A Novel Displacement of the Nitro-group from *p*-Nitrotoluene and Related Compounds

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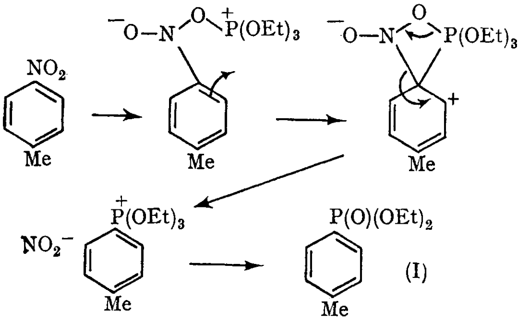
WHILE displacement of the nitro-group from activated aromatic compounds, such as *o*-dinitrobenzene,[1] is well known, such a displacement from unactivated nitro-compounds such as *p*-nitrotoluene has not been reported.

We now report that reaction of boiling triethyl phosphite with *p*-nitrotoluene gives diethyl toluene-*p*-phosphonate (I; 5%), in addition to diethyl 4-methyl-3*H*-azepine-7-phosphonate (6%), diethyl *N*-ethyl-*N*-*p*-tolylphosphoramidate (24%), and diethyl *N*-*p*-tolylphosphoramidate (26%).[2] *p*-Nitroanisole and *p*-ethylnitrobenzene give similar products in similar yields. Reactions involving *o*-[2] and *m*-nitro-analogues do not give rise to the corresponding diethyl arenephosphonates, thus indicating a fine balance between the various possible reaction paths.[2,3]

It is considered that the diethyl arenephosphonates produced in these reactions do not arise by direct nucleophilic displacement of the nitro-group, this being precluded by the presence of electron donating substituents. Instead, the route outlined in the Scheme is preferred, whereby nucleophilic attack on the oxygen of the nitro-group leads to the creation of an electrophilic phosphorus atom close to the aromatic ring now activated towards electrophilic substitution, and in a position favourable for the formation of a four-membered intermediate of the type common in organophosphorus chemistry. Collapse of this intermediate can then lead to the observed products.



SCHEME

(*Received, July 9th,* 1968; *Com.* 927.)

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[2] *Cf.* J. I. G. Cadogan, R. K. Mackie, and M. J. Todd, *Chem. Comm.*, 1968, 736.
[3] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.