

Reactions of Dimethyl Sulphoxide with Sulphur Electrophiles

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In a recent Paper¹ the reaction between dimethyl sulphoxide and an aromatic sulphonyl chloride to give chloromethyl methyl sulphide and the corresponding sulphonic acid is described. We now report our preliminary findings concerning the reactions of dimethyl sulphoxide with sulphenyl, sulphinyl, and sulphonyl chlorides.

Refluxing equimolar amounts of trichloromethanesulphenyl chloride and dimethyl sulphoxide in acetonitrile leads to the evolution of HCl and the formation of trichloromethyl methyl disulphide in 60% yield. The corresponding reaction between trichloromethanesulphenyl chloride and dibenzyl sulphoxide requires heating to 130° in the absence of solvent and affords trichloromethyl benzyl disulphide in 51% yield.

When equimolar amounts of 2,2,2-trichloroethanesulphinyl chloride and dimethyl sulphoxide are mixed, an exothermal reaction ensues with evolution of HCl. Distillation affords a fraction boiling at 80°/2 mm. The product solidifies and after recrystallisation from petroleum, 37% of 2,2,2-trichloroethanesulphonyl chloride, m.p.

42.5—44°, is obtained. Similarly, trichloromethanesulphinyl chloride is oxidised by dimethyl sulphoxide to trichloromethanesulphonyl chloride. On the other hand, benzenesulphinic acid anilide is recovered unchanged after several hours at 80—90° in excess of dimethyl sulphoxide.

The mixing of equimolar amounts of methanesulphonyl chloride and dimethyl sulphoxide gives also rise to an exothermal reaction with HCl evolution. After the spontaneous reaction has subsided, the mixture is kept at 100° for several hours. Distillation affords methanesulphonic acid in 55% yield. This reaction may have some preparative value for the conversion of aliphatic sulphonyl chlorides into their corresponding anhydrous acids.

No attempt was made to characterise the more volatile products. Extension of this work, especially with sulphoxides other than dimethyl sulphoxide, is in progress.

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¹ R. E. Boyle, *J. Org. Chem.*, 1966, **31**, 3880.