

A STUDY OF REACTIONS  
LEADING TO THE SYNTHESIS  
OF  
3,3,3-TRIFLUOROPROPENE

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OF  
3,3,3-TRICHLOROPROPENE

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TABLE OF CONTENTS

Introduction	1
Historical	3
Experimental	6
Discussion	19
Bibliography	21
Biography	23

## INTRODUCTION

In recent years, much work has been done on the synthesis of fluoro-hydrocarbons, special emphasis being given to this work in the development of the atomic bomb.

While monofluoro compounds are rather unstable, it is known that polyfluoro groups exhibit unusual stability, and the effect of this stability may be extended to other portions of a molecule. It was thought that a liquid polymer of 3,3,3-trifluoropropene would exhibit properties making it desirable for use under conditions requiring a stable, non-inflammable liquid with a relatively low freezing point. Such a material might be used in place of ethylene glycol as an antifreeze, in situations where fire presents an unusual hazard.

The object of this investigation was to determine the feasibility of preparing 3,3,3-trifluoropropene by substitution methods involving agents other than elemental fluorine or hydrogen fluoride gas, both of which are hazardous to use and require special equipment. As far as could be ascertained from the literature, no attempt has been made to prepare a liquid polymer from 3,3,3-trifluoropropene.

The proposed steps for the preparation of the desired polymer were:

- (a) Dehydration of chloral hydrate to chloral.
- (b) Addition of methylmagnesium bromide to chloral to form 1,1,1-trichloro-2-propanol.
- (c) Dehydration of the alcohol to give 3,3,3-trichloropropene.
- (d) Fluorination of the chloro analog to 3,3,3-trifluoropropene using an inorganic fluorine compound, such as antimony pentafluoride.

- (e) Polymerization of the fluoro compound using benzoyl peroxide as a catalyst.
- (f) Mild hydrogenation to saturate the remaining double bonds in order to stabilize the polymer.

A proposed alternate method to prepare the 3,3,3-trichloropropene was:

- (a) Reaction of bromotrichloromethane and ethylene in the presence of benzoyl peroxide to give 1,1,1-trichloro-3-bromopropane.
- (b) Dehydrohalogenation of the bromochloro compound to give 3,3,3-trichloropropene.

## HISTORICAL

3,3,3-Trifluoropropene has been synthesized and reported in the literature (7, 15), but only as incidental steps in the preparation of other fluorohydrocarbons. This synthesis involved the use of hydrogen fluoride in special pressure equipment. A homolog of this compound, 2-methyl-3,3,3-trifluoropropene, has been synthesized and polymerized to give a solid material (5).

Chloral hydrate has been dehydrated by shaking with concentrated sulfuric acid and distilling (14, 21, 22). 1,1,1-Trichloro-2-propanol (isopral, trichloroisopropyl alcohol) has been prepared from chloral using a Grignard reaction (9). Kharasch and co-workers (11) reported that the use of catalysts, such as manganous chloride or metallic manganese, in the reaction of the Grignard reagent with the chloral, increased the yield of the alcohol. However, considerable quantities of tar were obtained.

Vitoria (23) reported that 3,3,3-trichloropropene is obtained by treating the alcohol with phosphorus pentoxide. Kharasch and co-workers (12) reported an 84% yield of 3,3,3-trichloropropene along with some 1,1-dichloroallene by treating 1,1,1-trichloro-2-propanol with 10% excess phosphorus pentoxide and distilling. The allene was removed from the propene by careful fractionation at reduced pressure, using a Podbielniak column.

Kharasch and co-workers (10) have performed addition reactions of carbon tetrabromide and bromotrichloromethane to carbon-carbon double bonds, using either benzoyl peroxide or acetyl peroxide as a catalyst. With the bromotrichloromethane, they found, in all cases in which the structure of the product was determined, that the bromine added to one



carbon of the double bond and the trichloromethyl group to the other carbon. The structure of the addition product of ethylene and bromotrichloromethane was not determined, but it was assumed to be 1,1,1-trichloro-2-bromopropane "in view of the highly improbable validity of any other formulation". In order to form this compound, both the bromine and trichloromethyl radical must add to the same carbon, with, presumably, the migration of a hydrogen atom to the other carbon of the double bond. Such a mechanism seems unlikely in view of the manner of addition in the other examples given. A more reasonable product would seem to be 1,1,1-trichloro-3-bromopropane, and this compound is shown in the equations given in the article. However, they report the observed physical constants for the product formed to be: refractive index at 20°, 1.5127; and boiling point at 104 mm., 113.5-114°. In an earlier paper, Kharasch and co-workers (12) report the preparation of 1,1,1-trichloro-3-bromopropane by adding hydrogen bromide to 3,3,3-trichloropropene and the observed physical constants of the product, which are: refractive index at 20°, 1.5345; boiling point at 103 mm.; 115-16°; and boiling point at 751 mm., 184-86°.

The physical constants given for 1,1,1-trichloro-2-bromopropane (12) are: refractive index at 20°, 1.5060; and boiling point at 751 mm., 171-172°. These do not match those of the product of the ethylene-bromotrichloromethane addition.

Henne and co-workers (8) attempted to prepare 3,3,3-trifluoropropene from the chloro analog by heating with antimony trifluoride, but no exchange of halogen occurred and the reagents were recovered unchanged. No pentavalent antimony salt was used as a "fluorine carrier". Kharasch and co-workers (12) found that hydrogen halides add to the double bond

in 3,3,3-trichloropropene only slowly and under drastic conditions; they concluded that the latter is inactive toward addition.

McBee and co-workers (18) report that pentavalent antimony salts, such as antimony trifluorodichloride, are more active fluorinating agents than is antimony trifluoride, although the pentavalent salts cause considerable decomposition. Gilman (4) states that organic polyhalides with several halogen atoms located on the same carbon atom are best treated with antimony trifluoride, pentavalent antimony fluorochlorides, or similar inorganic fluorides. Antimony trifluoride seldom is efficient by itself, but a small amount of pentavalent salt, acting as a "fluorine carrier", hastens the halogen exchange. Antimony (V) fluorochloride is used for difficult substitutions. Benner (2) and McBee (16) report the successful use of fluorides such as mercurous fluoride, silver difluoride, cobalt trifluoride, and manganese trifluoride in halogen-exchange reactions.

Henne and Ruh (6) and Belmore (1) have successfully polymerized fluoro-olefinic compounds using benzoyl peroxide as a catalyst.

## EXPERIMENTAL

I. The method for preparing 3,3,3-trichloropropene as given by Kharasch (12) was selected. This procedure involved three steps: (a) dehydration of chloral, (b) addition of methylmagnesium bromide to chloral to form tri-chloroisopropyl alcohol, and (c) dehydration of the alcohol to 3,3,3-trichloropropene.

A. Dehydration of chloral hydrate.

The method of Vanino (22) was used to dehydrate chloral hydrate. Three hundred twenty-five grams of chloral hydrate was shaken in a separatory funnel with 250 ml. of concentrated sulfuric acid. The temperature of the mixture decreased during the dehydration. When solid chloral hydrate was no longer visible, the two layers were separated. The chloral was placed in a flask containing a small amount of calcium carbonate and distilled, care being taken to keep the equipment free of moisture, since chloral takes up water quite readily. A yield of 92.3% of the theoretical was obtained.

B. Preparation of 1,1,1-trichloro-2-propanol.

The method given by Kharasch (11) was used to prepare the chloro alcohol. The procedure consisted of the addition of methylmagnesium bromide to chloral in the presence of a manganous chloride catalyst, and then hydrolysis of the complex.

First run: The equipment consisted of a one-liter, three-neck distilling flask, provided with a stirring motor, a Friedrichs condenser, and a capillary tube for admitting methyl bromide gas.

Ground-glass joints were used throughout for connections.

A 200-ml. portion of dry ether and 47.7 g. of magnesium turnings

were placed in the flask, and methyl bromide admitted as a gas through the capillary tube. This was found to be unsatisfactory since the capillary tube became plugged after a short time, so 190 g. of methyl bromide was dissolved in 275 ml. of dry ether and added dropwise through a separatory funnel. This procedure was not entirely satisfactory due to pressure developed by the methyl bromide (boiling point,  $4.6^{\circ}$ ). The methyl bromide was added over a period of four hours and stirring was continued for thirty minutes after the addition was completed. The solution of the Grignard reagent had a dark color.

One and one-half grams of anhydrous manganous chloride was added as a catalyst, and 180 g. of chloral dissolved in 120 ml. of benzene was added dropwise to the methyl magnesium bromide solution with ice cooling over a period of two and one-half hours. The reaction was violent initially, but all visible evidence of a reaction disappeared after about 140 g. of chloral had been added. The mixture, which had become black, was stirred for forty-five minutes after the addition had been completed, and then allowed to stand at room temperature for eight hours. The Grignard complex, which had become rather viscous, was filtered through glass wool to remove the excess magnesium and hydrolyzed by pouring slowly into a cracked ice-sulfuric acid mixture. The ether and water layers were separated and the water layer thrice extracted with 30-ml. portions of ether. The ether layers were combined and ether removed by distillation. The remaining material was steam-distilled until no more oil came over. The oil layer of the distillate was yellow in color and had a sharp, distinctive odor. The residue in the flask was a black, tar-like mass. Kharasch (11) reported the formation of considerable quantities of tar in this reaction.

The oil layer was dried overnight with Drierite, and then distilled at atmospheric pressure in a Todd column with a Podbielniak-type packing. Considerable decomposition was in evidence, so the distillation through the long column was discontinued, and then resumed through a Snyder three-ball column. The material boiling up to  $150^{\circ}$  (chloral, benzene, and chloral hydrate) was removed. The remaining material was then fractionated in the Todd column at 29 mm. pressure. A  $67-71^{\circ}$  fraction (I) and a  $71-73^{\circ}$  fraction (II) were collected. Both fractions were clear, but began turning dark immediately. Fraction I was distilled at 742 mm. pressure using a Snyder three-ball column and a fraction came over at  $150-157^{\circ}$  with a tar-like residue remaining in the flask. This product was again distilled and a  $153-157^{\circ}$  fraction (III) collected. Fraction II (boiling at  $71-73^{\circ}$  at 29 mm.) was redistilled at 742 mm. and a fraction (IV) boiling at  $153-156^{\circ}$  was collected. The latter had a melting point of  $21-35^{\circ}$ , indicating that some impurities were still present, probably trichloroethanol (boiling at  $151^{\circ}$  at 742 mm.) formed by reduction of chloral by the Grignard reagent (3). This material was distilled twice again, the  $153-156^{\circ}$  fraction (V) being collected.

Second run: The reaction between chloral and methylmagnesium bromide was repeated with different amounts of reactants and a larger proportion of ether. Fifty-seven and one-half grams of magnesium turnings and 225 ml. of ether were placed in a flask and 200 ml. of methyl bromide in 310 ml. of ether was added as before. The excess magnesium was not filtered out. After the reaction between the magnesium and methyl bromide was completed, two grams of anhydrous manganese chloride was then added, and 180 g. of chloral in 130 ml. of

benzene was added dropwise as before. The Grignard complex was hydrolyzed as before, and the layers separated. The water layer was thrice extracted with ether, and the ether layers were combined. The ether was removed by distillation. The mixture was then steam-distilled, and the recovered oil was distilled at atmospheric pressure to remove chloral hydrate, chloral, and benzene. The remaining material was then distilled in the Todd column and the following fractions collected at 32 mm.: 65-69° (VI), 6.01 g.; 69-73° (VII), 4.68 g.; 74-75° (VIII), 12.33 g.; and 75-76° (IX), 24.63 g. A tar-like residue remained in the still pot. The combined weight of these fractions was 47.65 g. These fractions were distilled at 742 mm. pressure and two fractions collected as products: 149-155° (X) (trichloroethanol) and 155-157° (XI). The 155-157° fraction (XI) was collected as the trichloroisopropyl alcohol and the yield was 19.38 g., which represents a yield of about 10%. Kharasch (11) reported yields as high as 50% using carefully purified reagents, including especially resublimed magnesium obtained from Dow Chemical Company.

An attempt was made to dehydrate a portion of the Grignard product by the method of Roleff (19), but it did not yield any of the desired olefin. The method consists of: (a) evaporation of the ether from the methylmagnesium bromide under anhydrous conditions, (b) dissolving the residue in benzene, (c) addition of chloral dropwise, and (d) decomposition of the product with hydrochloric acid.

Third run: For this run, a two-liter flask was used. Four hundred ten milliliters of dry ether and 113 g. of magnesium turnings were added to the flask, and 400 g. of methyl bromide in 800 ml. of

ether was added dropwise. Three and eight-tenths grams of anhydrous manganous chloride was added, and 202 g. of chloral in 500 ml. of ether added dropwise with ice cooling. The complex was hydrolyzed as in the first run, the layers separated, the water layer thrice extracted, and ether removed by distillation. The remaining material was steam-distilled, separated, and the oil dried over anhydrous sodium sulfate. The materials boiling under  $150^{\circ}$  were removed by distillation, and the remaining material was set aside to be fractionated with the same material from the fourth run.

Fourth run: This run was similar to the other Grignard reactions, except that more ether and benzene were used, in an attempt to reduce the amount of tar-like residue formed in the reaction between the methyl Grignard reagent and the chloral, and to improve the yield of the product. The amounts of reactants used were: 113 g. of magnesium in 500 ml. of ether, 380 g. of methyl bromide in one liter of ether, and 238 g. of chloral in 500 ml. of benzene. Despite the fact that the water that circulated through the condenser was cooled with ice, some of the ether escaped owing to the high room temperature. Small portions of ether were added during the reaction. The product was hydrolyzed, steam-distilled and then fractionated as before. Fifty-eight and one-tenth grams of material remained after removing material boiling below  $150^{\circ}$ .

The materials from the third and fourth runs were combined and the trichloroisopropyl alcohol removed by fractionally distilling at reduced pressure in the Todd column. The yield was 54.1 g. (11% of the theoretical), which was not significantly better than in the second run.

Fifth run: The Grignard reaction was run once more, this time using a five-liter flask, and increased amounts of ether and benzene. The amounts of reagents used were: one liter of ether and 166 g. of magnesium, 591 g. of methyl bromide in two liters of ether, and 315 g. of chloral in 1375 ml. benzene. The Grignard complex was hydrolyzed and the trichloroisopropyl alcohol recovered from the oil layer as before.

C. Dehydration of 1,1,1-trichloro-2-propanol.

Preliminary runs: A 16.5-g. sample of n-octyl alcohol was dehydrated by adding a 10% excess of phosphorus pentoxide and distilling. A yield of 67% was obtained, and there was evidence of some decomposition in the still pot.

A 24.5-g. sample of n-amyl alcohol was dehydrated using phosphorus pentoxide with a yield of 47% of the olefin. Part of the product was lost because of its high volatility. Some decomposition occurred in the flask.

First run: A sample of the alcohol was placed in a distilling flask and an excess of phosphorus pentoxide was added. The flask was heated, but only a few drops of material distilled at  $108^{\circ}$  at 756 mm. pressure. This liquid has a pungent odor and gave positive tests for unsaturation. This distillate has a refractive index at  $20^{\circ}$  of 1.4590, as compared with a refractive index at  $20^{\circ}$  of 1.4780, reported by Kharasch (12). Much decomposition occurred in the distilling flask, leaving a solid tar-like residue. The yield of desired olefin was very poor.

Second run: Dehydration was attempted by admitting the trichloro alcohol below the surface of hot 85% phosphoric acid. Only a few drops



of material boiling in the range of the olefin was obtained, and some unchanged alcohol was recovered.

Third run: For this attempt, the theoretical amount of phosphorus pentoxide was added to 85% phosphoric acid to give 100% phosphoric acid, and the procedure was the same as in the second run. The yield was poor and some unchanged alcohol was recovered.

Fourth run: Dehydration was again attempted using 10% excess phosphorus pentoxide, but the results were again unsatisfactory.

Fifth run: A 10% excess of phosphorus pentoxide was added to a sample of the alcohol, and the material was distilled at 105 mm. The yield of olefin was not significantly improved by the reduced pressure.

Sixth run: An attempt was made to thermally dehydrate the alcohol by passing it through a heated tube. At lower temperatures, the unchanged alcohol was recovered. At higher temperatures, decomposition occurred and a black, rather viscous material was obtained.

Seventh run: Dehydration was then attempted by the method of Senderens (20), who reported that lower alcohols, such as isopropyl, dehydrate over fused sodium hydrogen sulfate at lower temperatures than when alumina is used. The vapors of the alcohol were passed through a heated tube containing fused sodium hydrogen sulfate, but decomposition occurred in the tube and none of the desired olefin was obtained.

Eighth run: The method of LeBel and Green (13) for dehydrating alcohols was then attempted. A portion of the alcohol was dropped on strongly heated zinc chloride. Only unchanged alcohol distilled, and some decomposition occurred in the reaction flask.

Ninth run: The alcohol vapors were passed over heated alumina, but no olefin was obtained. Above 200° decomposition of the alcohol occurred, leaving a black viscous material on the alumina.

II. The alternate method for preparing 3,3,3-trichloropropene was then attempted. This method involves two steps: (a) addition of bromotrichloromethane to ethylene, and (b) dehydrohalogenation to give 3,3,3-trichloropropene.

A. Reaction of ethylene with bromotrichloromethane.

First run: The equipment consisted of an ethylene generator, which catalytically dehydrated absolute ethanol over alumina heated to about 390°, and a reaction flask, provided with a sintered-glass, gas-dispersion disc, a manometer, and an ultraviolet lamp for illumination.

The ethylene was bubbled through 78.4 g. of bromotrichloromethane in the flask. One gram of benzoyl peroxide was added as a catalyst, and light from the ultraviolet lamp was directed on the flask. A valve on the gas outlet maintained a pressure of 140-200 mm. above atmospheric on the system. The run was continued for twenty-one hours, with fresh portions of benzoyl peroxide added occasionally. The material in the flask was then rectified, but only a trace of addition product was obtained.

Second run: The procedure was the same as in the first run, except that a larger flask was used and the system was initially swept with nitrogen gas. Four hundred eighty-three grams of bromotrichloromethane and four grams of benzoyl peroxide were placed in the flask, and ethylene was bubbled through the mixture for twenty hours. The yield was about five grams of addition product.

Third run: The equipment used for this and succeeding runs consisted of a Farr low-pressure hydrogenation apparatus.

A 172-g. portion of bromotrichloromethane was added to the flask along with four grams of benzoyl peroxide. Ethylene gas was admitted until the pressure reached 24.5 pounds per square inch, and the flask was then shaken, while being heated by an infrared lamp. After about an hour, the pressure dropped to 20 pounds per square inch. One more gram of benzoyl peroxide was added and the pressure brought to 55 pounds per square inch by the addition of more ethylene. After about an hour, the pressure dropped about 10 pounds per square inch. Addition of catalyst and recharging were repeated twice more. This product was then set aside for later rectification.

Fourth run: This run was essentially the same as the third run, except that freshly recrystallized benzoyl peroxide was used. One hundred fifty-six and one-half grams of bromotrichloromethane was used to charge the reaction flask. More ethylene seemed to be absorbed for each addition of recrystallized benzoyl peroxide than when unrecrystallized benzoyl peroxide was used. The resulting material was set aside for later rectification.

Fifth run: This run was essentially the same as the fourth run. A 227-g. portion of bromotrichloromethane was used to charge the flask.

The products from the third, fourth, and fifth runs were combined and fractionated. Two hundred fifty grams of unchanged bromotrichloromethane, boiling at  $102-106^{\circ}$ , was recovered. The material remaining in the flask was distilled at 104 mm. pressure; the fraction boiling at  $112-116^{\circ}$  was collected as the addition product, 1,1,1-trichloro-3-bromopropane. The yield was 232 g. or 42% of the theoretical.

B. Dehydrohalogenation of 1,1,1-trichloro-3-bromopropane.

1. An attempt was made to remove hydrogen bromide from the polyhalide using triethylamine (10).

First run: A 20.4-g. portion of the 1,1,1-trichloro-3-bromopropane was mixed with 20% excess of triethylamine and refluxed for ten hours. The liquid became brown and a heavy white precipitate formed. Water was added to dissolve the amine salt, the layers were separated, and the water layer was twice extracted with ether. The combined ether and oil layers were distilled. After the ether and unreacted amine distilled, the temperature rose rather rapidly, and no flat was noted at 114-115°, the boiling point of 3,3,3-trichloropropene. The material remaining in the flask was then distilled at reduced pressure and a fraction boiling at 113-116° at 10 $\frac{1}{2}$  mm. was collected (unchanged 1,1,1-trichloro-3-bromopropane).

Second run: Since no product was obtained in the first run using triethylamine, N,N-diethylaniline was used for the second run. A 10-ml. portion of the polyhalide was added dropwise to diethylaniline in a distilling flask which was maintained at 170°. Only a few drops of material distilled and the material in the flask became dark and viscous. The distillate was fractionally distilled, and was found to be composed mostly of unchanged 1,1,1-trichloro-3-bromopropane and a small amount of lower-boiling material. No flat in the distillation curve was noted at the boiling point of the desired olefin.

Third run: A 19.1-g. portion of 1,1,1-trichloro-3-bromopropane was used, and an equivalent amount of triethylamine was added. The reflux time was cut to two and one-half hours. The white solid (XII)

which formed was removed by filtration. The filtrate was washed with twice its volume of 10% sulfuric acid, then with an equal volume of 10% sodium carbonate solution, and was dried overnight with anhydrous sodium carbonate. This material was then distilled through a 25-cm. Vigreux column. After the ether was removed, the temperature rose steadily until it reached  $188^{\circ}$ ; only unchanged reactant was recovered. No flat was noted at  $114-115^{\circ}$ , the boiling point of the desired olefin. The white solid (XII) melted at  $245-248^{\circ}$ . The melting point of triethylamine hydrobromide is  $248^{\circ}$  and that of triethylamine hydrochloride is  $253-254^{\circ}$ . The salt gave a positive bromine test with dilute Schiff reagent.

Fourth run: A 14.7-g. portion of 1,1,1-trichloro-3-bromopropane was dissolved in 16 ml. of hexane and the equivalent amount of triethylamine added. The mixture was refluxed for six and one-half hours. Less solid was formed than in the last run. The mixture was washed and distilled as in the third run, but again no desired product was obtained, and some of the original polyhalide was recovered.

Fifth run: A 17.5-g. portion of the polyhalide was treated with a 30% excess of triethylamine and refluxed 12 hours. The mixture was acidified with dilute sulfuric acid and steam-distilled. The layers were separated, and the oil layer was dried over anhydrous sodium carbonate and distilled. No flat was noted in the boiling range of the desired olefin.

2. Alcoholic potassium hydroxide was then employed in the attempt to remove hydrogen bromide from 1,1,1-trichloro-3-bromopropane.

As a preliminary trial, 32.8 g. of sec.-amyl bromide was dissolved in 50 ml. of ethanol and an equivalent amount of 20% alcoholic

potassium hydroxide solution was added. A white precipitate formed slowly. Water was then added until an oil appeared, and the layers were separated. Upon distillation, some amylene was recovered.

First run: An equivalent amount of 10% alcoholic potassium hydroxide solution was added dropwise to a 14-g. portion of 1,1,1-trichloro-3-bromopropane and a precipitate began forming immediately. After the reaction mixture had stood for thirty minutes, water was added until an oil separated. The oil layer was removed, dried, and distilled. On distillation, no flat was noted at the boiling point of the desired olefin.

Second run: A 15-g. portion of the polyhalide was dissolved in 33 g. of absolute ethanol and an equivalent amount of 2.5% alcoholic potassium hydroxide solution was added dropwise. A white precipitate began to form in a few minutes. After standing four hours, the solid was removed by filtration, and water added to the solution until an oil appeared. The oil was taken up in ligroin, the layers separated, and the organic layer then distilled. About 2.5 ml. of material boiled at 112-120°, (XIII). This was set aside for further purification.

Third run: A 54.3-g. portion of the polyhalide was dissolved in 135 g. of absolute ethanol and an equivalent amount of 3% alcoholic potassium hydroxide solution was added in small portions with stirring. The precipitate was filtered and weighed; 19.9 g. of solid was recovered. (The theoretical yield of potassium bromide was 28.5 g.) The oil was recovered as in the second run, and this was distilled. The 112-120° fraction (XIII) was collected, and some unreacted 1,1,1-trichloro-3-bromopropane was recovered.

The combined 112-120° fractions (XIII) of runs two and three were

distilled, and the 114-116° fraction (XIV) collected: refractive index at 20°, 1.4655. Kharasch (12) reported the refractive index at 20° as 1.4872 for 3,3,3-trichloropropene and the refractive index at 20° as 1.4680 for 1,1-dichloroallene.

3. An attempt was made to remove hydrogen bromide from 1,1,1-trichloro-3-bromopropane by thermal cracking.

The polyhalide was passed through a heated tube packed with glass beads. At 250°, unchanged material was recovered. The temperature was gradually increased, but no hydrogen bromide was split out until a temperature was reached at which the polyhalide began to decompose to a black gummy film on the tube packing. None of the desired olefin was obtained.

III. An attempt was made to fluorinate 1,1,1-trichloro-3-bromopropane using a mixture of antimony trifluoride (90%) and antimony pentachloride (10%).

The reaction proceeded in the cold, with evidence of some decomposition. Water was added and the mixture steam-distilled. The layers were separated, and the water layer extracted with ether. The ether extract was added to the oil layer and the mixture dried over Drierite. Distillation yielded a fraction boiling at 95-100°, which represented a drop of about 85° from the boiling point of the original compound. Seventeen grams of the trichlorobromo compound were used, and the 95-100° fraction obtained weighed 6.5 g.

## DISCUSSION

The results of this investigation indicate that the synthesis of 3,3,3-trichloropropene by dehydration of 1,1,1-trichloro-2-propanol is unsatisfactory. Considerable quantities of tar were formed in the Grignard reaction between chloral and methylmagnesium bromide. The 1,1,1-trichloro-2-propanol obtained was unstable, becoming dark on standing, even when protected from light and in the presence of an anti-oxidant. Whenever the alcohol was distilled, even at reduced pressures, a tar-like residue remained. It was not possible to reproduce the yields reported by Kharasch (11). However, special reagents were not used in this investigation.

The various attempts at dehydration of the alcohol failed to produce satisfactory yields of 3,3,3-trichloropropene. 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. It is believed that extensive polymerization occurred in the attempts to prepare the olefin by dehydration of the alcohol, using phosphorus pentoxide.

The reaction of bromotrichloromethane and ethylene in the presence of a benzoyl peroxide catalyst was difficult to start, and required repeated additions of the catalyst. It is believed that this reaction would proceed in a more satisfactory manner if higher pressures were used, since the Parr apparatus gave improved yields over those obtained using lower pressures. This seems to be a satisfactory method of introducing a trichloromethyl group into a compound.

The reaction of the 1,1,1-trichloro-3-bromopropane and triethylamine failed to produce the desired olefin, 3,3,3-trichloropropene. The reaction of 1,1,1-trichloro-3-bromopropane with alcoholic potassium hydroxide



produced only traces of material boiling in the range of the desired olefin, but gave a moderate yield of material indicated to be 1,1-dichloroallene by its physical constants. Thus, it was not possible, by the methods used, to selectively remove hydrogen bromide without also removing hydrogen chloride from the bromotrichloro compound.

The fluorination product of 1,1,1-trichloro-3-bromopropane has a boiling point about  $80^{\circ}$  lower than the original compound. Calculations indicate that a drop of approximately  $40^{\circ}$  in the boiling point may be expected for each chlorine atom replaced by a fluorine atom. Had the drop been about  $120^{\circ}$ , an attempt would have been made to determine whether or not any 1,1,1-trifluoro-3-bromopropane had been produced, since hydrogen bromide might possibly be removed from this compound to give 3,3,3-trifluoropropene. Although the structure of the fluorination product was not determined, it is probably 1,1-difluoro-1-chloro-3-bromopropane. McBee (15) obtained a 32% yield of 1,1,1-trifluoro-2-chloropropane and an 8% yield of 1,1-dichloro-1-fluoro-2-chloropropane when 1,1,1,2-tetrachloropropane was fluorinated with mercury as a catalyst. Gilman (4) states that a trichloromethyl group is easily transformed to a difluorochloromethyl group.

Workable amounts of the 3,3,3-trifluoropropene could not be prepared by the methods tried, and therefore the polymerization and hydrogenation steps were not attempted.

This investigation produced no alternate method for the production of 3,3,3-trifluoropropene. The use of hydrogen fluoride and special high-pressure equipment still seem necessary for the synthesis of this compound.

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He entered the naval service in the fall of 1943, attended the Naval Reserve School at the United States Naval Academy, and received a commission as Ensign in the Naval Reserve in December of 1943. In January of 1944, he was married to Winona Maddox. He attended the Naval Diesel Engineering School at Penn State College, State College, Pa., in the spring of 1944, and was then assigned to the USS LST 681, which served in the Pacific area.

After his discharge from the navy in the spring of 1946, he attended the summer session at Northwestern State College, and that fall he entered Oklahoma A. and M. College. In the fall of 1947 he was appointed a Graduate Fellow in the Chemistry Department, and served in that capacity for two years. In the summer of 1949, a son, Steven Merrill, was born.

Typed by:

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