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 Zbirovský[4] have reported the isolation of dichloromethylene sulphoxide as an intermediate in the aqueous hydrolysis of trichloromethanesulphenyl chloride The alkaline hydrolysis of trichloromethanesulphenyl chloride[2] also leads to the production of inorganic compounds (S, CO_2, 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 $RSO_2{\cdot}S{\cdot}CCl_3$ 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 G[5]) 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 $(CHCl_2SO_2)^+$ and the absence at *m/e* 181 $(CCl_3SO_2)^+$ indicate that the formula is $CHCl_2SO_2SCCl_3$ and not $CCl_3SO_2SCHCl_2$. The i.r. spectrum of compound (II) was similar to that of trifluoromethylsulphenylsulphonyltrifluoromethane.[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 $CHCl_2SO_2SCCl_3$ and the reaction may be described by the equation (1).

$$\underset{\text{(I)}}{2CCl_3SCl} + 3NaOH \rightarrow \underset{\text{(II)}}{CHCl_2SO_2SCCl_3} + 3NaCl + H_2O \qquad (1)$$

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

$$2CCl_3SCl + 2NaOH \rightarrow 2Cl_3CSO^- + 2NaCl + 2H^+ \qquad (2)$$

$$2Cl_3CSO^- \rightarrow Cl_3CSO_2^- + Cl_3CS^- \qquad (3)$$

$$Cl_3CSO_2^- \xrightarrow{-Cl^-} Cl_2C{=}SO_2 \xrightarrow{Cl_3CS^-} Cl_2\bar{C}SO_2SCCl_3 \qquad (4)$$

$$Cl_2\bar{C}SO_2SCCl_3 + H^+ \rightarrow Cl_2CHSO_2SCCl_3 \qquad (5)$$

The first two steps [equations (2) and (3)] are analogous to the mechanism suggested by Haszeldine and Kidd in the hydrolysis of F_3CSCl.[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.

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