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Catalytic Removal of Hydrogen Chloride from Some Substituted α-Trichloroethanes[1]

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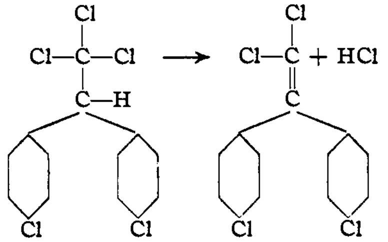
It has long been known that hydrogen chloride is eliminated from 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT) by alcoholic caustics.[2] We have now found that hydrogen chloride may be removed from this compound and several analogs by the use of various catalysts in accordance with the equation



For this purpose anhydrous ferric oxide, iron, and in particular anhydrous ferric and aluminum chlorides were found to be catalysts. As little as 0.01% of anhydrous ferric chloride will catalyze this reaction. Other materials, such as fuller's earth and some mineral products, showed catalytic activity, which was probably due to the presence of small amounts of iron compounds. Of the group, aluminum chloride was the most active. Its use is limited, however, because the evolution of hydrogen chloride is accompanied by charring.

On this basis the following procedure was developed. To a carefully dried 6-inch Pyrex U-tube containing 2 mg. of anhydrous ferric chloride and immersed to a depth of 3 inches in an oil-bath held at 110–120°, 2 g. of the trichloroethane derivative was added. A slow stream of dry air was drawn through the U-tube and then through a gas-washing bottle with a fused-in disk of fritted glass, containing 75 ml. of water. Hydrogen chloride was at once evolved and the reaction usually was complete in fifteen minutes. The aqueous solution was then titrated and found to contain within about 1% the amount of hydrogen chloride calculated for complete elimination. The cooled reaction product was extracted with ether, the extract washed with water, the ether removed and the residue crystallized from alcohol and dried in vacuum at room temperature. The results obtained with the individual derivatives were as follows:

2,2-Bis-(*p*-chlorophenyl)-1,1-dichloroethylene.—This melted at 88–89° and showed no depression of the melting point when mixed with the product prepared from the same trichloroethane derivative by the method of Zeidler.[1] Both samples gave a yellow colored solution in tetranitromethane.

2-*p*-Chlorophenyl-2-phenyl-1-1,1-dichloroethylene.—This melted at 110–111°.

Anal. Calcd. for $C_{14}H_9Cl_3$: C, 59.29; H, 3.20. Found: C, 59.16, 59.41; H, 3.53, 3.44.

When the reaction was carried out without a catalyst by refluxing 1 g. of the trichloroethane derivative in 100 ml. of 0.1 *N* alcoholic potash for one-half hour, the product had the same melting point and showed no lowering of the melting point when mixed with some of the product prepared by the above catalytic method.

2,2-Diphenyl-1,1-dichloroethylene.—This was prepared as above except that the heating lasted an hour. It melted at 80–81°, which was not lowered on mixing with a sample of this substance prepared according to Baeyer.[1]

2,2-Ditolyl-1,1,1-trichloroethane was similarly treated. After heating for one-half hour 94% of the hydrogen chloride was evolved. Further heating evolved additional hydrogen chloride. In neither case could a clearly defined product be isolated.

This reaction was found to proceed at an even lower temperature when a solution in chlorobenzene, naphthalene, nitrobenzene, or 1-chloronaphthalene was used. On the other hand, solvents such as stearic acid, *n*-octadecyl alcohol, and petroleum fractions (b. p. over 100°) inhibited the reaction.

That the elimination of hydrogen chloride may be accomplished catalytically is of especial interest because of the insecticidal properties of the α-trichloro-β-disubstituted ethanes and the possibility that catalytic decomposition by naturally occurring catalysts may be involved in their toxic action. This is indicated by the marked decrease in toxicity of the α-dichloro-β-disubstituted ethylenes.

Summary

Anhydrous ferric and aluminum chlorides, iron, iron oxides and certain mineral materials have been found to act catalytically to eliminate hydrogen chloride from certain α-trichloro-β-disubstituted ethanes to form the corresponding α-dichloro-β-disubstituted ethylenes.

This catalytic action may be inhibited by some solvents and promoted by others.

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(1) Not copyrighted.

(2) Baeyer, *Ber.*, **6**, 223 (1873); Zeidler, *ibid.*, **7**, 1181 (1874); Brand and Busse-Sundermann, *ibid.*, **75**, 1819 (1942).