Biphilic Insertions into a Sulphur–Oxygen Bond by Tervalent Phosphorus Compound

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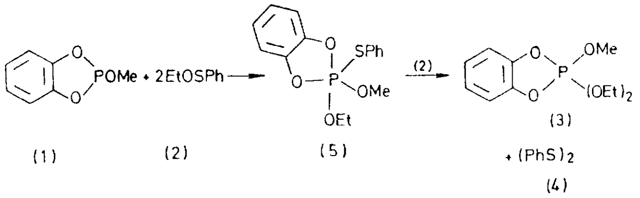
Summary Tervalent phosphorus compounds often react with ethyl benzenesulphenate to give ethoxythiophenoxyphosphoranes; these can react with another mole of ethyl benzenesulphenate to give ethoxyphosphoranes and diphenyl disulphide, or they can decompose by ionic pathways.

The phosphite (**1**) reacts with ethyl benzenesulphenate (**2**) to give the phosphorane (**3**) and diphenyl disulphide (**4**) in essentially quantitative yield. The formation of (**5**) as the first reaction product is strongly supported by the observation that an absorption in the ^{31}P n.m.r. spectrum at $\delta + 22$ relative to 85% phosphoric acid forms early in the reaction and then is replaced by the absorption for (**3**) at $+49$. In the available examples, introduction of a sulphur atom into an oxyphosphorane leads to a downfield shift in the ^{31}P n.m.r. spectrum of *ca.* 30[1] and thus the structural assignment is reasonable. No evidence has been obtained as yet as to how (**5**) is converted into (**3**).

Compounds $(EtO)_3P$ (**6**), $(EtO)_2PPh$ (**7**), $EtOPPh_2$ (**8**), and Ph_3P (**9**) were allowed to react with (**2**). In each instance oxyphosphoranes were observed as products. In these cases varying amounts of phosphoryl compounds containing ethoxy- and thiophenoxy-groups were also found. Triphenylphosphine yielded 90% diethoxytriphenylphosphorane and 10% triphenylphosphine oxide.[2] This may well be the method of choice for the synthesis of this material and for its further application as a synthetic reagent.[3] Mixed alkylarylphosphines react with (**2**) to give the corresponding phosphine oxides and phenyl ethyl sulphide.

The relative reactivities of (**6**)—(**9**) towards (**2**) were determined for individual reactants by following the changes in their ^{31}P n.m.r. spectra as a function of time. The order was established as (**7**) $>$ (**8**) $>$ (**6**) $>$ (**9**). Similar results were obtained when equimolar mixtures of the various reactants were allowed to react in excess with (**2**). There were no differences in products when the reactions were conducted in this manner. The ratio of remaining starting materials gave, with (**9**) $= 1$, (**8**) $= 11{\cdot}2$, (**7**) $= 20{\cdot}5$, and (**6**) $= 1{\cdot}35$. These results do not follow the observed rate variations for these compounds in a variety of nucleophilic displacement reactions. They have been found to be (**9**) $\geqslant$ (**8**) $>$ (**7**) $>$ (**6**).[4] The results suggest therefore that the rate-controlling process is not a normal $S_{\mathrm{N}}2$ reaction. Deviations from the normal nucleophilic behaviour of tervalent phosphorus compounds has been observed in their reactions with diethyl peroxide and these have been associated with a transition state in which the tervalent phosphorus compound is behaving as a biphile and inserting into the sigma oxygen–oxygen bond.[5] The results obtained with (**2**) are highly suggestive of a similar process.



Although many oxyphosphoranes are known, mixed oxythiophosphoranes are elusive and only a few are known.[1,6] Apparently the greater ease with which sulphur can accept a negative charge over oxygen allows more ready ionization with subsequent decomposition by ionic paths. Several mixed thiofluorophosphoranes are known, and they show varying degrees of stability.[1b]

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