

Observation of a Three-membered Ring Containing Phosphorane

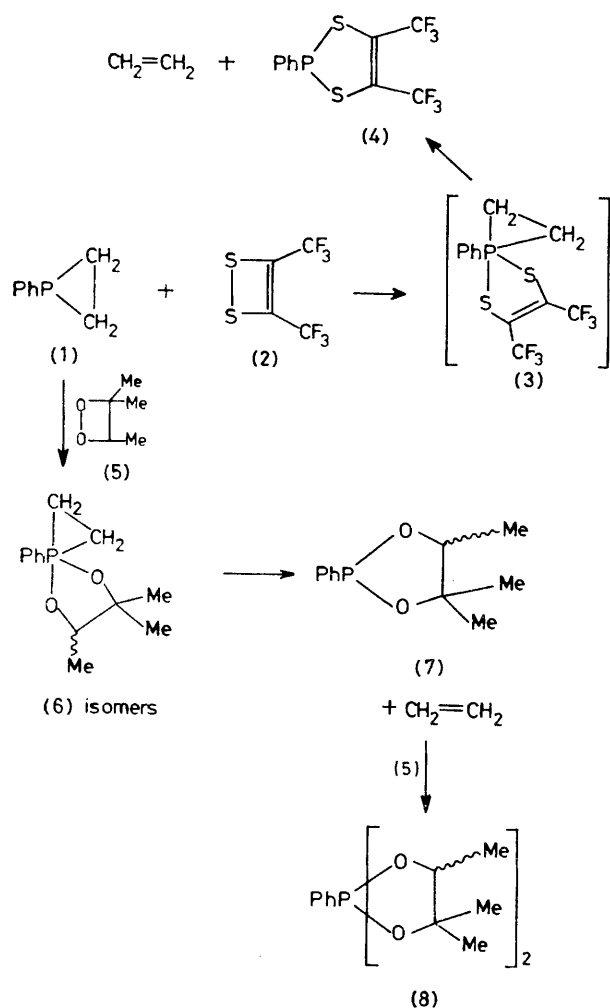
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Summary Phenylphosphiran (**1**) reacts with 3,3,4-trimethyl-1,2-dioxetan (**5**) at -78°C to give a mixture of three-membered ring containing phosphoranes (**6**).

SEVERAL years ago, it was reported that phenylphosphiran (**1**) reacts with the dithiet (**2**) to give the cyclic dithiophosphonite (**4**) and ethylene by a stereospecific process.¹ Since it is well known that (**2**) often reacts with trivalent phosphorus compounds to give phosphoranes,² it was

suggested that (**3**) was formed as an intermediate during the reaction. The isolation or observation of a three-membered ring containing phosphorane has not been accomplished. Recently it has been shown that dioxetans react readily with trivalent phosphorus compounds to give five-membered ring containing phosphoranes.^{2b,3} It is well known that five-membered ring containing oxyphosphoranes are significantly more stable than their acyclic counterparts.⁴ It seemed likely that (**1**) might react with a dioxetan to give an observable three-membered ring containing phosphorane.



3,3,4-Trimethyl-1,2-dioxetan (5) (1.3 mmol) was added to a frozen mixture of (1) (1 mmol) in benzene- CDCl_3 at -78°C . The mixture was allowed to warm to -45°C at which point a colourless solution resulted. On some occasions additional (5) was added because it decomposes in competition with its reaction with (1). The ^{31}P n.m.r. spectrum† of the mixture at -78°C had resonances at +162, -20 and -28 (broad absorption), and -87 p.p.m. These absorptions are assigned to the cyclic phosphonite (7), the mixture of phosphoranes (8), and the three-membered ring containing phosphoranes (6), respectively.‡ In the case of (6), it seems likely that intramolecular ligand exchange is occurring and that there will be two isomers present. It is not clear whether a trigonal bipyramidal or square pyramidal structure is favoured. In some reactions very little (7) and (8) were formed and the major components were (1) and (6).

The mixture of isomers (6) is quite stable at -80°C ; there was no significant change in the ^{31}P n.m.r. spectrum after 2 weeks. When the solution was allowed to warm slowly to room temperature, a gas was evolved. The i.r. spectrum of this gas had the characteristic absorptions of ethylene at 1440 and 948 cm^{-1} . There were also absorptions for tetramethylsilane and a carbonyl absorption for decomposition products, acetone and acetaldehyde, of the dioxetan. The ^{31}P n.m.r. spectrum showed that the -87 p.p.m. resonance had disappeared and that the +162 and -20 and -28 p.p.m. resonances remained.

These results strongly support the contention that the absorption at -87 p.p.m. is due to (6), and that it also undergoes fragmentation in the same manner as the postulated (3). The results also indicate that three-membered ring containing phosphoranes are quite unstable.

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† ^{31}P N.m.r. data are reported relative to 85% phosphoric acid with positive values downfield and negative values upfield.

‡ The high upfield shift observed for (6) is not unexpected for such a structure. The phosphiran (1) absorbs upfield of 85% phosphoric acid at δ 235 p.p.m.

¹ D. B. Denney and L. S. Shih, *J. Amer. Chem. Soc.*, 1974, **96**, 317.

² (a) N. J. De'Ath and D. B. Denney, *J.C.S. Chem. Comm.*, 1973, 856; (b) B. S. Campbell, N. J. De'Ath, D. B. Denney, D. Z. Denney, I. S. Kipnis, and T. B. Min, *J. Amer. Chem. Soc.*, 1976, **98**, 2924.

³ P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. Lerman, *J. Amer. Chem. Soc.*, 1975, **97**, 3850.

⁴ R. Luckenbach, 'Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements,' G. Thieme, Stuttgart, 1973.