

An Aromatic Nitrene-induced 1,4-Methoxyl Shift

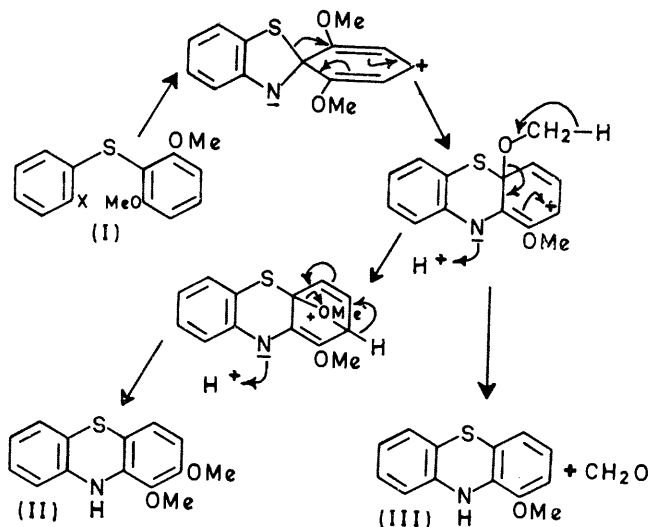
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Summary 2,6-Dimethoxyphenyl 2-nitrophenyl sulphide (I; X = N) gives 1,2-dimethoxyphenothiazine, via a novel 1,4-dimethoxyl shift, and 1-methoxyphenothiazine and formaldehyde.

Reaction via a nitrene (I; X = N), as in the Scheme, seems likely.

NOVEL rearrangements occurring during the course of triethyl phosphite deoxygenations¹ of aryl 2-nitroaryl sulphides and decomposition of their 2-azido-analogues have recently been described.² We now report that thermal decomposition of 2-azidophenyl 2,6-dimethoxyphenyl sulphide (I; X = N₃) in decalin, or the triethyl phosphite deoxygenation of 2,6-dimethoxyphenyl 2-nitrophenyl sulphide (I; X = NO₂) proceed at 150°, via a novel 1,4-methoxyl shift, with a concurrent demethoxylation, to give 1,2-dimethoxyphenothiazine [II; 39% (I; X = N₃) or 47% (I; X = NO₂)] and 1-methoxyphenothiazine [III; 20% (I; X = N₃) or 11% (I; X = NO₂)] by direct comparison (i.r., n.m.r., mass spectrum, correct analysis, m.p.) with authentic specimens synthesised by (a) addition of sulphur to 2-methoxydiphenylamine, (b) triethyl phosphite deoxygenation of 2-methoxyphenyl 2-nitrophenyl sulphide, and (c) a similar reaction of 2-nitrophenyl 2,3-dimethoxyphenyl sulphide. At 190° decomposition of (I; X = N₃) gives a slightly different ratio of products (II, 33% and III, 32%). The yield of demethoxylated product is exactly paralleled by the formation of formaldehyde (33%).



SCHEME

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¹ J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.

² J. I. G. Cadogan, S. Kulik, and M. J. Todd, *Chem. Comm.*, 1968, 736; J. I. G. Cadogan and S. Kulik, *ibid.*, 1970, 233; J. I. G. Cadogan, S. Kulik, and C. Thomson, *ibid.*, 436; M. Messer and D. Farge, *Bull. Soc. chim. France*, 1968, 2832.