Deoxygenation of 2-Nitrophenyl Phenyl Sulphides by Triethyl Phosphite: A New Aromatic Rearrangement

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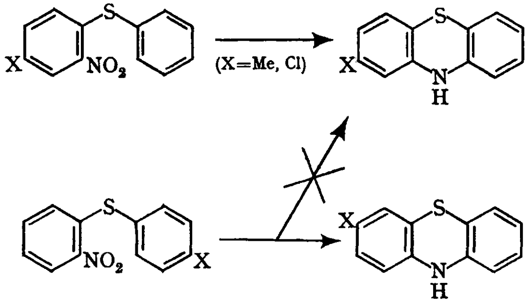
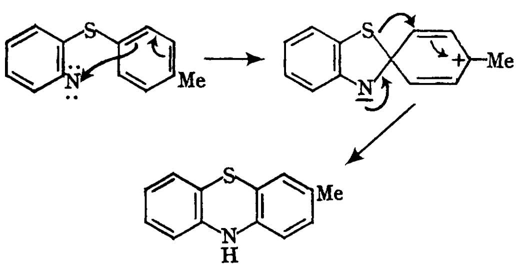
THE reaction of triethyl phosphite with 2-nitrophenyl phenyl sulphide gives phenothiazine in good yield.[1] A detailed investigation of this reaction has now revealed a new molecular rearrangement. Thus, under the normal conditions for deoxygenation by triethyl phosphite,[2] while 4-methyl-2-nitrophenyl phenyl sulphide gives 2-methylphenothiazine (36%) and *N*-ethyl-2-methylphenothiazine (25%), the latter produced by ethylation of the first formed phenothiazine, the isomeric 4-methylphenyl 2-nitrophenyl sulphide gives 3-methylphenothiazine and its *N*-ethyl derivative, as shown by comparison with authentic samples. By effecting the reaction in solution in cumene, 4-chloro-2-nitrophenyl phenyl sulphide gives 2-chlorophenothiazine (55%) while 4-chlorophenyl 2-nitrophenyl sulphide gives 3- (63%) rather than 2-chlorophenothiazine (Scheme 1), as shown by comparison with authentic samples. These observations suggest that the six-membered ring is being formed after rearrangement of a five-membered intermediate formed by electrophilic attack at the electron-rich 1′-position. Such attack may involve a nitrene (Scheme 2) by analogy with other deoxygenations by triethyl phosphite.[3] It is significant, in this connection, that we find that thermal decomposition of 2-azidophenyl 4-chlorophenyl sulphide gives 3-chlorophenothiazine, it being generally accepted that such decompositions of azides proceed *via* nitrenes. It is probable that ring closure involving cyclisation on to an unsubstituted ring also proceeds by such a rearrangement, which is similar to that involved in the Hayashi rearrangement of carboxybenzophenones in strong acid.[4]



Scheme 1



Scheme 2

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[1] J. I. G. Cadogan, R. K. Mackie, and M. J. Todd, *Chem. Comm.*, 1966, 491.

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

[3] J. I. G. Cadogan and M. J. Todd, *Chem. Comm.*, 1967, 178; J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.

[4] *Cf.* R. B. Sandin, R. Melby, R. Crawford, and D. McGreer, *J. Amer. Chem. Soc.*, 1956, **78**, 3817.