Nitrene-induced Rearrangements Leading to Phenoxazines and the 5,11-Dihydrodibenzo[*b*,*e*][1,4]oxazepine Ring System

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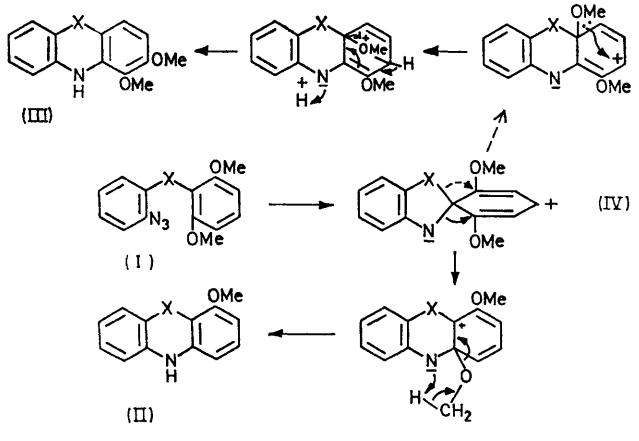
Summary By use of blocked *ortho*-positions in the starting 2-nitrenoaryl aryl ethers, the first successful conversions of these into phenoxazines and 5,11-dihydrodibenzo-[*b*,*e*][1,4]oxazepines have been achieved.

ALTHOUGH 2-nitrenoaryl aryl sulphides react *via* cyclisation and rearrangement to give phenothiazines,[1] the corresponding reaction of 2-nitrenoaryl ethers has not been achieved [2]

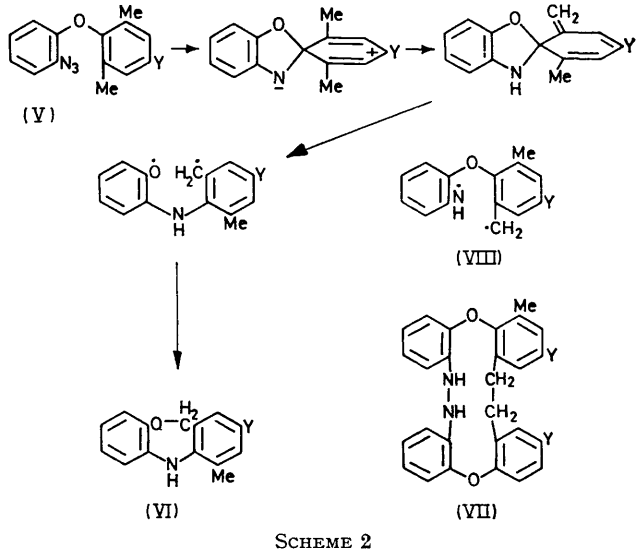
We now report, however, that blocking of the free *ortho*-positions in 2-nitrenoaryl aryl ethers leads to new syntheses of certain phenoxazines and 5,11-dihydrodibenzo[*b*,*e*][1,4]oxazepines.

Thus, thermolysis in decalin at 160° of 2-azidophenyl 2,6-dimethoxyphenyl ether (I; X=O) gave 4-methoxyphenoxazine (II; X=O) (35%), formaldehyde (15%), and 1,2-dimethoxyphenoxazine (III; X=O) (15%). The route in Scheme 1 is obvious. It is noteworthy that while the corresponding sulphide (I; X=S) behaved similarly in giving 1,2-dimethoxyphenothizaine (III; X=S) it gave 1- rather than 4-methoxyphenothiazine.[3] This is in accord with the expected higher migratory aptitude of sulphur over nitrogen in the intermediate (IV; X=S), whereas that of oxygen and nitrogen in (IV; X=O) would be more nearly equal.

Thermolysis of 2-azidophenyl 2,4,6-trimethylphenyl ether (V; Y=Me) gave 5,11-dihydro-2,4-dimethyldibenzo[*b*,*e*]-[1,4]oxazepine: (VI; Y=Me) (15%), M^+ 225·115246 and the bis ether (VII; Y=Me) (1%), M^+ 450·230114, (M $-C_{15}H_{16}NO)^+$ 224·106708; τ 8·04 (s, Me), 7·76 (s, Me), 7·70 (s, CH_2), 4·17br (s, NH), and 2·7—3·3 (m, ArH × 6). The 2,6-dimethyl analogue (V; Y=H) behaved similarly. A likely route to the oxazepines (VI) is depicted in Scheme 2.



SCHEME 1



SCHEME 2

The genesis of the bis ether (VII) is less obvious; Scheme 2 shows a possible diradical (VIII) route from the intermediate spirodiene (VI) but it is not clear why the radical (VIII), if formed, should not cyclise to give the isomeric **10,11**-dihydrodibenzo[*b,f*][1,4]oxazepine, which we could not detect.

All assignments of structures were supported by the correct analysis, mass-, and n.m.r.-spectroscopic data.

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[2] P. A. S. Smith, B. B. Brown, R. K. Putney, and R. R. Reinisch, *J. Amer. Chem. Soc.*, 1953, **75**, 6335.
[3] J. I. G. Cadogan and S. Kulik, *Chem. Comm.*, 1970, 792; *J. Chem. Soc.* (*C*), 1971, 2621.