Curtius-type Rearrangement of a Sulphonyl Azide

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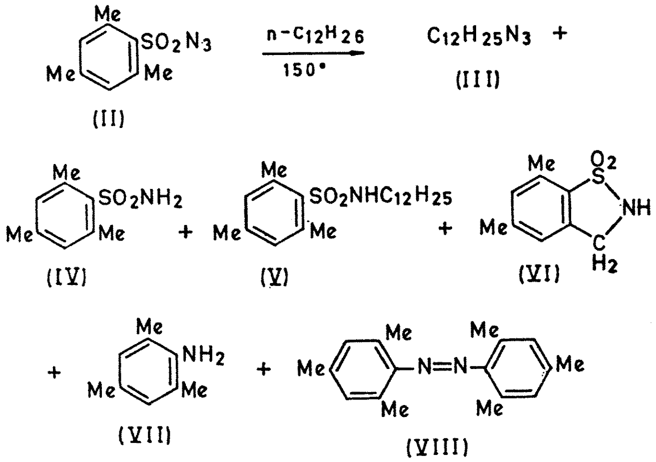
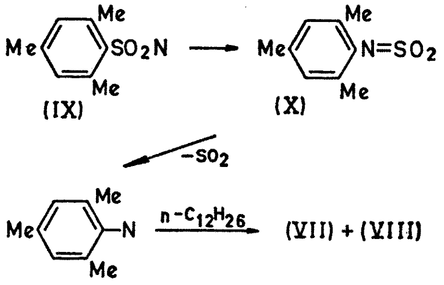
Summary Six products have been identified from the thermolysis of mesitylene-2-sulphonyl azide in dodecane: two are derived from a Curtius-type rearrangement of the corresponding sulphonyl nitrene.

UNTIL recently, sulphonyl azides were thought to be 'rigid' (Curtius' "starre" azides[1]) and not to undergo Curtius-type rearrangements. Photolysis of benzenesulphonyl azide (I) in methanol did give *N*-methoxybenzenesulphonamide and methyl *N*-phenylsulphamate,[2] and decomposition of the triethylammonium salt of *N*-*p*-nitrobenzenesulphonoxybenzenesulphonamide in methanol, ethanol, and aniline gave products derived from a Lossen-type rearrangement to sulphurylaniline.[3] It was felt[2] that these rearrangements involved a protonated species and not a free sulphonyl nitrene. The vapour-phase pyrolysis of (I) at 625° gave a 17·5% yield of azobenzene,[3] and trace amounts of the latter could be obtained from (I) in boiling cyclohexanone.[4] A nitrene mechanism was suggested[4] to account for the formation of azobenzene, but an alternative pathway involving elimination of sulphur dioxide and formation of phenyl azide[5] which is known to give azobenzene, is a possibility.[6] We now report evidence which suggests that sulphonyl nitrenes do undergo Curtius-type rearrangements.

In connection with a study of the synthesis of cyclic sulphonamides,[7] the thermolysis of mesitylene-2-sulphonyl azide (II), b.p. 79—80°/0·022 mm., at 150° in n-dodecane under nitrogen was studied. It gave seven products, six of which have been identified,[8] there being too little of the seventh to characterize. The mixture of dodecyl azides (III), b.p. 50°/20 μm. (2·3%) undoubtedly arises by a mechanism similar to that suggested by Breslow *et al.*[5] Sulphonamides (IV) (1·1%) and (V) (23·1%) are the expected hydrogen-abstraction and intermolecular C–H insertion products,[7] and the sultam (VI), m.p. 114·5—116°, (2·0%) is the expected[7] intramolecular insertion product, all of which undoubtedly arise from an intermediate sulphonyl nitrene (IX). The formation of the aniline (VII) (20·7%) and the azobenzene (VIII) (0·35%) is best accounted for by a rearrangement of (IX) to the unstable sulphonylaniline (X) which loses SO_2 to give the aryl nitrene which dimerises or abstracts hydrogen from the solvent.





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[1] T. Curtius, *Z. angew. Chem.*, 1914, **27**, 213; A. Bertho, *J. prakt. Chem.*, 1929, [2] **120**, 89; T. Curtius, *ibid.*, 1930, [2] **125**, 303.

[2] W. Lwowski and E. Scheiffele, *J. Amer. Chem. Soc.*, 1965, **87**, 4359.

[3] W. T. Reichle, *Inorg. Chem.*, 1964, **3**, 402.

[4] G. P. Balabanov, Yu. I. Dergunov, and V. A. Gal'perin, *J. Org. Chem.* (*USSR*), 1966, **2**, 1797.

[5] By analogy with the thermolysis of aliphatic sulphonyl azides in hydrocarbon solvents: D. S. Breslow, M. F. Sloan, N. R. Newburg, and W. B. Renfrow, *J. Amer. Chem. Soc.*, 1969, **91**, 2273.

[6] D. S. Breslow, personal communication. On the other hand, toluene-*p*-sulphonyl azide undergoes clean first-order thermolysis and little or no SO_2 is evolved.

[7] R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Amer. Chem. Soc.*, 1969, **91**, 1219.

[8] All new compounds were characterized by microanalysis, i.r., n.m.r., and mass spectral analysis. Authentic samples of known compounds were prepared for comparison.