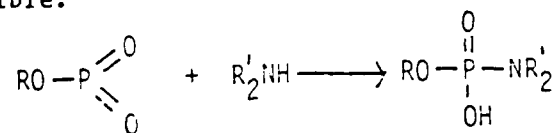
The P species is the desired highly reactive metaphosphate; its chemistry is being investigated by performing its generation in the presence of trapping agents. Major observations include the following.

1. The loss of the P bridge is complete in a few hours at temperatures below 110°. The exact framework used has some influence on the rate; phosphole dimers are less stable than Diels-Alder adducts from N-phenylmaleimide. Degradation is complete and clean, forming the dienes and polymerized forms (unidentified) of the metaphosphate.

2. In the presence of alcohols, the trapping of ROPO_2 is nearly complete, forming dialkyl phosphates; several have been isolated or characterized. The process is potentially of value in the small-scale synthesis of special phosphates.

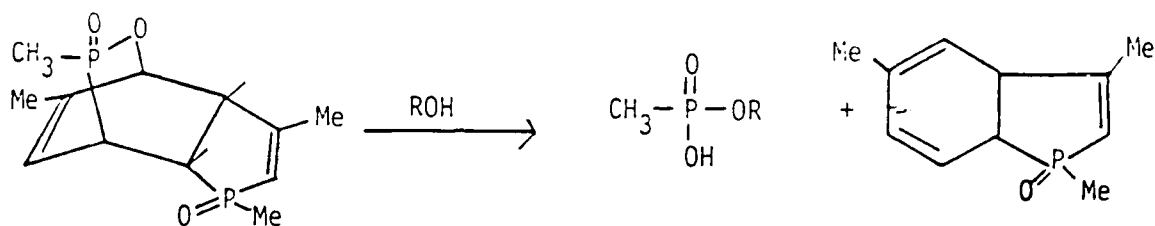


3. Amines react similarly and thus a synthesis of mixed phosphoric acid ester amides is possible.

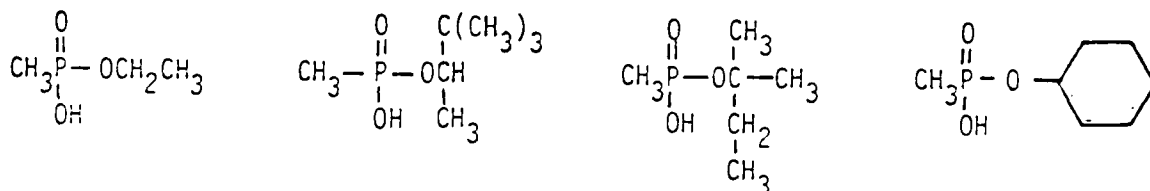


4. As originally noted by Westheimer's laboratory¹³, metaphosphates are capable of performing electrophilic substitution on the benzene ring in anilines. We have now found that pyrroles are excellent substrates for this reaction; attack occurs exclusively at the α -position, with over 80% utilization of the ROPO_2 generated. A typical product has been isolated (as the diester 10) and fully characterized.

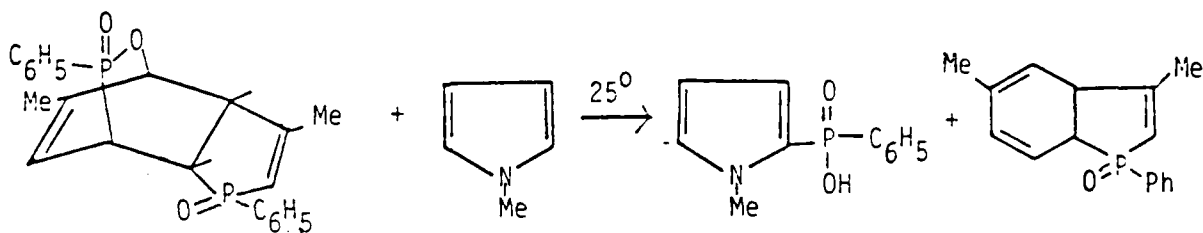
report on the bicyclic precursors even mentions the possibility of their use as RPO_2 generators¹⁵. These compounds, available from our previous work⁷, indeed were found to decompose smoothly in the presence of alcohols; monoalkyl phosphonates were formed in excellent yields. Several have been isolated as amine salts and characterized. The process is of synthetic value as a means of making special phosphonates on a small scale.



Phosphonates prepared include:



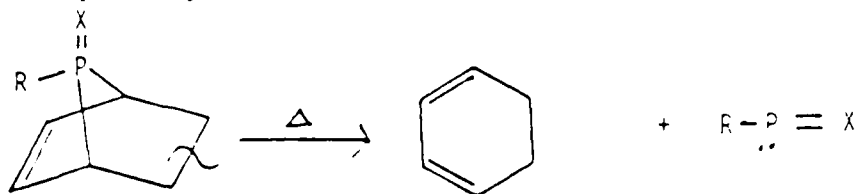
A striking new discovery is that the RPO_2 species is an excellent electrophilic agent and has given pyrrole derivatives in excellent yield



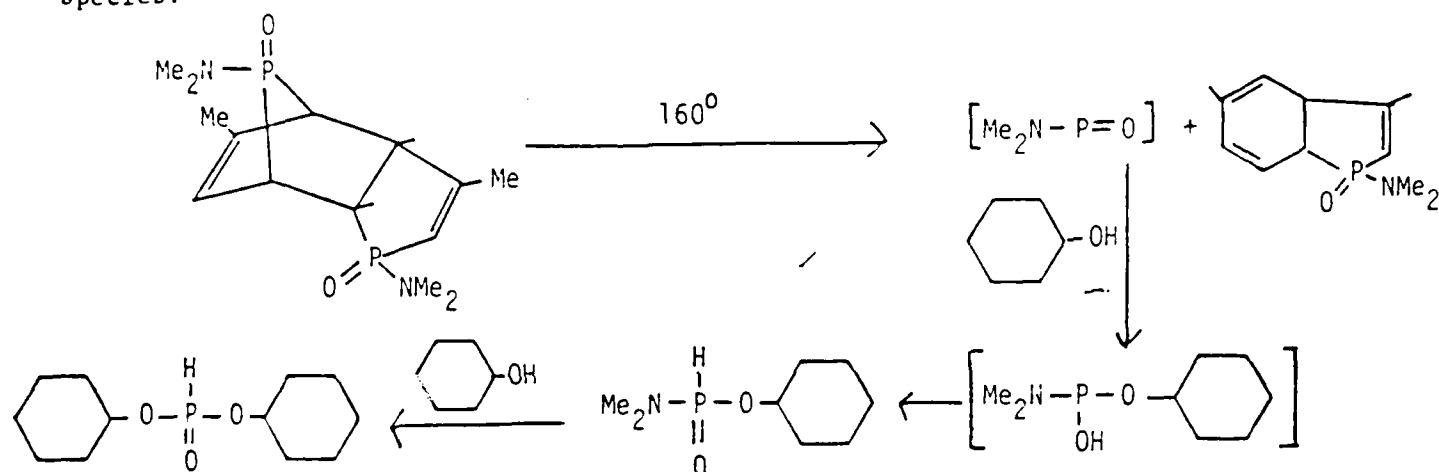
Again a process with synthetic utility is at hand and will be further explored. A report on this work has been published⁹

D. Elimination of P Fragments on Thermolysis of 7-Phosphanorbornene Derivatives.

Retro-cycloadditions of a different type are possible with the bicyclo[2.2.1]heptene system. With P(IV) derivatives, degradation may occur as follows:

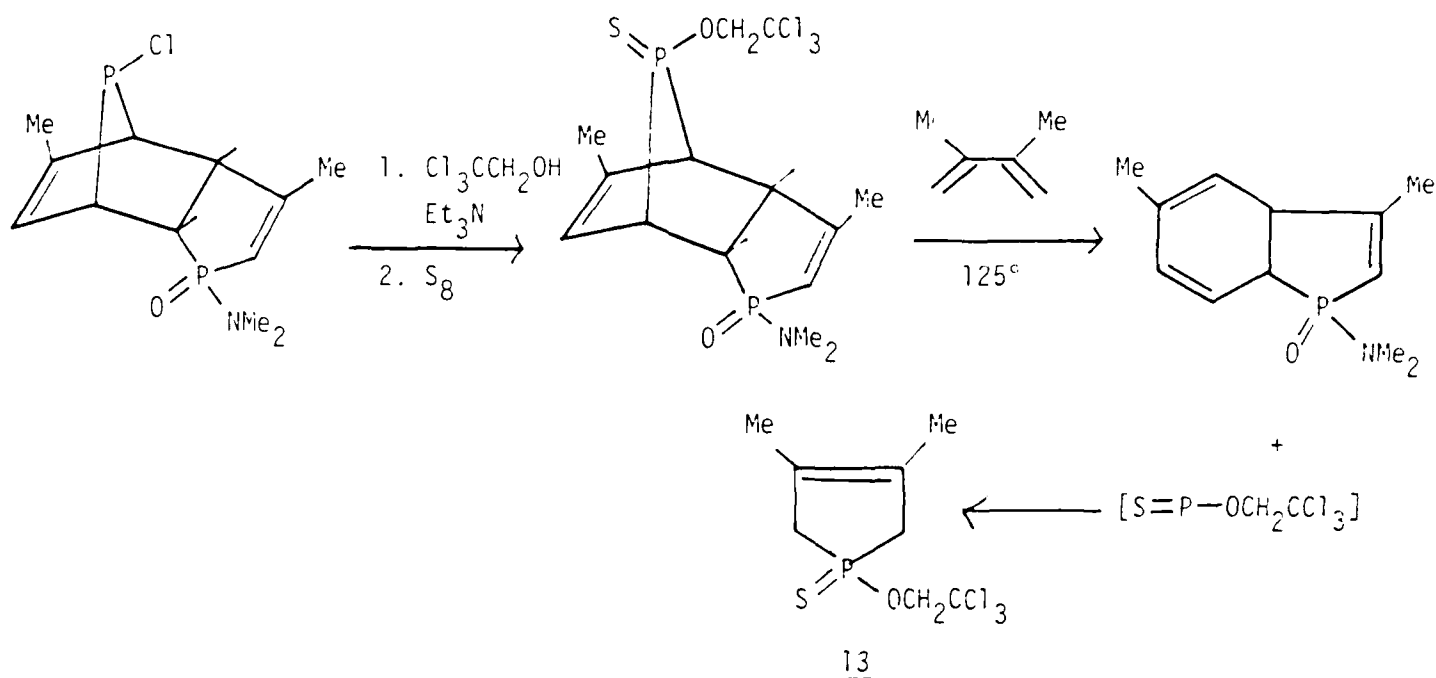


The product would possess a true double bond and would be a highly reactive electrophilic species. We have succeeded in generating and trapping such a species:



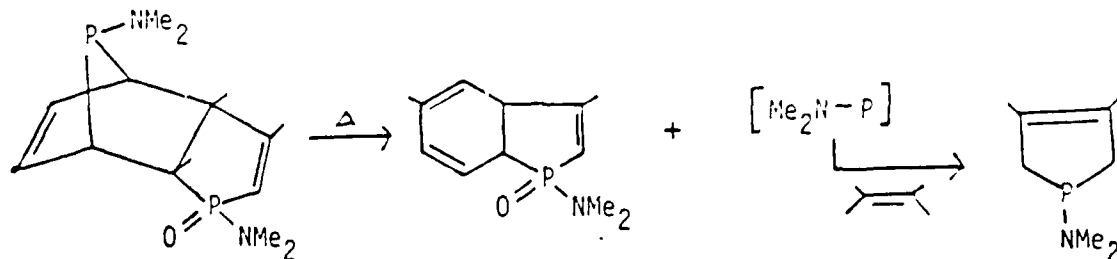
Amines also trap the fragment. In all cases, the original Me₂N group is simultaneously displaced by the trapping nucleophile, probably after ejection from the ring. Trapping was not successful with dienes. We have therefore demonstrated that the new species R₂N-P=O can be made available for study of its reactivity. (Other workers have since¹⁶ used this approach to prepare R-P=S).

Another application of this process that has been successfully demonstrated is the generation of the new species RO-P=S, as indicated below.



Product 13 has been isolated and fully characterized, and attests further to the utility of the framework for the generation of low-coordination number species.

Less success has attended our efforts to prepare P(I) derivatives (phosphinidenes) by this approach. We had previously studied the thermolysis of tertiary phosphines in the 7-PNB series and concluded that their decomposition did not proceed by a simple unimolecular ejection of R-P¹⁷. We have now studied the possibility that RO-P and R₂N-P may be generated from the corresponding 7-PNB derivatives and can be trapped with dienes, as illustrated below.



Although thermal degradation of the aminophosphine occurs, there is no evidence that the free phosphinidene is formed, and no trapping product has been obtained. MeO-P generation has also not been confirmed in trapping experiments.

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III. Publications resulting from this Grant

1. J. Szewczyk, J.R. Lloyd, and L.D. Quin, "Direct Transformation of Phosphinic Acids in the 3-Phosholene Series to Phosphinamides", Phosphorus Sulfur **21**, 155 (1984).
2. L.D. Quin and J. Szewczyk, "The Formation of P(III) Products from Phosphinamides with Silicon Hydrides", Phosphorus Sulfur **21**, 161 (1984).
3. L.D. Quin and J. Szewczyk, "Unusual Properties of Chloro- and Amino-phosphines in the 7-Phosphanorbornene Series", J. Chem. Soc., Chem. Commun. 1551 (1984).
4. L.D. Quin, C.C. Henderson, N.S. Rao, and J.C. Kisalus, "A Two-Step Method for the Transformation of 3-Phosholene Oxides to 1,4-Dihydro-1,4-azaphosphorine Oxides", Synthesis **12**, 1074 (1984).
5. L.D. Quin and J. C. Kisalus, "Two-Step 3-Phosholene to Phosphorinone Transformation", Phosphorus Sulfur **22**, 35 (1985).
6. L.D. Quin and B.G. Marsi, "Metaphosphate and Metaphosphonic Anhydride Formation by Thermolysis of 5,6-Oxaphosphabicyclo[2.2.2]octenes: Electrophilic alpha-Substitution on a Pyrrole", J. Amer. Chem. Soc. **107**, 3389 (1985).

Papers Accepted for Publication

7. L.D. Quin and K.C. Caster, "Thermal Degradation of Dimers of Phospholes", Phosphorus Sulfur.
8. G. Keglevich and L.D. Quin, "Reaction of Grignard Reagents with Phosphinous Chlorides Having the anti-7-Phosphanorbornene Framework", Phosphorus Sulfur.
9. A.L. Crumbliss, R.J. Topping, J. Szewczyk, A.T. McPhail, and L.D. Quin, "The Synthesis, X-Ray Crystal Structure and Solution Characterization of a

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IV. Participating Scientific Personnel

1. L.D. Quin, Research Director, Aug. 1982 - July 1985.
2. György Keglevich, Post Doctoral Research Associate, April 1984 - Jan. 1985.
3. John R. Lloyd, Post Doctoral Research Associate, Aug. 1982 - Jan. 1983.
4. Jerzy Szewczyk, Post Doctoral Research Associate, Jan. 1983 - Nov. 1984.
5. Kenneth C. Caster, Predoctoral Research Assistant, Nov. 1982 - June 1982.
6. John C. Kisalus, Predoctoral Research Assistant, Aug. 1982 - Feb. 1985.
7. Brian G. Marsi, Predoctoral Research Assistant, May 1983 - Sept. 1983.
8. Xiao-Ping Wu, Predoctoral Research Assistant, Jan. 1985 - July 1985.

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