

Reactions of Trichloromethanesulphenyl Chloride: Formation of Trichloromethylsulphenylsulphonyldichloromethane

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Summary Trichloromethylsulphenylsulphonyldichloromethane (II)¹ is formed by the reaction of dilute aqueous sodium hydroxide solution on trichloromethanesulphenyl chloride (I).

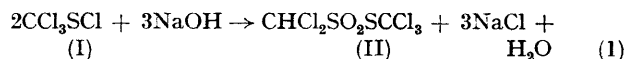
THE hydrolysis of trichloromethanesulphenyl chloride at elevated temperature in aqueous or acidic media gives hydrochloric acid, sulphur, and carbon dioxide.^{2,3} Šilhánek and Zbirovský⁴ have reported the isolation of dichloromethylene sulphoxide as an intermediate in the aqueous hydrolysis of trichloromethanesulphenyl chloride. The alkaline hydrolysis of trichloromethanesulphenyl chloride² also leads to the production of inorganic compounds (S, CO₂, Cl⁻). We found that the reaction of trichloromethanesulphenyl chloride with sodium hydroxide gave a crystalline substance trichloromethylsulphenylsulphonyldichloromethane (II). This is the first reported preparation of this compound although other compounds in the series RSO₂S·CCl₃ are known.³

Compound (II) was formed by addition of aqueous 0.5N-sodium hydroxide to well stirred trichloromethanesulphenyl chloride at 18–20 °C and at pH 6–7. After ca. 3 h a crystalline substance is formed (82%) m.p. 76 °C (from hexane). T.l.c. (Kieselgel G⁵) with hexane or hexane-methylene chloride (1:1) as eluant gave a single spot [*R_F* 0.15 (hexane); 0.75 (solvent mixture)].

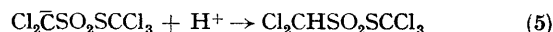
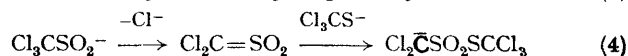
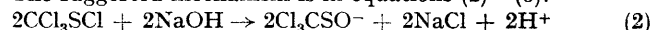
Determination of the structure was based mainly on microanalysis, n.m.r., i.r., and mass spectra. The presence

of an ion at *m/e* 147 (CHCl₂SO₂)⁺ and the absence at *m/e* 181 (CCl₃SO₂)⁺ indicate that the formula is CHCl₂SO₂SCCl₃ and not CCl₃SO₂SCHCl₂. The i.r. spectrum of compound (II) was similar to that of trifluoromethylsulphenylsulphonyl-trifluoromethane.⁶ The n.m.r. spectrum showed a single resonance at τ 3.41. The appearance of a low field resonance is expected from the deshielding effects of adjacent sulphonyl and chloro-groups.

The material, therefore, has the formula CHCl₂SO₂SCCl₃ and the reaction may be described by the equation (1).



The suggested mechanism is in equations (2)–(5).



The first two steps [equations (2) and (3)] are analogous to the mechanism suggested by Haszeldine and Kidd in the hydrolysis of F₃CSCl.⁶

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¹ The nomenclature used was proposed by W. E. Savige and J. A. Maclaren, 'The Chemistry of Organic Sulfur Compounds,' Pergamon Press, Oxford, 1966, vol. 2, p. 395.

² E. Rathke, *Annalen*, 1873, **167**, 201.

³ G. Sosnovsky, *Chem. Rev.*, 1958, **58**, 512.

⁴ J. Šilhánek and M. Zbirovský, *Chem. Comm.*, 1969, 878.

⁵ G. Zweig, 'Analytical Methods for Pesticides Plant Growth Regulations and Food Additives', Academic Press, New York, 1967, vol. V, p. 303.

⁶ R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 1955, 2901.