the simultaneous formation of an indene glycol and consequently some 2-indanone makes a quantitative interpretation of the results difficult.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 28, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Preparation and Properties of Certain Trifluoromethyl Compounds[1]

BY J. H. SIMONS, R. L. BOND AND R. E. MCARTHUR

Although compounds containing the trifluoromethyl radical are of considerable interest and have important uses, the number of them that are known is relatively small. Only a few methods of synthesis are available, and these are usually specific in nature, so that any one of them is capable of use in producing only a limited number of compounds. Many of the trifluoromethyl compounds that have been reported are prepared from benzotrifluoride. This is produced from benzotrichloride by either the Swarts[1a] reaction or by the action of hydrogen fluoride.[2] As the trifluoromethyl group is both stable and unreactive, many aromatic derivatives of benzotrifluoride can be and have been made. By the oxidation of one of these, aminobenzotrifluoride, Swarts[3] obtained trifluoroacetic acid. With this acid as the starting material and the use of known methods of organic chemistry, he prepared a considerable number of other compounds that can be considered as derivatives of trifluoroacetic acid, such as the amide, cyanide, esters, etc. By electrolysis[4] of the acid in aqueous solution he obtained hexafluoroethane.

Other methods for preparing trifluoromethyl compounds are: the reaction of fluorine with carbon,[5] the reaction of fluorine with hydrocarbons or halogen derivatives of hydrocarbons,[6] the action of a carbon arc on carbon tetrafluoride or difluorodichloromethane,[7] and the reaction of mercurous or mercuric fluoride with polyhalogen derivatives of methane.[8] A patent disclosure[9] indicates the possible formation of trifluorochloromethane from the reaction of antimony fluoride with carbon tetrachloride. The Swarts reaction has been used to produce a few other trifluoromethyl compounds such as trifluorodimethyl ether.[10]

It was the purpose of this investigation to search for other methods of synthesis. A new one was found for the preparation of trifluorochloromethane. It was hoped that this compound would operate in the Grignard synthesis or one of its variations. Many such reactions were studied. Attempts were made to prepare trifluorobromo- and trifluoroiodomethane. New syntheses were found for the preparation of fluoroform. Studies were made of the reaction of fluorine with carbon tetrachloride and difluorodichloromethane, several reactions of iodine pentafluoride were performed, reactions in a carbon arc were studied, and the thermal decomposition of barium trifluoroacetate was investigated.

Experimental

Apparatus.—Parts of the apparatus used in this work have been described previously. These are the fluorine generator,[11] the low temperature distilling column,[12] the vapor density balance[13] and the magnetic stirrer reaction vessel.[14] Other special equipment was constructed for this work and some of it will be described in connection with its use.

The Reaction of Fluorine and Carbon Tetrachloride.—A reaction vessel made of copper was used. This carried a reflux condenser, from the top of which the gaseous products were obtained. The shaft of a mechanical stirrer extended through the reflux condenser and rotated in a lead bearing so designed that it could be tightened like a packing gland. The fluorine gas entered through a tube, the outlet of which was below the level of the liquid. An additional inlet tube was provided to supply carbon tetrachloride. The open end of this tube was above that of the fluorine tube so that it served as an indicator for the level of the liquid, and more liquid could be supplied before the

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[1] Portions of the material contained herein were included in a paper presented in the Symposium on Fluorine Chemistry at the meeting of the American Chemical Society in Detroit, Sept. 11, 1940.

[1a] Swarts, *Bull. sci. acad. roy. Belg.*, **35**, 375 (1898).

[2] Simons and Lewis, THIS JOURNAL, **60**, 492 (1938).

[3] Swarts, *Bull. sci. acad. roy. Belg.*, **8**, 343 (1922).

[4] Swarts, *ibid.*, **17**, 27 (1931).

[5] (a) Ruff and Keim, *Z. anorg. allgem. Chem.*, **192**, 249 (1930); (b) Simons and Block, THIS JOURNAL, **61**, 2962 (1939).

[6] (a) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934); (b) Calfee and Bigelow, THIS JOURNAL, **59**, 2072 (1937); (c) Calfee, Fukuhara and Bigelow, *ibid.*, **61**, 3552 (1939).

[7] (a) Ruff and Bretschneider, *Z. anorg. allgem. Chem.*, **210**, 173 (1933); (b) Thornton, Burg and Schlesinger, THIS JOURNAL, **55**, 3177 (1933).

[8] (a) Ruff, Bretschneider, Luchsinger and Miltschitzky, *Ber.*, **69**, 299 (1936); (b) Henne, THIS JOURNAL, **59**, 1200 (1937).

[9] Kinetics Chemicals, Inc., Brit. Pat. 391,168 (April 13, 1933).

[10] Booth and Burchfield, THIS JOURNAL, **57**, 2070 (1935).

[11] Simons, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, Inc., New York, N. Y., 1939, p. 142.

[12] Simons, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 29 (1938).

[13] Simons, *ibid.*, **10**, 587 (1938).

[14] Simons, *ibid.*, **10**, 638 (1938).

end of the fluorine tube was above the level of the liquid. The gas, which came from the exit at the top of the reflux condenser, passed first through a glass tube containing wood shavings to detect the escape of fluorine and then through an alkali scrubbing tower. It was finally caught in carboys by water displacement. Two hundred and fifty cc. of carbon tetrachloride and 25 g. of arsenic were placed in the vessel and fluorine was passed through at the rate of about one-sixth mole per hour. The carbon tetrachloride liquid was kept at about 70°, and the reflux condenser was cooled with salt–ice. Under these conditions the reaction proceeded without explosions and the gas found in the carboys was 74% carbon tetrafluoride and 17% trifluorochloromethane. Using the same catalyst Ruff and Keim[15] found their gaseous products to contain 20% of carbon tetrafluoride and 54% trifluorochloromethane.

Preparation of Fluorotrichloromethane.—In an attempt to increase the yield of trifluorochloromethane a change was made in the catalyst. For the same amount of carbon tetrachloride the arsenic was reduced to 11 g. When crackling indicated a tendency toward explosion, bromine was added in small portions to a total of 3 to 4 cc. The condenser was cooled with tap water. The product obtained under these conditions was practically pure fluorotrichloromethane.

The addition of bromine was expected to reduce the yield of carbon tetrafluoride and increase the yield of compounds containing less fluorine. The reasoning is as follows. Bromine fluoride is a much more reactive substance than arsenic fluoride and the energy of activation in its reaction with carbon tetrachloride would be expected to be less. Due to this lower energy of activation the reaction takes place with lower concentrations of reactants, and the rate of production of the energy of reaction at any one point is less and can be more easily dissipated. In the presence of a large excess of carbon tetrachloride multiple substitution would, therefore, be expected to be less likely with a catalyst that provides a mechanism requiring a lower energy of activation. This reasoning amply explains the results obtained. However, the effect was much greater than was desired, and trifluorochloromethane was not obtained in high yield by this method.

The Formation of Hexachlorobenzene.—A brownish-red residue was found in the reaction flask after the treatment of carbon tetrachloride with fluorine. Repeated fractional crystallization gave a crop of fine white needles. These gave no test for fluorine or arsenic, but chlorine by a Carius determination was 81.56% and the melting point was 221. C_6Cl_6 has m. p. 229 and Cl 79.87%. The formation of hexachlorobenzene in this reaction is certainly unexpected. There are, however, other experimental results which are similar. Hexachlorobenzene has been detected in the residue resulting from passing carbon tetrachloride through a high tension electric arc.[16] Calfee, Fukuhara, Young, and Bigelow[17] obtained difluorodichloroethylene by the action of fluorine on ethyl chloride.

The Reaction of Fluorine and Difluorodichloromethane.—The use of arsenic as a catalyst for the reaction of fluorine and carbon tetrachloride in which both carbon tetrafluoride and trifluorochloromethane were formed suggested the possible use of this catalyst for the reaction of fluorine and difluorochloromethane. A mixture of these gases was passed over arsenic maintained at 100°. The yield of trifluorochloromethane was very low.

Silver fluoride was tried as a catalyst for this reaction. The mixed gases were passed over the salt maintained at different temperatures between 200 and 400°. There was no appreciable reaction. Bromine added to liquid difluorodichloromethane and fluorine bubbled through the liquid at −80° resulted in no reaction.

Trifluorochloromethane was made in very high yield by conducting the reaction between the gases over a mercury catalyst in a copper tube. The technique was similar to that of Simons and Block[5b] for the reaction between carbon and fluorine. By maintaining a temperature of 340 to 370° and a slight excess of difluorodichloromethane the reaction proceeded smoothly without explosions and no appreciable amount of carbon tetrafluoride was found in the products.

Reactions of Trifluorochloromethane.—As the carbon–fluorine bond is stronger than the carbon–chlorine bond, it was hoped that reactions could be found in which the chlorine atom of trifluorochloromethane could be replaced without disrupting the rest of the molecule. An apparatus was constructed to withstand five atmospheres pressure. It had a reaction vessel with a sealed-in magnetic stirrer. In a number of experiments magnesium in ethyl ether was treated with the compound, and the usual practice of starting a Grignard was employed. No apparent reaction resulted. This is also true for experiments in which lithium in benzene was used. A reaction occurred with magnesium in dimethylamine, but the product gave no test for an active Grignard compound. A slow reaction between lithium and trifluorochloromethane in trimethylamine was found at 0° and at about two atmospheres pressure. This appeared to give the desired product. After a number of experiments it was found that a small amount of dimethylamine was necessary to initiate this reaction and that the dimethylamine was consumed. About forty-eight hours were required for 0.2 mole of CF_3Cl to react with 0.4 mole of lithium. The product of this reaction was treated with carbon dioxide in the hope of obtaining trifluoroacetic acid, but vaporization from sulfuric acid did not give the acid and treatment with phosphorus trichloride did not give the acid chloride. When the product was treated with water or methyl alcohol, fluoroform was not obtained. Reaction with acetyl chloride gave 2–3 cc. of a liquid boiling 25–28°, which could not be identified positively as trifluoroacetone.

From the above it is evident that the chlorine in trifluorochloromethane is somewhat too firmly bonded to undergo the desired reactions. If the chlorine could be replaced by iodine, the resulting compound would possibly be sufficiently reactive. In attempting to make this compound CF_3Cl was passed over heated calcium iodide. At 100° a slight reaction occurred. Distillation and examination of the gaseous products showed a small amount of carbon tetrafluoride and some hexafluoroethane in addition to the starting material. The solid products showed in addition to calcium iodide: carbon, calcium fluoride, calcium

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(15) Ruff and Keim, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).

(16) Schall, *Z. physik. Chem. Untervicht*, **21**, 385 (1910).

(17) Calfee, Fukuhara, Young and Bigelow. THIS JOURNAL, **62**, 267 (1940).

chloride, and iodine. Postulating chemical equations to include the known products, we have $2CF_3Cl + CaI_2 = C_2F_6 + I_2 + CaCl_2$ and $2CF_3Cl + 2CaI_2 = CF_4 + CaF_2 + CaCl_2 + 2I_2 + C$. This experiment was repeated at 50° temperature intervals up to 500° with increasing rapidity of reaction but the same products.

Trifluoroiodomethane is apparently not obtainable in the above reaction. The reason may be a coupling reaction at the temperatures required. Because of this, the synthesis of the bromo compound was tried using anhydrous calcium bromide. Temperatures between 300 and 400° were employed, and the products were analogous to those using calcium iodide except that the proportion of carbon tetrafluoride to hexafluoroethane was much greater.

Experiments in which trifluorochloromethane was treated with potassium cyanide in the temperature range 400–500° gave carbon tetrafluoride as the only volatile product.

Reactions of Iodine Pentafluoride.—As reactions depending on the replacement of chlorine with iodine failed to produce trifluoroiodomethane, replacement reactions with fluorine were tried with iodomethanes. Ruff and co-workers[8a] replaced iodine in iodoform with fluorine, and Ruff and Keim[15] found that iodine pentafluoride reacted with benzene to form both iodo and fluoro benzenes. A copper vessel was made to study the reaction of iodine pentafluoride with iodoform and with carbon tetraiodide. This vessel was entirely enclosed except for a 3/8-inch (9.5-mm.) outlet tube at the top. All joints were made by fusing the copper together. A 3/8-inch (9.5 mm.) tee compression fitting connected to this outlet tube. A 1/4-inch (6.4-mm.) copper tube entered the vessel through the compression fitting and served both as an entry tube for the iodine pentafluoride and as a stirrer. It was longitudinally sawed into quarters at the lower end, so that when inserted and pressed against the bottom of the vessel, the quarters spread and formed the blades of the stirrer. Intermittent stirring was accomplished by slightly loosening the compression nut and rotating. Small holes drilled in this tube gave free entrance to the incoming materials. The side opening of the tee served as the outlet for gaseous products. These were first passed through sodium fluoride tubes at 0° to remove hydrogen fluoride and iodine and were then collected in traps at low temperature. A copper vessel that contained the iodine pentafluoride connected to the entry tube. Passing an inert gas through it would carry the vapor of the reagent into the reaction vessel or tipping it by bending the copper tube enabled the reagent to flow into the reaction vessel. The former technique was used to start the reaction and the latter after the initial vigor had subsided.

When iodine pentafluoride was caused to react with iodoform in this vessel in approximately molal quantities, the reaction would begin at salt–ice temperature. The temperature was gradually raised as the reaction proceeded until 80 to 90° was obtained. The products were fluoroform and difluoroiodomethane in a ratio of about 15 to 1.

As it is evident that iodine pentafluoride is not a sufficiently powerful fluorinating agent to remove the hydrogen in fluoroform, carbon tetraiodide was selected for experiment. The material was made by the method of Walker[18] and the identical technique as used for the fluoroform was employed. The product was hexafluoroethane.

Reactions in the Carbon Arc.—Ruff and Bretschneider[7a] prepared hexafluoroethane and tetrafluoroethylene by the action of a carbon arc on carbon tetrafluoride, and Thornton, Burg and Schlesinger[7b] found trifluorochloromethane, tetrafluorodichloroethane, carbon tetrafluoride, and chlorine in difluorodichloromethane that had been acted upon by a high tension arc. Reasoning from the above experiments the CF_3 radical might be expected to be formed from carbon tetrafluoride in a carbon arc and that it then could be caused to react with other substances. A mixture of carbon tetrafluoride and iodine was treated in an arc of 5000 to 7500 volts between graphite electrodes, but nothing corresponding to trifluoroiodomethane was obtained. About eight grams of fluorophosgene resulted by passage of a four to one ratio of carbon monoxide and carbon tetrafluoride at a pressure of 5 cm. through a hot arc of 7500 volts for one hundred hours.

An arc apparatus was constructed in which the upper graphite electrode could be raised or lowered mechanically. The lower electrode was drilled longitudinally through the center, and the entering gas passed through this hole. Gas pressures from 1 mm. to 1 atmosphere were tried and voltages from 1000 to 25,000 The best results were obtained with 1200 volts, 0.5 ampere, and a gas pressure of 3 cm. Carbon tetrafluoride was passed and repassed through an arc of this kind for about one hundred hours. Some hexafluoroethane was obtained in a distillation of the products, which also contained about 4 cc. of liquid boiling above −40°. Of this about half was octafluoropropane and the remainder higher boiling fluorocarbons. No unsaturated compounds were found by absence of bromine absorption. This is not in agreement with the experiments of Ruff and Bretschneider.

The Thermal Decomposition of Barium Trifluoroacetate.—Swarts[3] decomposed sodium trifluoroacetate and obtained trifluoroacetyl fluoride, trifluoroacetic anhydride, and perhaps fluorophosgene. His experiments were conducted at atmospheric pressure. It is possible that at low pressures, where the gaseous products are rapidly removed from the heated region and with the use of the barium salt that hexafluoroacetone could be obtained. At 3 mm. pressure and 282° the barium salt decomposed smoothly. However, the products were apparently the same as found by Swarts, and no substance the properties of which would correspond to a ketone, was found.

Summary

The reaction of fluorine and carbon tetrachloride has been studied. In the presence of arsenic some trifluorochloromethane is formed, but the addition of bromine caused an almost complete formation of fluorotrichloromethane. Difluorodichloromethane reacted with fluorine in the presence of mercury to form trifluorochloromethane quantitatively.

Trifluorochloromethane has been found unsuitable for Grignard reactions or for the formation of trifluoromethyllithium. Trifluorobromomethane

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[18] Walker, *J. Chem. Soc.*, **85**, 1090 (1904).

and trifluoroiodomethane are judged to be unstable after numerous attempts at their preparation. Reactions of trifluorochloromethane with calcium iodide and with calcium bromide yielded carbon tetrafluoride, hexafluoroethane and iodine.

In an electric arc carbon tetrafluoride reacted with carbon monoxide to form fluorophosgene. Carbon tetrafluoride alone in an arc formed a mixture of fluorocarbons including octafluoropropane.

Iodine pentafluoride reacted with iodoform to yield fluoroform and difluoroiodomethane and with carbon tetraiodide to yield hexafluoroethane.

STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 16, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

The Kinetics of the Thermal Isomerization of *trans*-Dichloroethylene

BY J. LESLIE JONES AND ROBERT L. TAYLOR*

There have been few studies made of the mechanism of homogeneous gaseous isomerization reactions. Of the studies, only those of Kistiakowsky and co-workers are quantitative. Kistiakowsky, *et al.*, have studied the gas phase isomerization of methyl maleate,[1a] methyl cinnamate,[1b] isostilbene[1c] and *cis*-butene-2.[1d] They found that the activation energy of the isomerization of dimethyl maleate to dimethyl fumarate was 26,500 cal. as compared to the values of 41,600 cal. and 43,000 cal. for the isomerization of *cis*-methyl cinnamate to *trans*-methyl cinnamate and isostilbene to stilbene, respectively. The research on the isomerization of *cis*-butene-2 to *trans*-butene-2 led to the conclusion that the reaction involved a chain mechanism. The widely separated values of the activation energies for the aliphatic ester and the aromatic derivatives were striking. In addition, the attempt to determine the mechanism of geometrical isomerization in the absence of groups contributing appreciably to resonance structures was unsuccessful, as the results obtained with the butene-2 indicated. In view of these facts, it was decided to investigate the gaseous isomerization of *trans*-dichloroethylene.[2]

This molecule represents the simplest example of a *cis–trans* isomer with significant differences in the physical properties of the two isomers. The contribution of resonance structures to the strength of the double bond is a minimum. Wood and Dickinson[3] recently published a study of the iodine catalyzed isomerization of the *trans* form in the liquid phase and in solution, but the research cast no light upon the simple thermal isomerization mechanism.

Experimental Section

Preparation of Dichloroethylene.—The *trans*-dichloroethylene used in this work was obtained in a fairly pure form from the Eastman Kodak Company. It was further purified by repeated fractionation in a three-foot column, packed with glass helices. Starting with 1500 cc. of material, 400 cc. was obtained with a boiling point range of 47.85 to 47.87° at 769.5 mm. pressure. The *cis* isomer was prepared by treating 300 g. of the *trans* form with 18 g. of bromine and allowing it to stand in the dark for twenty-four hours. The resulting equilibrium mixture was washed with 10% potassium hydroxide, several portions of distilled water dried over calcium chloride and fractionally distilled. About 40 cc. of *cis*-dichloroethylene was obtained which boiled at 59.9° at a pressure of 768.0 mm. (boiling range less than 0.1°). The boiling points obtained by Wood and Dickinson[3] were 59.6° for the *cis* isomer and 47.2° for the *trans* isomer at 745 mm. pressure.

Apparatus.—The apparatus used in the experimental study was the static type, employing a quartz spiral manometer as a null point indicator. A Pyrex glass hollow-barrel stopcock was employed to close the reaction vessel and was greased with a high melting lubricant. This particular stopcock together with the small amount of capillary tubing extending out of the furnace was heated with nichrome wire to prevent condensation of dichloroethylene. The reaction vessel was enclosed in an aluminum sheathing within the furnace in order to minimize temperature gradients and a thermocouple inserted into the sheathing. The alumel–chromel thermocouple was calibrated against condensing naphthalene and benzophenone. The temperature was usually constant within ±0.1°.

Because of the possible reaction between mercury vapor and dichloroethylene, particular precautions were taken to

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* A portion of this material is taken from the thesis submitted by Robert L. Taylor in partial fulfillment of the requirements for the Master of Science degree in chemistry.

(1) (a) Kistiakowsky and Nelles, *Z. physik. Chem.*, *Bodenstein Festband*, **152**, 369 (1931); Kistiakowsky and Nelles, THIS JOURNAL, **54**, 2208 (1932); (b) Kistiakowsky and Smith, *ibid.*, **57**, 269 (1935); (c) Kistiakowsky and Smith, *ibid.*, **56**, 638 (1934); (d) Kistiakowsky and Smith, *ibid.*, **58**, 766 (1936).

(2) Ebert and Bull, *Z. physik. Chem.*, **A152**, 451 (1931), announced that they intended to study the kinetics of the gaseous isomerization, but no results have been published to date.

(3) Wood and Dickinson, THIS JOURNAL, **61**, 3259 (1939).