Preparation of Novel Sulphur Containing Phosphoranes

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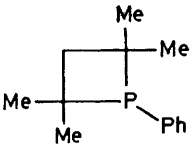
Summary Reaction of small ring containing phosphines and phosphites with 3,4-bis(trifluoromethyl)-1,2-dithieten leads to stable sulphur containing phosphoranes in high yields.

Little is known about the chemistry of phosphoranes in which sulphur is bonded to phosphorus. There are only a few examples of these compounds, and in these only one sulphur is bonded to phosphorus.[1] Here we report a new reaction which leads to a new class of sulphur containing phosphoranes.



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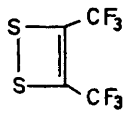

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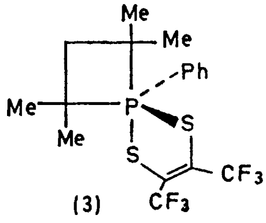

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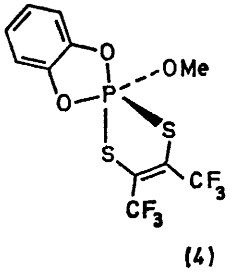
Reaction of the phosphetan (**1**) with the dithieten (**2**) occurred rapidly in methylene chloride at −78° to give a yellow precipitate which was recrystallized from CCl_4 to give yellow crystals, m.p. 109—112°.†

The mass spectrum had a molecular ion at *m/e* 432, calc. 432. The ^{31}P n.m.r. spectrum in methylene chloride showed a single absorption at −17·5 p.p.m. relative to 85% phosphoric acid, and the ^{19}F n.m.r. spectrum a doublet at +53·9 p.p.m. (J_{PF} 0·2 Hz) relative to trichlorofluoromethane. The ^1H n.m.r. spectrum showed a doublet at δ 1·30 (J_{PCCH} 21 Hz) and another doublet at 1·80 (J_{PCCH} 19 Hz). Other absorptions in this region were noted, as were absorptions for aromatic hydrogens. The n.m.r. data strongly support the structure (**3**), provided permutational isomerization is allowed, but is restricted to apical-equatorial exchange of the two rings, *i.e.*, the phenyl group remains in an equatorial position.[2] Thus, under these conditions the fluorine atoms become equivalent and there are two kinds of methyl group hydrogen atoms. The ^1H n.m.r. did not change from −50 to 147° at which temperature fairly rapid decomposition of (**3**) occurred.

Reaction of methyl catechol phosphite and methyl ethylene phosphite with (**2**) at −78° gave substances, (**4**) and (**5**), which are assigned phosphorane structures. The compound, (**4**), has b.p. 100—102°/0·05 mm. The mass spectrum showed a molecular ion at *m/e* 396, calc. 396. The ^{31}P n.m.r. had one absorption at −17·5 p.p.m. The ^1H n.m.r. spectrum had a doublet at δ 3·76 (J_{POCH} 17 Hz,



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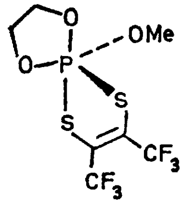

(5)

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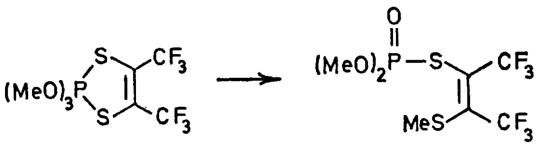
† Satisfactory analyses were obtained for all new compounds.

CH_3). Absorptions for aromatic hydrogens were also found, δ 6·8—7·15. The ^{19}F n.m.r. showed a doublet at +54 p.p.m., (J_{PF} 3·2 Hz).

(**5**) was not isolated. It had a ^{31}P chemical shift of −16·5 p.p.m. The ^{1}H n.m.r. spectrum had a doublet at δ 3·75 (J_{POCH} 17 Hz, CH_3). A complex multiplet was found at δ 3·8—4·6.

Treatment of (**2**) with trimethyl phosphite gave (**6**) initially which had a ^{31}P chemical shift of −1 p.p.m. The phosphorane (**6**), whose structure is assigned principally on the basis of the ^{31}P chemical shift, was unstable and decomposed readily at room temperature to (**7**) which was found as a mixture of geometric isomers. The structure of (**7**) is supported by its mass spectrum, ^{1}H and ^{31}P spectral data, and analysis.


(6) (7) *cis* and *trans*

Treatment of triphenylphosphine with (**2**) under a variety of conditions gave only triphenylphosphine sulphide.

The reaction of (**2**) with trisubstituted phosphorus compounds can yield phosphoranes with two sulphur atoms bonded to phosphorus. The phosphoranes show the same order of stability as has been noted for oxyphosphoranes, *i.e.*, 4- and 5-membered-ring containing materials are usually more stable and the greater the number of electronegative groups bonded to phosphorus, the greater the stability. In a qualitative way it appears that sulphur containing phosphoranes are less stable than the oxyphosphoranes. For example, the biacetyl–trimethyl phosphite adduct is quite stable, whereas (**6**) decomposed quite rapidly.

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