[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

The Preparation and Fluorination of Addition Products of Bromotrichloromethane and Bromo- and Chloroölefins[1]

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Bromotrichloromethane has been found to react with a number of haloölefins to give simple addition products. The addition proceeds readily in the cases studied except whenever the halogen atoms are located both on a carbon atom having a double bond and on the carbon atom adjacent to it. Fluorinations of some of the adducts have been carried out.

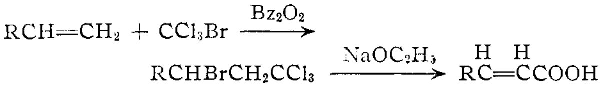
The peroxide-induced addition of bromotrichloromethane to olefins having a terminal double bond has been shown by Kharasch and co-workers[2,3] to proceed as

$$CH_2{=}CHR + CCl_3Br \longrightarrow CCl_3CH_2CHBrR$$

The high yields of one-to-one addition products obtained from bromotrichloromethane and olefins seemed to warrant an investigation of the reaction of the bromide with haloölefins as a general means of preparing substances containing the trichloromethyl group which might be converted to various fluorine compounds. Since the preparation of fluorobutanes was desired, this study was limited to the reaction of bromotrichloromethane with chloro- or bromoölefins which would give a butane or isopentane derivative.

Of twelve haloölefins treated with bromotrichloromethane in the present study, nine formed simple addition products. The properties of the adducts are shown in Table I. Perfluoroallyl chloride, 1,1-dichloropropene and 1,2-dibromo-3-chloropropene failed to form addition products.

Kharasch and his colleagues established the structures of a number of addition products of bromotrichloromethane and hydrocarbon olefins by hydrolysis to known unsaturated acids.



$$RCH{=}CH_2 + CCl_3Br \xrightarrow{Bz_2O_2} RCHBrCH_2CCl_3 \xrightarrow{NaOC_2H_5} R\overset{H}{C}{=}\overset{H}{C}COOH$$

In the present study numerous attempts were made to obtain unsaturated β-haloacids by the use of this procedure, but no acids were isolated. Consequently, different methods were used for the proof of structure of the addition products.

Four of the olefins which reacted with bromotrichloromethane had the structure $CH_2{=}CX-$ where X is chlorine, bromine or the trifluoromethyl group. That these substituents had no effect on the direction of addition across the double bond is indicated by the compounds obtained by the fluorinations of the 2-chloro- and 2-trifluoromethylpropene adducts. The former led to the known[4] 1-chloro-1,1,3,3-tetrafluorobutane and to $CF_2ClCH_2CFClCH_3$ which was dehydrochlorinated to 1,1,3-trifluorobutadiene.[5] The 2-trifluoromethylpropane adduct gave $CF_3CH_2C(CF_3)BrCH_3$ and $CF_2ClCH_2C(CF_3)BrCH_3$ which was converted to $CF_2{=}CH{-}C(CF_3){=}CH_2$. Since the preferred method of attack of a trichloromethyl radical is on the terminal methylene group of a 1-alkene and the cases shown above indicate no abnormal effect due to chlorine or trifluoromethyl group, the additions to $CH_2{=}CBrCH_3$ and $CH_2{=}CBrCH_2Cl$ were assumed to give the straight-chain compound.

The addition compound with 1-chloropropene also was found to be the straight-chain compound $CCl_3CHClCHBrCH_3$ as it reacted with zinc to give an olefin. The isomeric $CCl_3CH(CH_3)CHClBr$ would not be expected to react with zinc to give an unsaturated compound. The properties of the dehalogenated adduct, $CCl_3CH{=}CHCH_3$, are in reasonable agreement, except for the refractive index, with the values of $CCl_3CH{=}CHCH_3$ reported in the patent literature.[6] It is somewhat surprising that 1-chloropropene gave a yield of addition product twice as great as that obtained from 2-chloropropene.

The structure of the addition product of 2-chloro-2-butene and bromotrichloromethane is believed to be $CCl_3CH(CH_3)CClBrCH_3$ on the basis of its fluorination to a pentafluoroisopentane. The alternate compound $CCl_3C(CH_3)ClCHBrCH_3$ would not be expected to exchange its halogen atoms for fluorine to give a pentafluoride as such replacements normally occur only with carbon atoms containing only halogen atoms.[7]

The structure of the adduct from 1,3-dichloro-2-butene was not established as it was obtained in a small yield. The addition to the symmetrical 1,4-dichloro-2-butene leads to a single addition product.

Kharasch has shown that allyl chloride reacts readily with bromotrichloromethane to give 3-bromo-1,1,1,4-tetrachlorobutane thus demonstrating that an allylic chlorine atom alone will not prevent the addition from occurring. Recent evidence[8-10] has indicated that bromotrichloromethane gives good yields of adduct with chlorotrifluoroethane from which it may be inferred that the trifluorovinyl group is capable of reaction with the methane derivative. It therefore seems logical to postulate, in the case of $CF_2{=}CFCF_2Cl$, that the unreactivity toward bromotrichloromethane is not

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[2] M. S. Kharasch, O. Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1105 (1947).

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[4] E. T. McBee and W. R. Hausch, *Ind. Eng. Chem.*, **39**, 419 (1947).

[5] P. Tarrant, A. M. Lovelace and M. R. Lilyquist, THIS JOURNAL, **77**, 2783 (1955).

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[8] A. L. Henne and D. W. Kraus, *ibid.*, **73**, 1791 (1951).

[9] W. T. Miller, Jr., and J. M. Howald, Abstracts of Papers 122nd Meeting, American Chemical Society, Atlantic City, N. J., September, 1952, p. 12-k.

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TABLE I

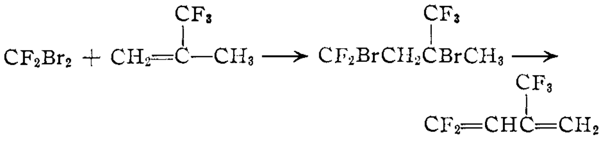
ADDITION PRODUCTS FROM HALOALKENES AND BROMOTRICHLOROMETHANE

Olefin	Addition product	Yield, %	B.p., °C.	Mm.	$n^{25}D$	d^{25}_4	MRD Calcd.	MRD Obs.	Ag equiv. Calcd.	Ag equiv. Obsd.
$CH_3CH{=}CClCH_3$	$CH_3CBrClCH(CCl_3)CH_3$	76	87	4	1.5352	1.7126	52.55	52.26	57.77	58.49
$CH_2{=}C(CF_3)CH_3$	$CCl_3CH_2C(CF_3)BrCH_3$	64	91	44	1.4573	1.7698	47.37	47.49	77.09	77.95
$CH_2{=}CBrCH_3$	$CCl_3CH_2CBr_2CH_3$	50	91	5	1.5528	2.0040	50.80	51.00	63.86	63.59
$CH_2{=}CBrCH_2Cl$	$CCl_3CH_2CBr_2CH_2Cl$	8	126	6	1.5764	2.0923	55.67	56.02	58.96	58.55
$CH_2ClCH{=}CClCH_3$	$C_5H_6BrCl_5$	8	109–113	3.5	1.5458	1.7748	57.42	57.70	53.88	53.81
$CH_2ClCH{=}CHC_2Cl$	$CH_2ClCH(CCl_3)CHBrCH_2Cl$	23	132–136	9	1.5480	1.8126	57.42	56.65	53.88	53.64
$CH_2{=}CClCH_3$	$CCl_3CH_2CBrClCH_3$	34	75	5	1.5293	1.7686	47.90	47.94	54.96	56.61
$CHCl{=}CHCH_3$	$CCl_3CHClCHBrCH_3$	65	82–85	8	1.5303	1.7530	47.90	48.45	54.96	55.02

caused by the trifluorovinyl group or the halogen atoms adjacent to the double bond alone but is the consequence of the effects of both factors. Additional support for the conclusion that halogen atoms when present in the 3-position and 1- or 2-position retard addition is given by the good yield of product from $CH_3CCl{=}CHCH_3$ and the low yield from $CH_3CCl{=}CHCH_2Cl$.

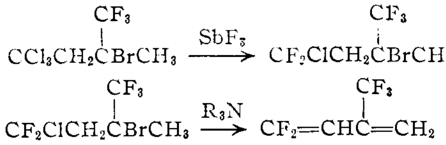
Kharasch and Sage[11] have shown that bromotrichloromethane and 3-bromopropene give 1,2,3-tribromopropane and 3,3,3-trichloro-1-butene when heated in the presence of benzoyl peroxide. 2,3-Dibromopropene reacts in a similar manner as 1,2,2,3-tetrabromopropane and 2-bromo-4,4,4-trichlorobutene apparently were formed.

It seemed probable that some of the adducts of bromotrichloromethane and the haloölefins might be useful for the synthesis of dienes containing fluorine. Efforts to prepare 1,1-difluoro-3-trifluoromethyl-1,3-butadiene through the reactions



$$CF_2Br_2 + CH_2{=}\overset{\overset{CF_3}{|}}{C}{-}CH_3 \longrightarrow CF_2BrCH_2\overset{\overset{CF_3}{|}}{C}BrCH_3 \longrightarrow CF_2{=}CH\overset{\overset{CF_3}{|}}{C}{=}CH_2$$

were not successful because no adduct was formed with CF_2Br_2. However, the diene was made by the method



$$CCl_3CH_2\overset{\overset{CF_3}{|}}{C}BrCH_3 \xrightarrow{SbF_3} CF_2ClCH_2\overset{\overset{CF_3}{|}}{C}BrCH_3$$

$$CF_2ClCH_2\overset{\overset{CF_3}{|}}{C}BrCH_3 \xrightarrow{R_3N} CF_2{=}CH\overset{\overset{CF_3}{|}}{C}{=}CH_2$$

The fluorination step required some study before conditions which gave the desired $CF_2ClCH_2C(CF_3)BrCH_3$ were found. Using a mixture of antimony trifluoride and antimony trifluorodichloride in a molar ratio of 3:1 at 60° for six hours gave a 43% yield of the chlorobromo compound. Increasing the amount of SbF_3Cl_2 gave more highly fluorinated material; with a $SbF_3:SbF_3Cl_2$ ratio of 2:1, a 66% yield of $CF_3CH_2C(CF_3)BrCH_3$ was formed. Several experiments were carried out using anhydrous hydrogen fluoride, sometimes in the presence of antimony pentachloride, at temperatures of from 100 to 250°. Fluorination occurred in each as indicated by the formation of low boiling material, but no product which could be conclusively identified was isolated. Material boiling about 30° was obtained; and due to its low refractive index and boiling point, it is believed to be chiefly 1,1,1,3-tetrafluoro-3-trifluoromethylbutane.

Tributylamine was used to dehydrohalogenate the $CF_2ClCH_2C(CF_3)BrCH_3$ to the diene, but the yield was only 36%. Apparently it is somewhat more difficult to remove hydrogen chloride than hydrogen bromide, for much better yields of dienes were obtained by dehydrobromination of compounds such as $CF_2BrCH_2CHBrCH_3$. The difficulty may also be due to the presence of the bromine atom on the carbon containing the trifluoromethyl group.

It was anticipated that a branched chain butadiene containing fluorine could be prepared by a process involving the addition of either dibromodifluoromethane to 3,3,3-trifluoro-2-butene or the addition of bromotrichloromethane to the olefin and fluorinating the adduct. However, it was found that neither methane derivative would add to this fluoroölefin. A method of preparing 3,3,3-trifluoro-2-butene by fluorinating $CF_2BrCH_2CHBrCH_3$ and dehydrobromination was developed.

A study also was made of the fluorination of $CCl_3CH_2CClBrCH_3$ with the expectation that 1,1-difluoro-3-chlorobutadiene could be prepared from it. Hydrogen fluoride gave a product boiling about 40° which is believed to be largely 1,1,1,3,3-pentafluorobutane.[12] The use of antimony trifluorodichloride gave two compounds, 1-chloro-1,1,3,3-tetrafluorobutane and 1,3-dichloro-1,1,3-trifluorobutane.

Experimental

In general, the procedure of Kharasch[2] was followed in the addition reaction; however, no effort was made to exclude oxygen from the reaction vessel. When the boiling point of the olefins permitted, the reactions were carried out at atmospheric pressure under reflux; the mixture was heated on a steam-bath for six hours after addition of all materials. The olefins having low boiling points were allowed to react in an autoclave. The 1.4-liter, stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath, the reactants were added, and the container was sealed and placed in the rocker. The mixture was heated, with rocking, to 100° and maintained at that temperature for about three hours.

The cooled reaction mixture was washed with a dilute solution of ferrous sulfate and hydrochloric acid to destroy any undecomposed peroxide that might be present. The mixture was then washed with water and dried over anhydrous calcium chloride or calcium sulfate. Distillation was carried out with a 20-inch fractionating column packed with 1/8-inch glass helices. Most of the unreacted bromotrichloromethane was removed at atmospheric pressure and the addition product was then obtained at a reduced pressure, usually about 5 mm.

Benzoyl peroxide, commercial grade, was used to initiate the addition reactions because it decomposes slightly below steam-bath temperature. For each mole of olefin, 0.06 mole of peroxide and 5 moles of bromotrichloromethane were employed. Yields were calculated on the basis of the amount of olefin used. The olefins were obtained from Co-

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[11] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 79 (1949).

[12] A. L. Henne and J. B. Hinkamp, THIS JOURNAL, **67**, 1197 (1945).

lumbia Organic Chemicals Co., Inc., or Distillation Products Industries.

1,1,1-Trichloro-2-butene.—Treatment of the adduct from bromotrichloromethane and 1-chloropropene with powdered zinc resulted in a 14% yield of an olefin, b.p. 78–81° (92 mm.), n^{21}_{D} 1.4719, d^{21}_{4} 1.2857; *MR*D calcd. for $CCl_3CH{=}CHCH_3$ 34.81, *MR*D found 34.64. 1,1,1-Trichloro-2-butene, prepared by the dehydrochlorination of the adduct of carbon tetrachloride and propene, is reported to have the constants: b.p. 79.8–80.3° (102 mm.), n^{20}_{D} 1.4819, d^{20}_{20} 1.2859, *MR*D found 35.41.[6]

The infrared spectrum of the dehalogenation product includes absorption at 3.26 and 6.15 μ, characteristic of the double bond with adjacent hydrogen atoms, and strong absorption near 12 μ which probably results from the carbon-chlorine stretching vibrations.

Addition of Bromotrichloromethane to 2,3-Dibromopropene.—The dibromopropene was redistilled and the portion which boiled at 79–89° (86–120 mm.) was used. The olefin (151 g., 0.75 mole) was mixed with bromotrichloromethane (740 g., 3.75 moles) and benzoyl peroxide (14 g., 0.06 mole) in a 1-liter flask and the reaction carried out in the customary manner. Distillation of the reaction mixture resulted in two portions: 37 g. (21% yield) of a material boiling at 98° (43 mm.), d^{25}_{4} 1.7722, n^{25}_{D} 1.5262, and 50 g. (14% yield) of a substance boiling at 98–101° (5 mm.), d^{25}_{4} 2.6400, n^{25}_{D} 1.6150. The higher boiling fraction is 1,2,2,3-tetrabromopropane.

Anal. Calcd. for $C_3H_4Br_4$: Br, 89.2. Found: Br, 89.2. The lower boiling material is believed to be $CCl_3CH_2CBr{=}CH_2$. Calcd. for $C_4H_4BrCl_3$: Ag eq., 59.6. Found: Ag eq., 62.2.

Fluorination of 3-Bromo-1,1,1-trichloro-3-trifluoromethylbutane (I). With Hydrogen Fluoride.—A 300-ml. stainless steel autoclave containing hydrogen fluoride (16 g., 0.8 mole) and I (80 g., 0.26 mole) was heated and agitated at 100° for 8 hours. The reaction vessel was cooled to room temperature and the excess hydrogen fluoride vented. The remaining material was poured on ice, neutralized with sodium carbonate and steam distilled. Fractionation gave some material boiling near room temperature and 27 g. of starting material.

The reaction was carried out at 125°, with hydrogen fluoride (54 g., 2.7 moles) and I (104 g., 0.338 mole) to give 25 g. of material, b.p. 36.2°, n^{5}_{D} 1.2982, d^{20}_{4} 1.2152, which contained only a trace of bromine or chlorine.

With Antimony Trifluoride and Chlorine.—The 300-ml. reaction vessel was charged with antimony trifluoride (160 g., 0.89 mole) and chlorine (34 g., 0.475 mole). After the reaction had subsided, compound I (160 g., 0.52 mole) was added and the vessel heated and agitated at 60° for 6 hours. The contents were poured into cool hydrochloric acid, the organic layer separated, neutralized and steam distilled. Distillation was carried out through a 50-cm. column packed with glass helices; 73 g. of 3-bromo-1,1,1-trifluoro-3-trifluoromethylbutane, b.p. 90–91°, n^{24}_{D} 1.3455, d^{24}_{4} 1.6556, was obtained.

Anal. Calcd. for $C_5H_6BrF_6$: Br, 30.95. Found: Br, 31.1.

Using I (96 g., 0.312 mole), antimony trifluoride (73 g., 0.436 mole) and chlorine (8.8 g., 0.123 mole) at 60° for 6 hours gave 40 g. of 3-bromo-1-chloro-1,1-difluoro-3-trifluoromethylbutane boiling at 120–123°. A center fraction had the properties b.p. 122°, n^{24}_{D} 1.3798, d^{24}_{4} 1.7639.

Anal. Calcd. for $C_5H_5BrClF_5$: Ag eq., 137. Found: Ag eq., 134.

1,1,1-Trifluoro-3-trifluoromethyl-2-butene.—To a flask equipped with a stirrer and a partial take-off condensing head was added 3-bromo-1,1,1-trifluoro-3-trifluoromethylbutane (25 g., 0.097 mole). The temperature was raised to 90° and a concentrated solution of potassium hydroxide (10 g., 0.18 mole) in ethanol was added dropwise. The low boiling material was removed by distillation as it formed and was washed, dried and fractionated to give 10 g. (58%) of the olefin, b.p. 31°, n^{10}_{D} 1.2973, d^{22}_{4} 1.2584.

Anal. Calcd. for $C_5H_4F_6$: F, 64.4. Found: F, 64.1.

1,1-Difluoro-3-trifluoromethylbutadiene.—Tributylamine was added to a flask equipped with a 15-cm. column packed with Berl saddles. The amine was heated to 180–190° and 3-bromo-1-chloro-1,1-difluoro-3-trifluoromethylbutane (75 g., 0.29 mole) was added dropwise. The reaction mixture began refluxing after approximately 10 ml. of the halide had been added. Product was removed at a rate sufficient to maintain a vapor temperature of 50–55°. The reaction was continued until all refluxing had stopped. Fractionation gave 16 g. (36%) of material boiling at 34.5–39°. An analytical fraction of 8 g. had b.p. 34.5°, n^{11}_{D} 1.3165, d^{11}_{4} 1.2420.

Anal. Calcd. for $C_5H_3F_5$: C, 37.99; H, 1.91. Found: C, 37.77; H, 2.02.

The Fluorination of 3-Bromo-1,1,1,3-tetrachlorobutane (II).—A 300-ml. stainless steel reaction vessel was charged with II (650 g., 2.36 moles) and hydrogen fluoride (310 g., 15.5 moles). The reaction was carried out at 90° for 8 hours. The product was poured on ice, the organic layer separated and steam distilled. Fractionation gave 24 g. of material boiling at 40°, n^{24} 1.3049, d^{24}_{4} 1.2619, believed to be chiefly 1,1,1,3,3-pentafluoropentane for which Henne has reported the properties b.p. 40.14, n^{20}_{D} 1.2824, d^{20}_{4} 1.2666.

A 1.4-liter stainless steel vessel was charged with antimony trifluoride (360 g., 2 moles), chlorine (71 g., 1 mole) and II (275 g., 1 mole). The vessel was agitated for 6 hours at 70°. After the purification procedure described above, the organic material was fractionated. The first compound isolated (20 g.) was 1-chloro-1,1,3,3-tetrafluorobutane, b.p. 70–71°, n^{24}_{D} 1.3321, for which McBee and Hausch report b.p. 69° at 745 mm., n^{26}_{D} 1.3340. 1,3-Dichloro-1,1,3-trifluorobutane (45 g.), b.p. 129°, n^{24}_{D} 1.4048, d^{24}_{4} 1.6640, was also obtained.

Anal. Calcd. for $C_4H_5Cl_2F_3$: Cl, 39.2. Found: Cl, 39.1.

The structure of this compound was established by dehydrohalogenation with triamylamine to 1,1,3-trifluorobutadiene, b.p. 16°, n^{1}_{D} 1.3430, d^{1}_{4} 1.1178; these physical constants agree with the reported value.[5] The infrared spectrum of the diene prepared in this manner was identical to that of 1,1,3-trifluorobutadiene.

3-Bromo-1,1,1-trifluorobutane (III).—The fluorination of $CF_2BrCH_2CHBrCH_3$[13] to the desired compound (III) was carried out under a variety of conditions. The best conversion obtained was 50% and the yield was 59% under the conditions described below.

A mixture of $CF_2BrCH_2CHBrCH_3$ (236 g., 0.93 mole), hydrogen fluoride (100 g., 5 moles) and antimony pentachloride (5.6 ml.) was heated and agitated in a stainless steel reaction vessel for 18 hours at 135°. About 130 g. of organic material was recovered by steam distillation to give $CF_3CH_2CHBrCH_3$, b.p. 84°, n^{24}_{D} 1.3740, d^{24}_{4} 1.5119; *MR*D calcd. 28.1, *MR*D found 28.6.

Anal. Calcd. for $C_4H_6BrF_3$: Br, 41.8. Found: Br, 40.9.

The $CF_3CH_2CHBrCH_3$ was converted to the known $CF_3CH{=}CHCH_3$[14] by treatment with alcoholic potassium hydroxide.

Fluorination of 2-Trichloromethyl-3-bromo-3-chlorobutane.—The following materials were placed in the autoclave, which had been cooled previously in a Dry Ice–acetone-bath: 267 g. (0.92 mole) of the organic compound and 105 g. (5.2 moles) of hydrogen fluoride. The autoclave was sealed, heated to 104° in 3 hours, and maintained at that temperature for 2 additional hours. The reaction mixture was distilled through an 8-inch column packed with 1/8-inch glass helices. The lowest boiling fraction had the constants: b.p. 59.0–59.3°, n^{25}_{D} 1.3054, d^{25}_{4} 1.2266; *MR*D calcd. for $C_5H_7F_5$ 24.76, found 25.10; it was assumed to be 2-trifluoromethyl-3,3-difluorobutane.

Anal. Calcd. for $C_5H_7F_5$: F, 58.6. Found: F, 57.9.

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(14) R. N. Haszeldine, *J. Chem. Soc.*, 2040 (1954).