
A Study of the Reactions Leading to the Synthesis of 3, 3, 3-Trifluoropropene

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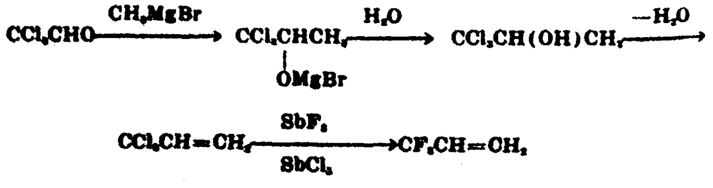
Compounds containing two or more fluorine atoms on a single carbon atom are known for their inertness. It was thought that a polymer of 3, 3, 3-trifluoropropene would have desirable properties such as non-inflammability and inertness. A liquid polymer of this compound would have a relatively low melting point and a wide liquid range, properties which would be desirable in a coolant for motors. The purpose of this investigation was to determine the feasibility of preparing 3, 3, 3-trifluoropropene by substitution methods involving agents other than elemental fluorine or anhydrous hydrogen fluoride, both of which are hazardous to use and require special equipment.

Two series of reactions were attempted for the preparation of 3, 3, 3-trifluoropropene:

METHOD A.



$$CCl_3CHO \xrightarrow{CH_3MgBr} \underset{OMgBr}{CCl_3CHCH_3} \xrightarrow{H_2O} CCl_3CH(OH)CH_3 \xrightarrow{-H_2O}$$

$$CCl_3CH{=}CH_2 \xrightarrow[SbCl_5]{SbF_3} CF_3CH{=}CH_2$$

Kharasch and co-workers (3) studied the reaction of methylmagnesium bromide and chloral and reported that the use of catalysts such as manganous chloride or metallic manganese increased the yield of the alcohol. The same workers (4) obtained an 84% yield of 3, 3, 3-trichloropropene by treating 1, 1, 1-trichloro-2-propanol with 10% excess of phosphorus pentoxide. Because our yields of the desired products in these reactions were very low, the following method was attempted.

METHOD B.

$$\mathrm{CH_2{=}CH_2} \xrightarrow{\mathrm{CBrCl_3}} \mathrm{CCl_3CH_2CH_2Br} \xrightarrow[\mathrm{KOH}]{\mathrm{alcoholic}}$$

$$\mathrm{CCl_3CH{=}CH_2} \xrightarrow[\mathrm{SbCl_5}]{\mathrm{SbF_3}} \mathrm{CF_3CH{=}CH_2}$$

Kharasch and his students (2) investigated the addition of bromotrichloromethane to carbon-carbon double bonds using benzoyl peroxide and acetyl peroxide as a catalyst. Henne (1) attempted to prepare 3, 3, 3-trifluoropropene from the chloro analog by heating with antimony trifluoride, but recovered the reagents unchanged. It was hoped that this exchange could be effected with a "fluorine carrier" such as a pentavalent antimony salt.

EXPERIMENTAL

METHOD A. Chloral hydrate was dehydrated to chloral with concentrated sulfuric acid by the method of Vanino (7). A yield of 92.3% of the theoretical was obtained.

The chloral was treated in anhydrous ether with methylmagnesium bromide in the presence of manganous chloride, followed by hydrolysis of the complex, according to the method of Kharasch (3). It was not possible to reproduce the yields of 1, 1, 1-trichloro-2-propanol claimed by Kharasch although five attempts were made. The average yield of this alcohol obtained by us was 11% of the theoretical.

The dehydration of 1, 1, 1-trichloro-2-propanol was attempted by several methods. Heating this alcohol with phosphorus pentoxide gave a negligible amount of 3, 3, 3-trichloropropene instead of the 84% yield claimed by Kharasch (4). According to Senderens (6) lower alcohols are dehydrated by passing them over fused sodium hydrogen sulfate. This method gave none of the desired olefin. In following the method of LeBel and Green (5) a portion of the alcohol was dropped on strongly heated zinc chloride. The alcohol distilled unchanged. Finally, vapors of the alcohol were passed over heated alumina in the well-known method of dehydrating alcohols, but none of the olefin was obtained. Failure to obtain the desired dehydration of 1, 1,1-trichoro-2-propanol forced us to abandon this line of attack.

METHOD B. Bromotrichloromethane was added to ethylene in the presence of benzoyl peroxide in a Parr low-pressure hydrogenation apparatus according to the method of Kharasch (2). Average yields of 1, 1, 1-trichloro-3-bromopropane were 42% of the theoretical.

Various methods of dehydrobromination of 1, 1, 1-trichloro-3-bromopropane were attempted. Triethylamine and N, N-diethylaniline did not remove hydrogen bromide. Alcoholic potassium hydroxide gave small amounts of 3, 3, 3-trichloropropene. Since these amounts were small, no attempt was made to fluorinate the olefin.

DISCUSSION

The results of this investigation indicate that the synthesis of 3, 3, 3-trichloropropene by the dehydration of 1, 1, 1-trichloro-2-propanol is unsatisfactory. Considerate quantities of tar were formed in the Grignard reaction of chloral and methylmagnesium bromide. The 1, 1, 1-trichloro-2-propanol obtained was unstable, becoming dark on standing, even when protected from light. Whenever the alcohol was distilled, even at reduced pressure, a tar-like residue remained. Various attempts to dehydrate the alcohol failed. With phosphorus pentoxide much decomposition occurred, and a heavy black tar-like residue was obtained. Phosphorus pentoxide has been reported as a catalyst for the polymerization of olefins, so that extensive polymerization may have occurred in the attempts to prepare the olefin.

The reaction of bromotrichloromethane and ethylene with benzoyl peroxide as the catalyst was difficult to initiate and required repeated additions of the catalyst. It is believed that this reaction would have proceeded faster if a higher pressure had been used. This seems to be a satisfactory method of introducing the trichloromethyl group into an olefin.

The reaction of 1, 1, 1-trichloro-3-bromopropane gave only traces of 3, 3, 3-trichloropropene because of the formation of other compounds such as 1, 1-dichloroallene. It did not appear possible to remove hydrogen bromide selectively from the 1, 1, 1-trichloro-3-bromopropane.

Although two series of reactions leading to the production of 3, 3, 3-trifluoropropene have been investigated, no new method for the production of this compound has been found.

LITERATURE CITED

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