Formation of Phosphoranes and Related Compounds in Trialkyl Phosphite Deoxygenations of 2,6-Dimethylaryl 2-Nitrophenyl Ethers and 2,6-Dimethylaryl-2-nitrophenylmethane

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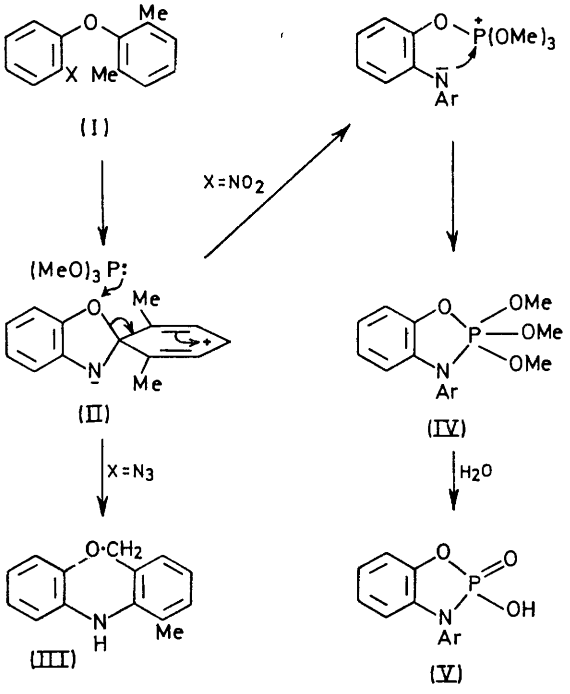
Summary Trialkyl phosphite deoxygenation of 2,6-dimethylphenyl 2-nitrophenyl ether gives the aminotextroxyphosphorane (IV) and that of 2-nitrophenyl-2,4,6-trimethylphenylmethane gives diethyl *o*-(2,4,6-trimethylphenylamino)benzylphosphonate, which novel products support the intermediacy of a spirodiene in these reactions.

We have reported previously[1,2] many examples of rearrangements occurring during the deoxygenation of nitro-compounds by triethyl phosphite. The course of these reactions can be interpreted in terms of a spirodienyl intermediate, *e.g.* (II), although direct evidence is lacking. We now report two new examples of the reaction which not only lead to new types of product hitherto undetected in the reaction series, but also provide strong support for the intermediacy of a spirodienyl intermediate.

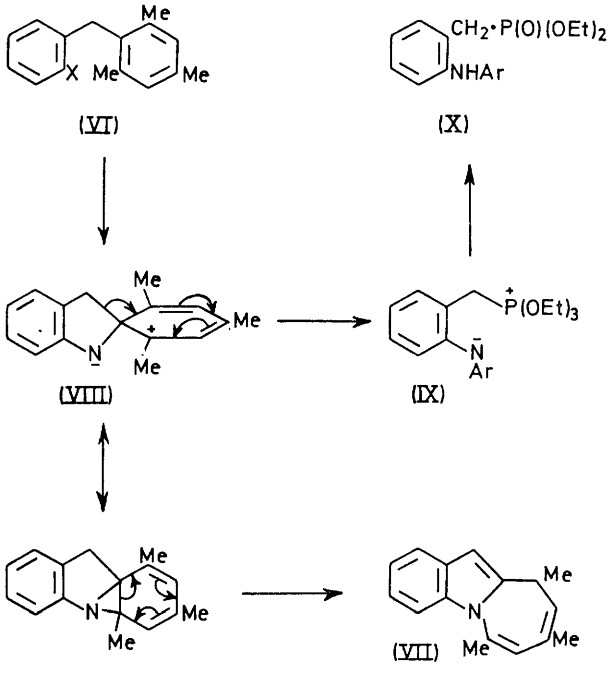


(Ar = 2,6 - $Me_2C_6H_3$)

Scheme 1.

Thus, while the ether (I; X = N_3) gives the dibenzoxazepine (III) (11%),[2] deoxygenation of the corresponding nitro-compound (I; X = NO_2) by excess of trimethyl phosphite gives the crystalline aminotetroxyphosphorane (IV) (50%). Reactions with triethyl phosphite or the 2,4,6-trimethylphenyl homologue proceed similarly and the structural assignment is supported by mass and ^{31}P and ^{1}H n.m.r. spectroscopy, and by progressive hydrolysis to the acid (V) and to 2′,6′-dimethylphenyl-2-hydroxyphenylamine. The isolation of this phosphorane system points to reaction as in Scheme 1 wherein the intermediate spirodiene (II) reverts to aromaticity *via* nucleophilic attack by tervalent phosphorus on the bridgehead oxygen. An alternative involves collapse of (II) to a quinoneimine and hence (IV) by reaction with phosphite.

Similarly, whereas (VI; X = N_3) gives various isomeric azepinoindoles [*e.g.* (VII)],[3] a result which we confirm, the corresponding 2-nitro-derivative (VI; X = NO_2) in the presence of triethyl phosphite gives, additionally, the phosphonate (X) (7%). This points to reaction *via* the spirodiene (VIII) in Scheme 2, analogous to Scheme 1, although it has still to be resolved whether (X) arises from (IX) *via* direct elimination of ethylene or *via* a rapidly decomposed phosphorane, analogous to (IV).



(Ar = 2,4,6 - $Me_3C_6H_2$)

Scheme 2.

Thus in both cases (I and VI; X = NO_2) the trialkyl phosphite has dual roles as a deoxygenating reagent and as a nucleophile towards the intermediate in the reaction, thereby acting as its own mechanistic probe.

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[1] J. I. G. Cadogan and S. Kulik, *J. Chem. Soc.* (*C*), 1971, 2621.
[2] J. I. G. Cadogan and P. K. K. Lim, *Chem. Comm.*, 1971, 1431.
[3] G. R. Cliff and G. Jones, *J. Chem. Soc.* (*C*), 1971, 3418.