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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.



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 CCl₄ to give yellow crystals, m.p. $109-112^{\circ}$.[†]

The mass spectrum had a molecular ion at m/e 432, calc. 432. The ³¹P n.m.r. spectrum in methylene chloride showed a single absorption at -17.5 p.p.m. relative to 85%phosphoric acid, and the ¹⁹F n.m.r. spectrum a doublet at +53.9 p.p.m. (JPF 0.2 Hz) relative to trichlorofluoro-

† Satisfactory analyses were obtained for all new compounds.

methane. The ¹H n.m.r. spectrum showed a doublet at $\delta 1.30$ (*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 ³¹P n.m.r. had one absorption at -17.5 p.p.m. The ¹H CF₃ n.m.r. spectrum had a doublet at δ 3.76 (JPOCH 17 Hz,



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(5) was not isolated. It had a ³¹P chemical shift of -16.5 p.p.m. The ¹H n.m.r. spectrum had a doublet at $\delta 3.75$ (JPOCH 17 Hz, CH₃). A complex multiplet was found at $\delta 3.8-4.6$.

Treatment of (2) with trimethyl phosphite gave (6) initially which had a ³¹P 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, ¹H and ³¹P spectral data, and analysis.

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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¹ A. P. Stewart and S. Trippett, Chem. Comm., 1970, 1279; E. Gaydon, G. Peiffer, and A. Guillemonat, Tetrahedron Letters, 1971, 239. ⁴ F. H. Westheimer, Accounts Chem. Res., 1968, 1, 70; F. Ramirez, *ibid.*, p. 168; K. Mislow, *ibid.*, 1970, 3, 321; E. L. Muetterties, *ibid.*, p. 266; I. Ugi. D. Marquarding, H. Khusacek, P. Gillespie, and F. Ramirez, *ibid.*, 1971, 4, 288, and references cited in these review articles.