The Reaction of Triethyl Phosphite with *o*-Dinitrobenzene: Evidence for Aromatic Substitution by Tervalent Phosphorus

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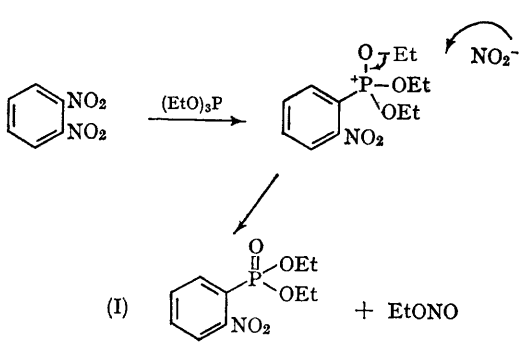
IN continuation of our studies of the reactions of tervalent phosphorus compounds with nitro-compounds,[1] it has now been shown that triethyl phosphite (1·5 mol.) reacts with *o*-dinitrobenzene (1 mol.) in boiling acetonitrile (8 hr.) to give diethyl *o*-nitrophenylphosphonate (I; m.p. 55—56°, b.p. 128°/0·02 mm.; 75%), ethyl nitrite, and a small quantity of triethyl phosphate, indicative of deoxygenation as a competing side reaction. In the absence of solvent a vigorous reaction occurs at 90° to give (I) (70%), tarry material, and ethyl nitrite (50%). Diethyl *o*-nitrophenylphosphonate was characterised by analysis, molecular-weight determination, hydrolysis to the known *o*-nitrophenylphosphonic acid,* and by comparison of its n.m.r., i.r., and u.v. spectra with those of an authentic sample of (I). Ethyl nitrite was characterised by comparison of its n.m.r., i.r., and mass spectra with those of authentic material.

Although the details of the mechanism have not yet been established, particularly with respect to the first step, the simplest route to the products is as follows:



* An authentic sample of *o*-nitrophenylphosphonic acid was generously provided by Dr. L. Freedman.

The reaction is of interest, not only because it affords a convenient route to diethyl *o*-nitrophenylphosphonate, which is a useful intermediate previously difficult to prepare, but also because established examples of heterolytic aromatic substitution by phosphorus compounds are rare. The reaction is relevant to observations previously recorded but unexplained. Thus Horner and Klüpfel[2] showed that *o*-dinitrobenzene and triethylphosphine gave a 1 : 1-adduct of unknown structure, while the reaction of triphenylphosphine with 4-nitropyridine 1-oxide at 200° has been reported to lead to the evolution of nitrous fumes, the fate of the remainder of the molecule being unknown.[3]

(*Received, June 22nd*, 1966; *Com.* 426.)

[1] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831; J. I. G. Cadogan, R. K. Mackie, and M. J. Todd, preceding Communication.
[2] L. Horner and K. Klüpfel, *Annalen*, 1955, **591**, 69.
[3] E. Howard and W. F. Olszewski, *J. Amer. Chem. Soc.*, 1959, **81**, 1483.