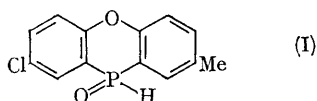


Duality in the Chemical Character of Secondary Phosphine Oxides

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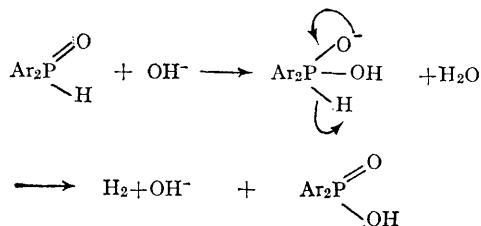
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SECONDARY phosphine oxides have been shown to act as nucleophiles, in the presence of base, either at oxygen or at phosphorus to give respectively derivatives of either ter- or quadri-covalent phosphorus;¹ we have discovered, however, that they act not only as nucleophiles in the absence of base but also as electrophiles towards bases.



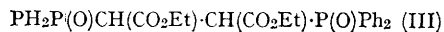
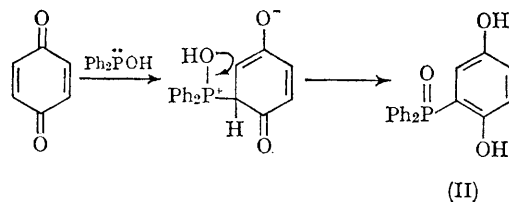
For example, the addition of excess of ethanolic sodium hydroxide or ethoxide to diphenylphosphine oxide at room temperature results in the rapid evolution of *hydrogen*, with conversion of the oxide into the sodium salt of diphenylphosphinic acid. This striking reaction is equally rapid with the cyclic oxide (I) and also occurs with di- α -naphthyl- and di-*n*-octyl-phosphine oxide although much more slowly even at 70°. We also find that the thiophenate anion reacts analogously; hydrogen is slowly evolved when aqueous sodium thiophenate is added to the oxide in ethanol at 60° with the production of the *S*-phenyl ester of diphenylphosphinothiolic acid, $\text{Ph}_2\text{P}(\text{O})\text{SPh}$.

This previously unreported reaction may be explained by addition of hydroxyl ion to an electrophilic phosphorus followed by expulsion of hydride ion.



Consistent with this hypothesis, when the reaction is carried out in dioxan- D_2O containing NaOD , HD is evolved together with D_2 in the proportion of approximately 1 : 20 (mass spectrometry). The preponderance of D_2 is not unexpected because the exchange $\text{P-H} \rightarrow \text{P-D}$ is known to occur with similar compounds, *e.g.*, mono- and di-alkylphosphonates.² In addition we have observed that in D_2O , in the presence of a trace of alkali, the infrared P-H band (2350 cm^{-1}) of diphenylphosphine oxide is readily replaced by the P-D absorption band (1685 cm^{-1}). Hydrogen is also evolved when the acetone adduct, $\text{Ph}_2\text{P}(\text{O})\text{C}(\text{OH})\text{Me}_2$, is warmed in ethanol with 4*N*-sodium hydroxide; sodium diphenylphosphinate and acetone (but *no* propan-2-ol) are produced.

While the anions of alkyl secondary phosphine oxides have been added to $\alpha\beta$ -unsaturated carbonyl compounds,³ we find that diphenylphosphine oxide reacts as a nucleophile in the complete absence of base and, in benzene, rapidly gives a high yield of the mono-adduct (II) with quinone and the di-adduct (III) with ethyl acetylenedicarboxylate. Although we have no direct evidence on the mechanism, the simplest way of explaining these uncatalysed additions is to postulate that the oxide reacts in its trivalent form as follows:—



All new compounds have been authenticated by analysis, and infrared and n.m.r. spectra.

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