ACTION OF CHLORINE ON UNSATURATED POLYCHLORO COMPOUNDS
IN AN ACID MEDIUM

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As we have shown previously [1], compounds of structure

\[ \text{CCl}_2 \equiv \text{CH} - \text{CH}_X \]

in which \( X = \text{OCH}_3, \text{N(C}_2\text{H}_5), \text{NO}_2, \) etc., combine smoothly with chlorine when the substituent \( X \) is an electron acceptor, whereas in cases in which this substituent is an electron donor, not only addition occurs, but also replacement of hydrogen by chlorine.

It was considered that replacement of allyl hydrogen occurred, but it has now been found that treatment of 1,1-dichloro-3-methoxypropene with chlorine gives mainly a product in which the methoxy group is chlorinated:

\[ \text{CCl}_2 \equiv \text{CHCH}_2\text{OCH} \rightarrow \text{CCl}_2 \text{CHClCH}_2\text{OCHCl}. \]

The structure of this product was proved by its conversion into 2,3,3,3-tetrachloro-1-propanol by the action of methanol in presence of hydrochloric acid. We also synthesized 1,1,1,2-tetrachloro-3-(chloromethoxy)propane by the chloromethylation of 2,3,3,3-tetrachloro-1-propanol. When compounds of the above structure containing an electron-donating substituent \( (\text{OCH}_3, \text{N(C}_2\text{H}_5}) \) are treated with chlorine in presence of hydrogen chloride, the substitution reaction predominates [1].

It was further shown [2] that compounds containing the \( \text{CCl}_2 \equiv \text{CH} \) group react with chlorine in a \( \text{H}_2\text{SO}_4 \) medium by "conjugated addition" with formation of \( \alpha \)-chloro carboxylic acids in accordance with the scheme:

\[ \text{RCH} = \text{CCl}_2 + \text{Cl}_2 \rightarrow [\text{RCHCl} - \text{CCl}_2\text{OSO}_2\text{H}] \rightarrow \text{RCHClO}_2. \]

In this way good yields were obtained of \( \alpha \)-chloro carboxylic, \( \alpha,\omega \)-dichloro carboxylic, and \( \alpha \)-chloro dicarboxylic acids from compounds of the type \( \text{CH}_2(\text{CH}_3)_n \text{CH} = \text{CCl}_2, \text{Cl}(\text{CH}_3)_n \text{CH} = \text{CCl}_2 \) and \( \text{HOOC(CH}_3)_n \text{CH} = \text{CCl}_2 \), respectively.

In the present investigation we have shown that the suppression of substitution on saturated carbon atoms of compounds of structure \( \text{CCl}_2 = \text{CH}(\text{CH}_2)_n \) \( X \) in chlorine treatments in presence of hydrogen chloride is of great general significance. For example, when 1,1,5-trichloro-1-pentene, 6,6-dichloro-5-hexenenitrile, and 8,8-dichloro-7-octenoic acid were treated with chlorine in chloroform at 0-15\(^\circ\), reaction went with brisk evolution of hydrogen chloride and formation of a mixture of chlorination products. In presence of hydrogen chloride these unsaturated compounds smoothly combined with chlorine at the double bond with formation in good yield of 1,1,1,2,5-pentachloropentane, 6,6,6-tetrachlorohexanoic acid, and 7,8,8,8-tetrachloroocatenoic acid, respectively.

In order to determine the relationship between the strength of an acid and the effect of the acid on the reaction between chlorine and compounds containing the \( \text{CCl}_2 = \text{CH} \) group, a study was made of the reaction of 1,1,5-trichloro-1-pentene and chlorine in media of glacial acetic acid, 90% phosphoric acid, concentrated sulfuric acid, and 70% perchloric acid at 0-15\(^\circ\) without irradiation. It was found that conjugated addition of
chlorine with formation (after treatment with water) of 2,5-dichlorovaleric acid occurred only in media of sulfuric (concentrated) and perchloric acids. In 70% sulfuric acid, as in presence of hydrogen chloride, addition of chlorine at the double bond occurred without appreciable substitution at saturated carbon atoms. In this respect there is a definite difference in behavior between dichlorovinyl compounds and olefins in these reactions. As is well known, olefins react with chlorine by "conjugated addition" not only in media of strong mineral acids, but also in other media (see, for example, [3,4]).

The preparation of α-chloro carboxylic acids by the action of chlorine on dichlorovinyl compounds in concentrated sulfuric acid is carried out under mild conditions, so that it is possible to prepare α-chloro carboxylic acids containing various substituents. In particular, in this paper we describe the action of chlorine on 1,1,5,5,5-pentachloro-1-pentene in concentrated sulfuric acid, in which a trichloromethyl group is preserved and 2,5,5,5-tetrachlorovaleric acid is obtained.

There are as yet no experimental data on the orienting effect of the trichloromethyl group on electrophilic addition at the double bond of a compound containing the grouping $\text{CCl}_3\text{C}=$. Attempts to investigate the reaction between hydrogen bromide and 3,3,3-trichloropropene with this object were not successful, since reaction occurred only in presence of aluminum chloride, which isomerized the original compound into 1,1,3-trichloropropene [5] (compare [13]), or in presence of benzylo peroxide, in which case reaction occurred with isomerization into an intermediate radical [6]. It was therefore of interest to study the electrophilic conjugated addition of chlorine to 3,3,3-trichloropropene.

According to Titov and Maklyaev [3], addition of chlorine to propene in a medium of acetic, formic, or benzenesulfonic acid results in the formation of a compound of the formula:

$$\text{CH}_3 - \text{CH} = \text{CH}_2\text{Cl}, \text{ in which } X = \text{CH}_3\text{CO}^-, \text{HCO}^-, \text{C}_6\text{H}_5\text{SO}_2^-, \text{OX}$$

so that the reaction is subject to the usual rules of electrophilic addition. When chlorine reacted with 3,3,3-trichloropropene in concentrated sulfuric acid or glacial acetic acid, in addition to 1,1,1,2,3-pentachloropropane, 2,3,3,3-tetrachloro-1-propanol was obtained in form of its sulfate or acetate, respectively. Hydrolysis of these esters gave 2,3,3,3-tetrachloro-1-propanol, which was found to be identical with the substance obtained as follows:

$$\text{CCl}_3\text{CH} = \text{CH}_2 + \text{CH}_3\text{COONa} \xrightarrow{\text{CH}_3\text{COOH}} \text{CCl}_2 = \text{CH} - \text{CH}_2\text{OCOCH}_3 \xrightarrow{\text{CH}_3\text{OH}} \text{HCl}$$

$$\rightarrow \text{CCl}_3 = \text{CH} - \text{CH}_2\text{OH} \xrightarrow{\text{CCl}_2\text{CHClCH}_2\text{OH}, \text{HCl}}$$

It was thus shown that the trichloromethyl group in 3,3,3-trichloropropene has an orienting effect in the direction opposite to that of the methyl group in propene. This result confirms the view of the electron-accepting character of the trichloromethyl group formed by two of the authors of this paper and Zakharkin [7] on the basis of a study of the dissociation constants of a series of acids of structure: $\text{CCl}_3(\text{CH}_2)_n\text{COOH}$.

**EXPERIMENTAL**

**Action of Chlorine on 1,1,5-Trichloro-1-pentene in Hydrochloric Acid.** Chlorine and hydrogen chloride were passed through a solution of 26 g of 1,1,5-trichloro-1-pentene in 15 ml of ether and 15 ml of saturated aqueous hydrogen chloride until no further reaction occurred. The mixture was diluted with water, and the organic layer was separated, washed with water, and dried over calcium chloride. Distillation gave 29 g (81%) of 1,1,1,2,5-pentachloropentane, b.p. 92-93° (2.5 mm); $\eta^0_D$ 1.5104; $d^0_4$ 1.4815; found MR 49.37; calculated MR 49.62.

For 1,1,1,2,5-pentachloropentane the literature [8] gives b.p. 121-122° (12 mm); $\eta^0_D$ 1.5135; $d^0_4$ 1.4807. The structure of 1,1,1,2,5-pentachloropentane was proved by its hydrolysis with nitric acid to 2,5-dichlo-