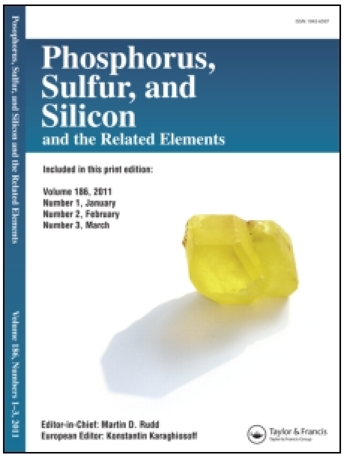

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Fragmentation Reactions of Bridged Heterocyclic Phosphorus Compounds as a Source of Low-Coordination Species

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FRAGMENTATION REACTIONS OF BRIDGED HETEROCYCLIC PHOSPHORUS COMPOUNDS AS A SOURCE OF LOW-COORDINATION SPECIES

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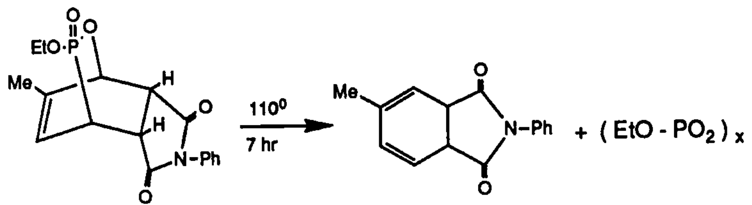
Abstract Several types of unsaturated, bridged structures have been prepared that can undergo retro-cycloaddition with the extrusion of phosphorus species having low coordination. By this technique, the species $RO-PO_2$, $R-PO_2$, $R_2N-P=S$, $RO-P=S$, and $R-P=CH_2$ have been generated and detected by trapping experiments.

During our research in heterocyclic phosphorus chemistry of the last few years, we recognized that some of the structural frameworks being examined had the potential of serving as generators of low coordination species of phosphorus when they were subjected to thermal or photochemical degradation. The important feature in these frameworks is the presence of a P-fragment in the 1,4-bridging position on a cyclohexene or cyclohexadiene ring. Retrocycloadditions can then occur, and the P fragment is expelled in a low-coordination state. Since we and others have developed various ways to modify the functionality and oxidation state of P in these bridged ring systems, a number of low-coordination species are potentially available. Indeed, some can be conceived of that have not yet been prepared by other methods. Some of the generation techniques are relatively mild, and consideration is being given to practical synthetic applications for special phosphorus compounds. Other laboratories (especially those of Mathey, Regitz, and Tomioka) have also recently employed compounds with bridged frameworks for the generation of low-coordination species.

METAPHOSPHATES[1]

A suitable precursor is 1, which is formed by O-insertion (MCPBA[2,3]) into the highly strained C-P bond of the 7-phosphanorbornene moiety of phosphole oxide - N-phenylmaleimide adducts. These compounds decompose thermally, forming the diene product (2) and condensed phosphates. Dimers of phosphole oxides give similar results.

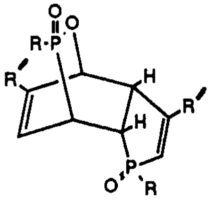


1 2

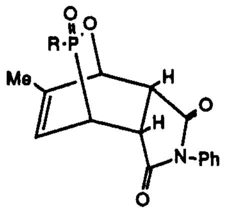
When alcohols or amines are present, about 70-80% of the metaphosphate is trapped as a stable phosphate [EtOP(O)(OH)(OR)] or phosphoramidate [EtOP(O)(OH)(NR_2)]. Metaphosphates are powerful electrophilic species[4] and we have found that they readily attack the α-position of N-methylpyrrole when this compound is present. Indoles also react with ethyl metaphosphate, but furan, thiophene and a phosphole are not reactive.

METAPHOSPHONIC ACID ANHYDRIDES[1]

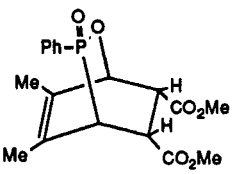
The species $C_6H_5PO_2$ and CH_3PO_2 have been generated from frameworks 3, 4, and 5, which were also prepared by the O-insertion reaction.



3 (R = Me or Ph
R' = Me or H)



4 (R = Me or Ph)



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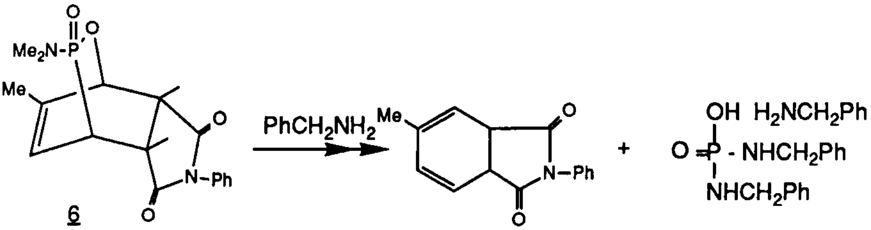
Decompositions were performed in solution at 60-80°C and gave a high transfer of P to alcohols or amines. The ability of RPO_2 to function as an electrophilic substituting agent was demonstrated by forming phosphinates from N-methylpyrrole and N-methylindole.

METAPHOSPHORAMIDATES

The compound 6 was prepared by the O-insertion process and on heating at 100° was completely converted to the expected diene and a phosphoramide polymer. Trapping was only successful when a large excess of benzylamine was present; however, it was found that the rate of the fragmentation was greatly increased. This implies that a reaction occurs with the amine before the expulsion of the P fragment. Also, compound 6 (in methanol) was photolyzed at 25° for 2.5 hr; no 6 remained, and all phosphorus was found in the form of dimethyl phosphate. Photolysis represents a new technique for generating metaphosphoric acid derivatives, perhaps of broader scope and with practical significance.



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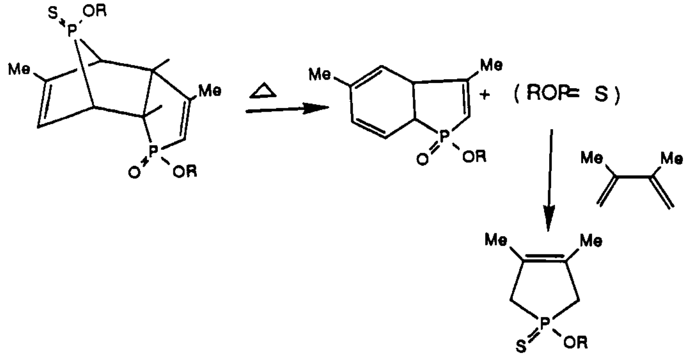
THIOPHOSPHENOUS ACID DERIVATIVES

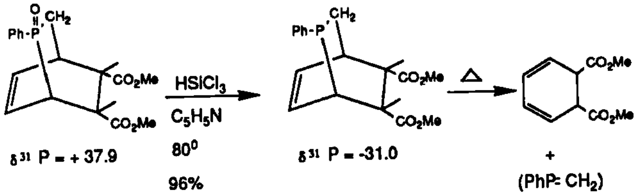
Structure 8 was smoothly decomposed at 110-120° in toluene.



When a diene trapping agent was present, the fragment was intercepted and appeared as a 3-phospholene. The transfer of P to dimethylbutadiene as a trap was 80-90% complete by ^{31}P NMR analysis; after isolation, actual yields of 3-phospholenes ranged from 30% (R = C_6H_5) to 40% (R = Cl_3CCH_2). Similar results were obtained in the generation and trapping of the species R_2N-P=S [R = Me, Et, $(CH_2)_5$].

PHOSPHAALKENES

Phosphine 9 was stable at room temperature; at 450° (0.01 mm) it was largely decomposed to the dihydrophthalate, presumably by ejection of PhP=CH_2.



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A phosphine with the phosphabicyclo[2.2.2]octadiene framework was much less stable; even when the reduction was performed at room temperature, extensive loss of the P bridge occurred and a benzene derivative was formed.

Acknowledgement

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