The temperature of the equilibration was 84.5°. The gas chromatographic analyses of the equilibration products are averages of several determinations.

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Preparation of Trichloromethanesulfonyl Chloride[1]

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Recently, it has been shown[2] that trichloromethanesulfonyl chloride is a very useful chlorinating agent. For instance, toluene was converted to benzyl chloride in high yield, *p*-bromotoluene was converted to *p*-bromobenzyl chloride without halogen interchange, and cyclohexane was chlorinated to cyclohexyl chloride. Chlorine and sulfuryl chloride react with *n*-alkanes and alkylbenzenes under free radical conditions to give a mixture of isomers, but trichloromethanesulfonyl chloride shows great selectivity. Thus, with *n*-hexane and ethylbenzene it gave only 2-chlorohexane and α-chloroethylbenzene, respectively. This work has prompted us to publish the present communication dealing with the preparation of trichloromethanesulfonyl chloride.

Trichloromethanesulfonyl chloride can be prepared by the action of moist chlorine on carbon disulfide[3,4] or by oxidation of trichloromethanesulfenyl chloride with nitric acid,[5,6] calcium hypochlorite,[7] or hydrogen peroxide.[8,9] The best yields and product quality are obtained by the peroxide oxidation, which was therefore investigated in more detail.

Peracetic acid was brought into contact with trichloromethanesulfenyl chloride at varying temperatures. The sulfenyl chloride was not attacked by 40% peracetic acid in acetic acid at 25–35°. It was oxidized smoothly to the sulfonyl chloride in *ca.* 40% yield when the peracetic acid was added slowly at 100°.

A 30% solution of hydrogen peroxide oxidized the sulfenyl chloride to the sulfonyl chloride in yields up to 78%. The sulfenyl chloride was dissolved in acetic acid and maintained at reflux during the peroxide addition.

Urea–hydrogen peroxide addition compound can also be used advantageously for this oxidation. A solution of the sulfenyl chloride in glacial acetic acid was heated to 110°, and solid urea–hydrogen peroxide was added at a rate to keep the reaction mixture boiling. Trichloromethanesulfonyl chloride was obtained in 50% yield. It is important that this reaction be carried out as rapidly as possible at 110°, as prolonged reaction (e.g., 10 hr.) lowers the yield appreciably.

During the course of these experiments no explosions occurred. Therefore, the reactions are regarded as safe under the described conditions.

EXPERIMENTAL

With 30% aqueous hydrogen peroxide. A solution of trichloromethanesulfenyl chloride (18.6 g., 0.1 mole) in glacial acetic acid (50 ml.) was brought to boiling, and 30% aqueous hydrogen peroxide solution was added slowly, with the reaction mixture being maintained at reflux. The addition of hydrogen peroxide (50 ml.) was stopped when a white sublimate appeared in the reflux condenser. The reaction mixture was diluted with water, and the snow-white product (17 g., 78%) was collected, dried, and recrystallized from alcohol, m.p. 140–141°.

With a 40% solution of peracetic acid in glacial acetic acid. A solution of trichloromethanesulfenyl chloride (5.16 g., 0.028 mole) in glacial acetic acid (5 ml.) was heated to 100°. A 40% solution (18 ml.) of peracetic acid in acetic acid was added drop by drop over a period of 8 hr. to the sulfenyl chloride solution. At this point the reaction mixture became nearly colorless, and it was cooled and diluted with water. The white precipitate collected (2.4 g., 40%) was identical with that prepared by the previous method.

With urea–hydrogen peroxide addition compound. To a solution of trichloromethanesulfenyl chloride (1.74 g., 0.0093 mole) in acetic acid (4 ml.) at 110° was slowly added powdered urea–hydrogen peroxide compound (2 g.). The rate of addition was adjusted to maintain the reaction mixture at boiling. The reaction mixture was diluted with water and the product (1 g., 50%) collected by filtration.

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