

Decomposition of Methanesulphenyl Chloride in the Presence of Amines

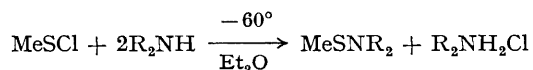
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Summary Methanesulphenyl chloride reacts in the presence of secondary amines by heterolytic cleavage of the sulphur-chlorine bond yielding sulphenamides, and by an elimination of hydrogen chloride giving thioformaldehyde, and thence further products.

THE reactions of arenesulphenyl chlorides indicate routes involving both heterolysis¹ and homolysis² of the sulphur-chlorine bond. This work indicates that alkanesulphenyl chlorides react in two distinct ways with secondary amines.

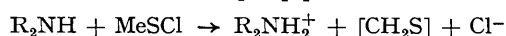
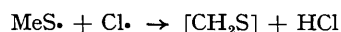
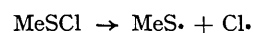
Four major volatile components are formed from the reaction of methanesulphenyl chloride³ with an excess of dialkylamine at -60° . Only one, the sulphenamide (30–40%), results from direct heterolysis of the sulphur-chlorine bond.



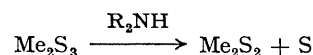
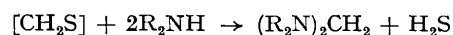
(R = Me, Et, and Prⁿ).

The others, bis(dialkylamino)methane $(\text{R}_2\text{N})_2\text{CH}_2$ (15–20%), dimethyl disulphide (20–25%), and dimethyl trisulphide (15–20%) result through a reaction sequence involving an intermediate $[\text{CH}_2\text{S}]$.

This intermediate may result by two elimination pathways. One involves the homolytic cleavage of the S-Cl bond followed by H abstraction from the methylthio-radical so generated. The other pathway considered is the base-catalysed 1,2 elimination of hydrogen chloride.



The *gem*-diamine and polysulphides result from the sequence formulated below. Support for the first step is found in the standard procedure for synthesising *gem*-diamines using formaldehyde and secondary amines.⁴



The condensation of methanesulphenyl chloride and hydrogen sulphide, in a manner similar to the synthesis of trisulphides from sulphur dichloride and a thiol,⁵ would give thermally unstable methyl hydrodisulphide.⁶ This dissociates into hydrogen sulphide and dimethyl trisulphide, originally characterised from the reaction of ammonia with methanesulphenyl chloride.⁷ Like other alkyl and aryl trisulphides, dimethyl trisulphide is desulphurised into the disulphide in the presence of dimethylamine.⁸

Further support for this thioaldehyde intermediate comes from the isolation of diethyl disulphide and trisulphide using ethanesulphenyl chloride and dimethylamine.

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