Mechanism of the Reaction of Methanesulphonylnitrene with Benzene

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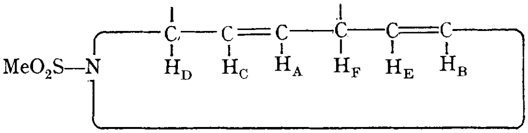
THE thermal decomposition of methanesulphonyl azide in benzene at 120° has been shown[1] to give *N*-methanesulphonylaniline (I) (54%) and methanesulphonamide (14·4%). In contrast to the reactions with ethyl azidoformate[2] and with cyanogen azide,[3] no seven-membered ring compound (II) could be detected. The results were rationalised in terms of a singlet sulphonylnitrene $\mathrm{RSO_2}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}$ which added to benzene in the rate-determining step to form the bicyclic aziridine intermediate (III). This then underwent ring opening and rearrangement to (I). The ring-opening of (III) to (I) rather than (II) could be explained if the sulphonyl group were better able to delocalise the developing negative charge than were either the nitrile or ethoxycarbonyl groups.

In an attempt to trap (III), the reaction was repeated at 120° in the presence of an excess of tetracyanoethylene (TCNE). A crystalline adduct $C_{13}H_9N_5O_2S$, m.p. 200° (decomp.), was obtained (30·4%) at the expense of (I) (6%). Methanesulphonamide (19%) was also obtained. The n.m.r. spectrum of the adduct indicated clearly that it was not the symmetrical product (IV), and spin-decoupling experiments confirmed that it was the 1,4-adduct (V) of *N*-methanesulphonylazepine (II) having part-structure (VI):



(VI)

The same product (V) was obtained from an authentic sample of *N*-methanesulphonylazepine

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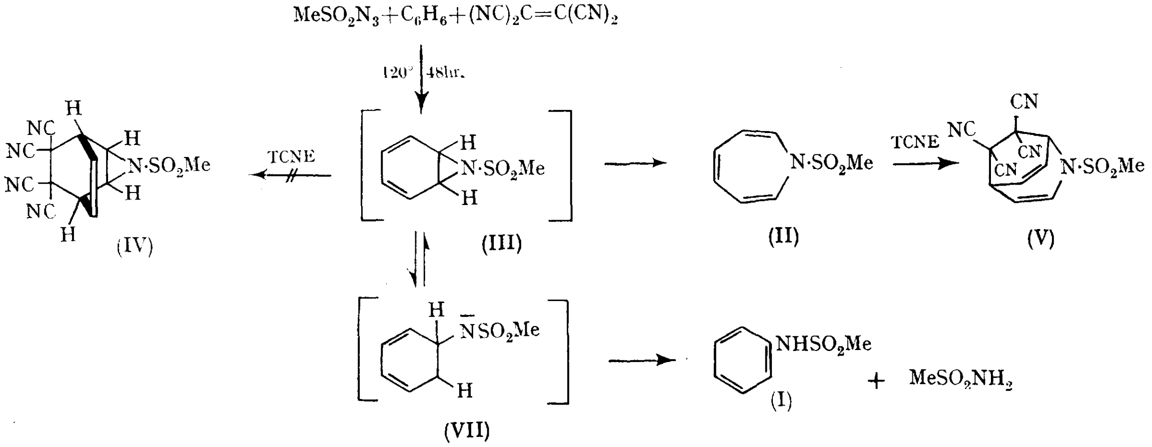
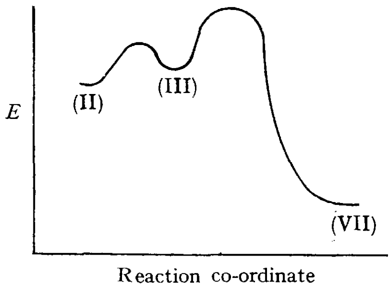
N.m.r. spectrum of tetracyanoethylene adduct (VI)

H_A	2·99 τ	(octet, J_{AC} 8·6, J_{AF} 7·3, J_{AD} 1·0 c/sec.)
H_B	3·33 τ	(octet, J_{BE} 8·6, J_{BD} 1·5, J_{BF} 0·5 c./sec.)
H_C	3·40 τ	(octet, J_{CD} 7·0, J_{AC} 8·6, J_{CF} 1·0 c./sec.)
H_D	4·32 τ	(octet, J_{CD} 7·0, J_{AD} 1·0, J_{BD} 1·5 c./sec.)
H_E	4·72 τ	(triplet, J_{EF} = J_{BE} 8·6 c./sec.)
H_F	6·09 τ	(complex multiplet, J_{AF} 7·3, J_{EF} 8·6, J_{CF} 1·0, J_{BF} 0·5 c./sec.)
H_{Me}	6·68 τ	(3H singlet)



(II)‡ and TCNE in benzene at 80°, thus further supporting structure (V). Corresponding adducts, or mixtures of adducts, were obtained from the reaction of methanesulphonyl azide and toluene, or chlorobenzene, at 120° in the presence of TCNE. No adduct was formed between (I) and TCNE in benzene at 120°. The structure of (V) is similar to that of the adduct formed from TCNE and *N*-ethoxycarbonylazepine.[5]

These results suggest that an equilibrium exists between (II), (III), and (VII): at 120° it lies mainly on the side of (VII) which rearranges irreversibly to (I). The situation can be depicted by a potential energy diagram. Thus, at 120° (II) is too unstable relative to (VII) to be isolated (thermodynamic control) [even after short reaction times no (II) could be detected by t.l.c.] though it is formed more readily than (VII) (kinetic control) and can, therefore, be intercepted if TCNE is present. This suggested that at lower temperatures (II) it might indeed be isolated. Unfortunately, methanesulphonyl azide does not thermolyse appreciably much below 120°. However, when a solution of methanesulphonyl azide in benzene was heated at 80° for 100 hr., compound (II) could be detected by t.l.c. in the mixture (R_f = 0·65), but not (I) (R_f = 0·35).



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