A New Aromatic Rearrangement Involving a Nitrene: Synthesis of the 5,11-Dihydrodibenzo[*b*,*e*]-1,4-thiazepine Ring System

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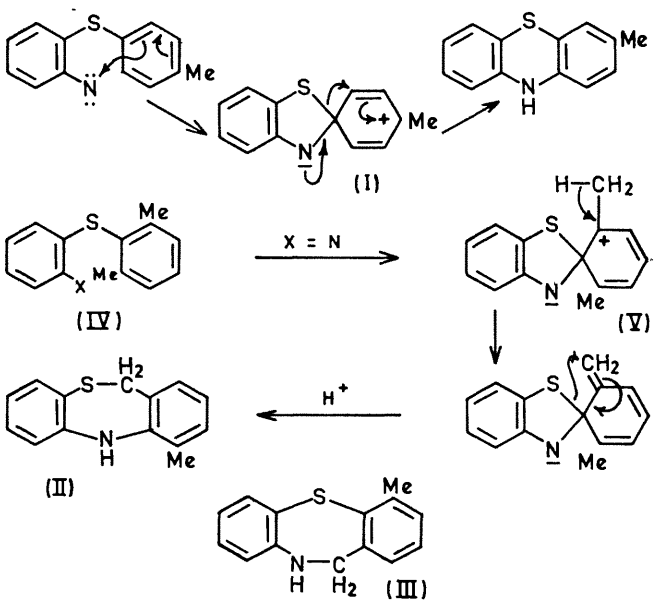
Summary Thermal decomposition of 2-azidophenyl 2,6-dimethylphenyl sulphide (IV; X = N_3) in decalin leads to 5,11-dihydro-4-methyldibenzo[*b*,*e*][1,4]thiazepine (II) *via* a novel rearrangement involving a nitrene.

WE have shown[1] that thermal decomposition of aryl 2-azidophenyl sulphides and phosphite deoxygenation[2] of 2-nitrophenyl aryl sulphides give "rearranged" phenothiazines probably *via* an intermediate of the type (I) derived from a nitrene. We now report a novel rearrangement which occurred during the thermal decomposition of 2-azidophenyl 2,6-dimethylphenyl sulphide (IV; X = N_3), a molecule in which the essential *o*-positions are blocked. Thus, the azide, in decalin at 180°, gave 5,11-dihydro-4-methyldibenzo[*b*,*e*][1,4]thiazepine (II) (74%) as shown by direct comparison with an authentic specimen [m.p. and mixed m.p. 74°, i.r., mass, and n.m.r. spectra (τ 7·74, CH_3; 6·07, $\cdot CH_2$; 4·30, NH; 2·8—3·5, 7ArH)] prepared by the method of Yale and his co-workers.[3] The isomeric [*b*,*f*]-[1,4]thiazepine (III) was not detected (g.l.c.).

Similar results were obtained *via* the nitrene produced by trimethyl phosphite reduction[2] of the nitro-compound (IV; X = NO_2).

These results point to the mechanism outlined in the Scheme, whereby the first formed nitrene (IV; X = N:), rather than undergo insertion into a methyl C–H bond to give the [*b*,*f*]thiazepine (III) attacks the adjacent benzene ring at the nucleophilic 1′ position to give the five-membered intermediate (V) analogous to that postulated in the phenothiazine rearrangement. This in turn undergoes a sigmatropic shift to give the observed product.



(*Received, December 22nd*, 1969; *Com.* 1923.)

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[2] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.
[3] H. L. Yale, F. A. Sowinski, and J. Bernstein, U.S.P. 3,188,322.