Ring Expansion during the Reaction of Simple Aromatic Nitro-compounds with Triethyl Phosphite

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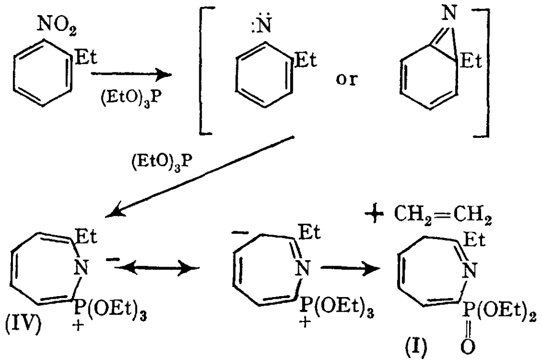
IN CONTINUATION of our studies[1] on the deoxygenation of nitro-compounds by triethyl phosphite, we find that the thermal reaction involving *o*-ethylnitrobenzene gives diethyl 2-ethyl-3-*H*-azepin-7-yl phosphonate (I) (12%), ethylene (50% based on the azepine), and, after hydrolysis, diethyl *N*-(*o*-ethylphenyl)phosphoramidate (II) (18%), indicating the precursor triethyl *N*-(*o*-ethylphenyl)phosphorimidate (III).[2] Diethyl *N*-ethyl-*N*-phenyl phosphoramidate is also formed. Control experiments showed that (II) and (III) were not precursors of (I). *o*-Nitrotoluene and nitrobenzene gave analogous products under these conditions. These results are in contrast to earlier failure to detect identifiable products, apart from a trace of the phosphorimidate, in the reaction of triethyl phosphite with nitrobenzene,[3,4] and with the report[5] that the corresponding reduction of *o*-ethylnitrobenzene gave only triethyl *N*-(*o*-ethylphenyl)phosphorimidate (44%).[5] Ring-expansion to 3-*H*-azepines during reduction of aromatic nitro compounds with diethyl methyl phosphite in the presence of an added nucleophile, diethylamine, has been reported, and has been adduced as evidence in favour of nitrene participation in the reaction.[6] Our present results indicate a bifunctional role of triethyl phosphite as a reducing agent and as the nucleophile responsible for ring expansion, probably *via* a quasiphosphonium intermediate (IV), which undergoes elimination of ethylene rather than an Arbusov-type isomerisation to give a *C*- or *N*-ethylated product.



$(EtO)_3P{=}NAr$
(III)

$(EtO)_2P(O){\cdot}NHAr$
(II)

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[1] J. I. G. Cadogan, S. Kulik, and M. J. Todd, preceding Communication and references therein.

[2] P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 42.

[3] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

[4] R. J. Sundberg, *J. Amer. Chem. Soc.*, 1966, **88**, 3781.

[5] R. J. Sundberg, *J. Org. Chem.*, 1965, **30**, 3604.

[6] J. I. G. Cadogan and M. J. Todd, *Chem. Comm.*, 1967, 178; *cf.* R. A. Odum and M. Brenner, *J. Amer. Chem. Soc.*, 1966, **88**, 2074.