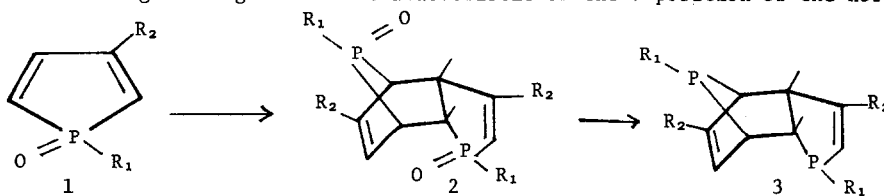


EVIDENCE FOR PENTAALKYLPHOSPHORANE INTERMEDIATES IN THE REACTION
 OF DIENES AT THE BRIDGING PHOSPHORUS IN P-METHYLPHOSPHOLE DIMERS

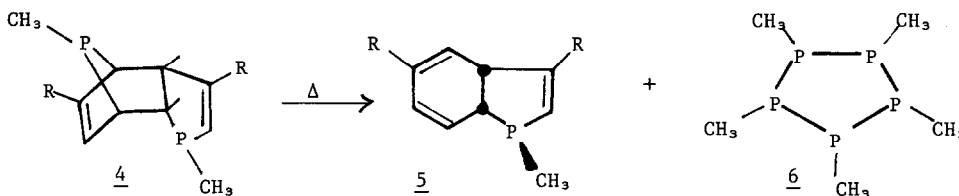
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The rate of loss of the phosphorus atom in the 7-phosphanorbornene moiety of P-methyl phosphole dimers is greatly increased when the dimers are heated in the presence of 1,3-dienes. The major products are 3-phospholenes and 3a, 7a-dihydrophosphindoles, formed in retrocycloaddition of the P(V) adduct of the diene and the phosphine.

Dimers of phospholes (prepared indirectly by dimerization of phosphole oxides¹ followed by deoxygenation with HSiCl₃-pyridine²) are of considerable interest in that they contain one phosphorus atom with the great angle strain characteristic of the 7-position of the norbornene system.



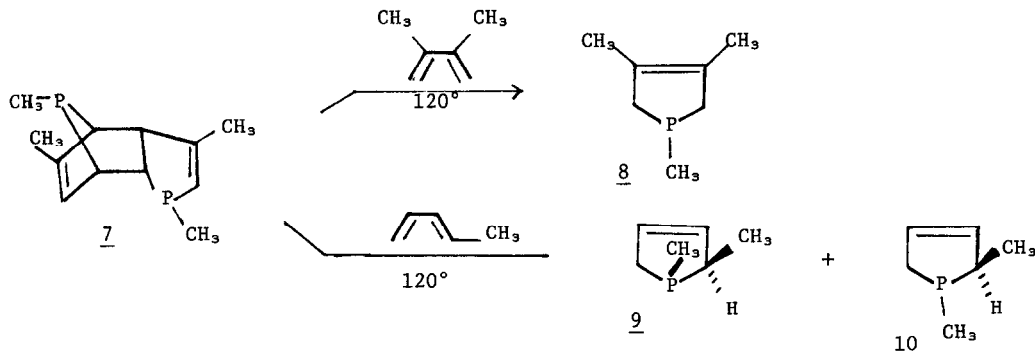
We had observed earlier that P-methyl derivatives of 3 could be safely distilled *in vacuo*, but that prolonged exposure to high temperature (e.g., 120° C for 16 hr.) caused complete decomposition. Among the products were the 3a,7a-dihydrophosphindole 5 and the cyclopolyphosphine 6.



It occurred to us that the latter substance may have been formed by polymerization of the phosphinidene (CH₃P:) ejected from the dimer in a retro-cycloaddition process; if so, the phosphole dimers could serve as useful generators of this scarcely known species³. We have explored this possibility by attempting to trap the phosphinidene before its polymerization. A variety of olefins was first used but gave no trapping products. 1,3-Dienes, however, gave significant yields of the expected 3-phospholenes. More careful consideration of the experiment has revealed that a very different process is involved in forming the 3-phospholene, wherein an unprecedented direct attack of a diene on a tertiary phosphine group takes place.

In a typical experiment, a mixture of 26 mmole of 2,3-dimethylbutadiene and 4.0 mmole of dimer 7 in 2 ml of p-xylene was heated at 115-120° C for 18 hr. Examination of the product by ³¹P NMR revealed that all of 7 was destroyed and that the main products were the dihydrophosphindole (5, R=CH₃, δ ³¹P +10.7) and 1,3,4-trimethyl-3-phospholene (8, δ ³¹P -48.8, lit.⁴ -50.3). The 3-phospholene

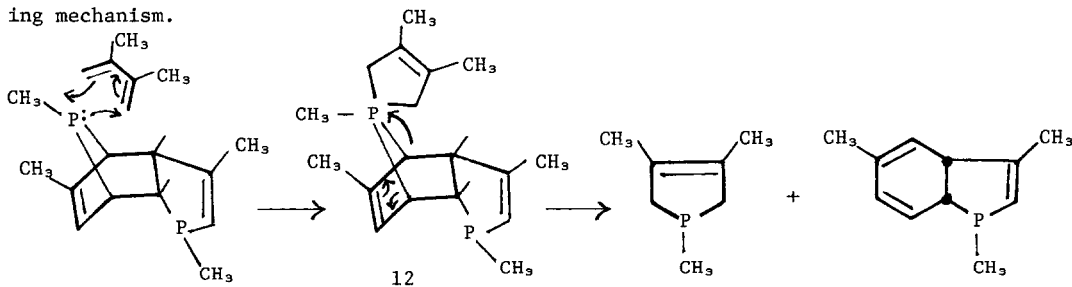
was easily removed by bulb-to-bulb transfer on a vacuum line; it formed a methiodide (m.p. 133-134°C: 28% yield from 7) also with the correct ^{31}P NMR shift (δ +36.4 (CDCl_3); lit.⁵ +36.6). In a similar experiment, trans-piperylene gave a 5:1 mixture of cis-1,2-dimethyl-3-phospholene (9, δ ^{31}P -25.7 (CDCl_3); an authentic specimen had -24.8 (CDCl_3), although -16.7 (neat) has been reported⁴) and trans-1,2-dimethyl-3-phospholene (10, δ ^{31}P -24.9 (CDCl_3); lit.⁴ -28.2 (neat); authentic sample in CDCl_3 , -23.7). A benzyl bromide salt (33% yield from 7) after recrystallization from methanol-ethyl acetate had the m.p. (202-204° C) expected for that from the major product 9 (lit.⁶ 202-203° C).



Phosphole dimer 4 ($\text{R} = \text{H}$) also reacted with trans-piperylene under the same conditions to form a similar mixture of phospholenes 9 and 10.

Heating $(\text{CH}_3\text{P})_2$ with the dienes at 120° for 16 hr failed to give any reaction, proving it is not a precursor of the 3-phospholenes. The striking observation was then made that the rate of destruction of 7 was much slower in the absence of a diene (Fig.1). Only 39% destruction of 7 occurred on heating a 0.03 M mesitylene solution at 121-125° C for 9.5 hr, whereas complete destruction occurred under the same conditions when piperylene was present. Furthermore, the reaction followed a somewhat different course in the absence of a diene; some de-dimerization gave 1,3-dimethylphosphole as the major product, along with dihydrophosphindole 5. The effect is even more striking with the anti isomer (11) of 7. This isomer is much more stable than the syn isomer; it is completely unaffected at 120° C, and requires temperatures in excess of 150° C for appreciable decomposition. With trans-piperylene present, however, 80% of the 11 was destroyed at 117-121° C after a 9.7 hr period. The main product was cis-1,2-dimethyl-3-phospholene along with 5.

These results are not consistent with dimer decomposition by extrusion of a free phosphinidene, but are indicative of the direct interaction between the dimer and the diene expressed by the following mechanism.

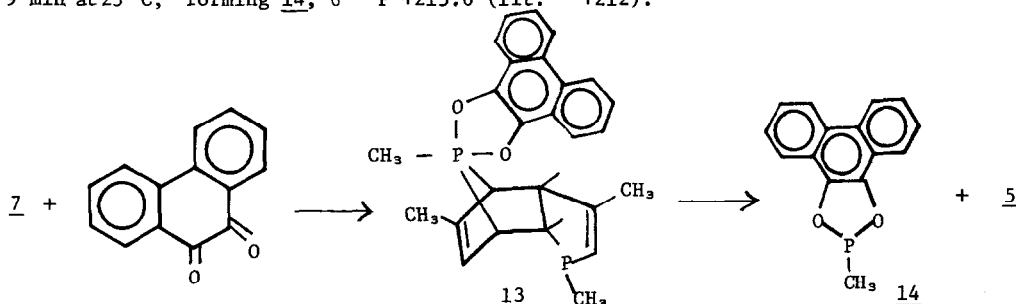


There is no precedent for the cycloaddition of a tertiary phosphine with a diene, although the well-known McCormack cycloaddition⁷ employs halo or alkoxy P(III) derivatives. The severe

contraction of the C-P-C angle at the bridging phosphorus (79° ; acyclic tertiary phosphines are usually around 100°) is partially relieved by the adoption of the P(V) intermediate, which allows an angle of 90° in the apical-equatorial disposition of the trigonal bipyramid (TBP). Similar reasoning has been used¹⁰ to explain the formation of the very rare pentaalkylphosphorane structure by attachment of a carbanion to a highly strained phosphonium salt, and in the isomerization of 7-phosphanorbornenes by alcohols¹¹. Structure 12 would be expected to decompose readily by retro-cycloaddition to the 3-phospholene, and attempts to observe it by ^{31}P NMR at various temperatures have been unsuccessful.

The stereoselectivity of the trans-piperylene interaction also speaks against a free phosphinidene mechanism, since there would be no reason for the more crowded cis-1,2-dimethyl-3-phospholene to form in such predominance over trans. Models show that the TBP formed with this diene has fewer non-bonded interactions if the C-methyl group projects away from the dimer framework, which leads to the cis-product.

That the bridging P of the phosphole dimers is especially prone to form the P(V) state was demonstrated by the virtually instantaneous reaction that occurred at 25°C with phenanthraquinone as a typical α -dicarbonyl reagent. The reaction with less than one equivalent of quinone to form the dioxaphosphorane¹² occurred specifically at the bridging P. The product 13 had $\delta^{31}\text{P} +24.6$ and $+0.6$ (d of d, $^3J_{\text{PP}} = 29.3$ Hz), but rapidly underwent retrocycloaddition¹³ with $t_{1/2}$ about 9 min at 23°C , forming 14, $\delta^{31}\text{P} +215.6$ (lit.¹³ $+212$).



Since these results cast doubt on a degradation mechanism for the dimers that involves phosphinidene extrusion, another mechanism must be operative. Its nature has been revealed by further experiments that showed the formation of dihydrophosphindole 5 to be very dependent on concentration and to be favored only from heating the neat dimer or a reasonably concentrated solution. In dilute solutions (less than 0.05M), or in the vapor phase, the decomposition takes a different course, and is simply that of de-dimerization to the monomeric phosphole. Data for the vapor phase reactions are reported elsewhere¹⁴. These results clearly show that intermolecular interactions lead to the extrusion of the bridging phosphorus.

Phosphole dimers with P-phenyl substitution have given less clearcut results; their rate of decomposition is not noticeably different when a diene is present, yet 3-phospholenes can be formed under conditions similar to those used for P-methyl dimers (32% of the methiodide of 1-phenyl-3,4-dimethyl-3-phospholenes, formed from the P-phenyl analog of 7). On the other hand, the product distribution from decompositions of the dimer does depend on concentration, and intermolecular processes are occurring. The mixtures are of great complexity and have not been fully analyzed. However, a major difference from the P-methyl dimers is obvious: very little de-dimerization to the phosphole occurs under any conditions. Also the tetramer $(\text{C}_6\text{H}_5\text{P})_4$ forms along

with the pentamer.

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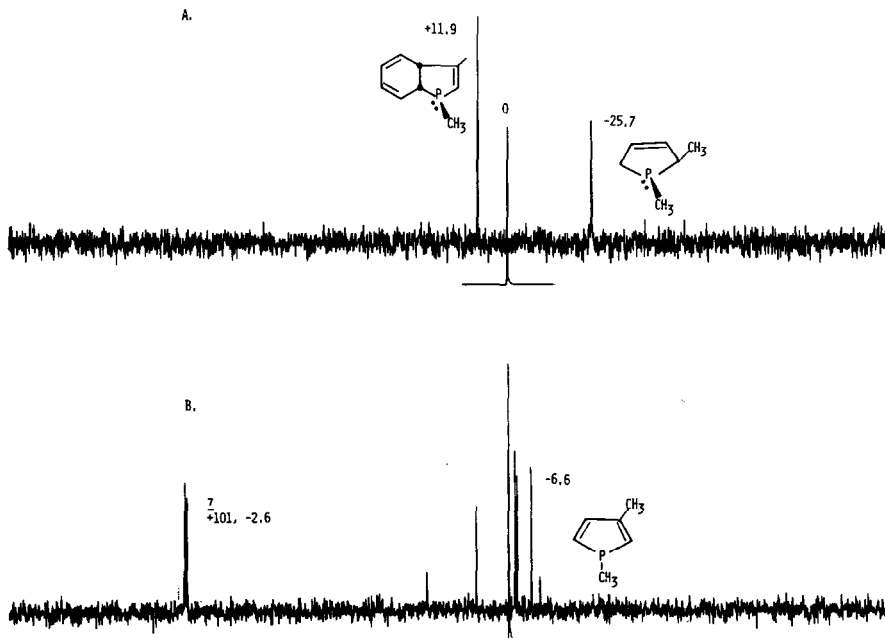


Fig. 1. ^{31}P NMR spectra showing the behavior of 0.032 M mesitylene solutions of phosphole dimer **7** at 121-125° C, 9.5 hr, in the presence (A) and absence (B) of piperylene.

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