## SYNTHESIS OF HALOBUTANES

### E. T. McBee and W. R. Hausch<sup>1</sup>

PURDUE UNIVERSITY AND PURDUE RESEARCH FOUNDATION, LAFAYETTE, IND.

SEVERAL new chlorofluorobutanes have been prepared by fluorination and by photochemical chlorination of appropriate halobutanes. Addition of hydrogen chloride to 3,3-difluoro-1-butene was directed so that only 1-chloro-3.3-difluorobutane was produced. Synthesis of chlorofluorobutanes by addition of hydrogen fluoride to chloro-olefins gives good yields only when the compound involved was a monochloro-olefin. The directive effect of CF<sub>2</sub>, CF<sub>2</sub>, and CClF groups on chlorine substitution was studied.

**HIS** paper is one of a series on the synthesis of certain fluorine-containing aliphatic compounds which were evaluated as anesthetics (7). Figure 1 summarizes the syntheses of the fluorine-containing derivatives of butane and the butenes. Since this work was completed, some of the reactions and new compounds have been reported (2, 3) with excellent agreement.

The starting material for the investigation was 2.3-dichlorobutane, made by addition of chlorine to 2-butene. This chlorination, conducted at 0°C. in carbon tetrachloride with an excess of butene, gave also small amounts of CH<sub>3</sub>CHClCHClCH<sub>2</sub>Cl and CH<sub>3</sub>CHClCCl<sub>2</sub>CH<sub>2</sub>. The latter compound and CH<sub>3</sub>CCl==CCl-CH<sub>3</sub> were primarily obtained by treating CH<sub>3</sub>CH=CClCH<sub>3</sub> with chlorine at  $0^{\circ}$  C. in the presence of sodium bicarbonate (8)

Addition of chlorine to CH<sub>3</sub>CCl=CClCH<sub>3</sub> gave CH<sub>3</sub>CCl<sub>2</sub>CCl<sub>2</sub>-CH<sub>3</sub> in 68% yield. This tetrachlorobutane, which melts at 174°C., is one of a series of substituted ethanes in which the six hydrogen atoms are substituted by chlorine or methyl groups. Nine of this series of ten compounds are known, and all but possibly one are camphoraceous solids with melting points ranging from 187 °C. for  $CCl_3CCl_3$  to  $104 \degree C$ . for  $C(CH_3)_3C(CH_3)_3$ .

#### PHOTOCHEMICAL CHLORINATION

Several compounds were chlorinated photochemically with anhydrous reagents in the vapor phase using a modified Muskat apparatus (5). This procedure is practical and easy to operate and may be illustrated as follows:

1. Sixty-six grams of  $CH_3CClFCH_2CH_3$  were added to the distilling flask of the Muskat apparatus. The material in the flask was boiled to maintain a take-off and reflux of  $CH_3CClFCH_2$ -CH<sub>3</sub> at the top of the column. The chlorination chamber was illuminated by two 200-watt bulbs and maintained at a tempera-ture near the boiling point of  $CH_3CClFCH_2CH_3$ . Chlorine was introduced into the researce of short 10 grams near here. ture near the bolling point of  $CH_3CClFCH_2CH_3$ . Chlorine was introduced into the reactor at the rate of about 10 grams per hour. The product was washed, dried, and rectified to give 11 grams of unreacted  $CH_3CClFCH_2CH_3$ , 32.4 grams of  $CH_3CClFCHClCH_3$ , 15 grams of  $CH_3CClFCH_2CH_2Cl_3$  and 17 grams of  $CH_3CCl_2CH ClCH_3$ . The latter compound probably resulted from the forma-tion of  $CH_3CCl=CHCH_3$  followed by addition of chlorine to the double bond. No  $CH_2ClCClFCH_2CH_3$  was observed, an in-dication that the alpha hydrogens are somewhat stabilized against substitution. against substitution. 2. Three bundre

Three hundred twelve grams of CH<sub>3</sub>CF<sub>2</sub>CHClCH<sub>3</sub> were chlorinated for 9 hours in the Muskat apparatus. During the last 3 hours the temperature at the top of the column was maintained at 89° C. in order to chlorinate some of the CH<sub>3</sub>CF<sub>2</sub>CCl<sub>2</sub>CH<sub>3</sub>. The reaction product was washed, dried, and rectified to give 100 grams of  $CH_3CF_2CCl_2CH_3$ , 65.0 grams of  $CH_3CF_2CHClCH_2Cl$ , 120 grams of  $CH_3CF_2CCl_2CH_2Cl$ , and 40 grams of  $CH_3CF_2CCl_2$ -CHCl₂.

Results of the chlorinations are very similar to those obtained by chlorinating in sunlight, in the presence of water (2). The chlorination of CH3CF2CH2CH2 gave 2 parts of CH3CF2CHClCH3 to about 2.5 parts of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, a higher proportion of the secondary isomer than was reported by Henne (2). This difference may have been due to a higher reaction temperature. A CCIF group is much less effective in directing substitutive chlorination away from the alpha position than CF<sub>2</sub> or CF<sub>3</sub> groups. For example, chlorination of CH<sub>2</sub>CClFCH<sub>2</sub>CH<sub>3</sub> in the modified Muskat apparatus yielded 44.9% CH<sub>3</sub>CClFCHClCH<sub>3</sub>, 20.8% CH3CCIFCH2CH2Cl, and 21.1% CH3CCl2CHClCH3. Chlorination of CH<sub>3</sub>CF<sub>2</sub>CHClCH<sub>3</sub> at 80-90 °C. gave 25.3% CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>-CH<sub>3</sub>, 16.4% CH<sub>2</sub>CF<sub>2</sub>CHClCH<sub>2</sub>Cl, 25.2% CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>CH<sub>2</sub>Cl, and 7.1% CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>CHCl<sub>2</sub>, an indication of increased reactivity of the secondary hydrogen atom under these conditions. Only beta hydrogen atoms were substituted in the partial chlorination of CH<sub>1</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, again an indication that hydrogen on a carbon atom is activated by the presence of a chlorine atom. Chlorination of CH3CF2CCl2CH3 gave CH3CF2CCl2CH2Cl and  $CH_3CF_2CCl_2CHCl_2$ . Further chlorination would probably have given CH<sub>3</sub>CF<sub>2</sub>CCl<sub>2</sub>CCl<sub>3</sub> as the only pentachloride. No trace of CH<sub>2</sub>ClCF<sub>2</sub>CCl<sub>2</sub>CH<sub>2</sub> was observed.

Dehydrochlorination of CH2CF2CH2CHCl2 with alcoholic potassium hydroxide at reflux temperature to yield CH<sub>2</sub>CF<sub>2</sub>CH= CHCl occurs with about the same ease as the formation of CH<sub>3</sub>-CF2CH==CH2 from CH2CF2CH2CH2CH2Cl (2). Also, CH2CF2CCl2-CH3 and CH3CF2CHClCH3 are similar in that neither reacts with alcoholic potassium hydroxide at reflux temperature. Dehydrohalogenation of CH<sub>3</sub>CF<sub>2</sub>CHClCH<sub>3</sub> occurs very slowly at 150° C., but substantial quantities of CH<sub>2</sub>CF<sub>2</sub>CH=CH<sub>2</sub> were formed with alcoholic potassium hydroxide at 200° C. Alcoholic potassium hydroxide at 24-40° C. converted CH<sub>3</sub>CClFCH<sub>2</sub>CH<sub>3</sub> to CH2=CFCH2CH3. The techniques used in these dehydrochlorinations are illustrated in the following examples:

1. Sixty-seven grams (0.411 mole) of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CHCl<sub>2</sub> were dripped into 28 grams (0.5 mole) of potassium hydroxide in 150 grams of 95% ethyl alcohol. The mixture was refluxed for one hour and steam-distilled, washed, dried, and rectified to give 35 grams of CH<sub>4</sub>CF<sub>2</sub>CH=CHCl. 2. Two moles of CH<sub>4</sub>CClFCH<sub>2</sub>CH<sub>2</sub> were treated with alco-holic potash at 25-40° C. for 18 hours. Six grams of CH<sub>2</sub>==CFCH<sub>2</sub>.

CH<sub>3</sub> were obtained, with the remainder of the material unreacted.

The effect of the electronegativity of the CF<sub>2</sub> group was further observed in the addition of hydrogen chloride to  $CH_3CF_2CH=-CH_2$ . Forty grams of CH<sub>2</sub>CF<sub>2</sub>CH=CH<sub>2</sub> and 10 grams of aluminum chloride were placed in a 12-inch test tube. The test tube was surmounted by a long dry-ice condenser, followed by a dry-ice trap. Dry hydrogen chloride was passed into the reaction mixture through a fritted glass disk for 8 hours, and the product then poured over cracked ice. The mixture was washed, steam-distilled, dried, and rectified to yield 10 grams of unreacted starting material and 37 grams of CH3CF2CH2CH2Cl. This addition of hydrogen chloride in the presence of aluminum chloride, to form exclusively CH<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, is the reverse of that predicted by Markownikoff's rule. Bromine added readily to CH<sub>3</sub>CF<sub>2</sub>CH= CH<sub>2</sub> to yield the expected product, CH<sub>3</sub>CF<sub>2</sub>CHBrCH<sub>2</sub>Br.

#### FLUORINATIONS

Some CH<sub>2</sub>CF=CHCH<sub>2</sub> was also formed, along with CH<sub>3</sub>CF<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>, in the treatment of CH<sub>2</sub>CCl=CHCH<sub>3</sub> with hydrogen

<sup>&</sup>lt;sup>1</sup> Present address, J. T. Baker Chemical Co., Phillipsburg, N. J.

		$T_{A}$	ble I.	Physical Properties and Analyses									
Compound	M.P., ° C.	B.P., °C. (745 Mm.)	° č.	d'4	$n \stackrel{t}{{}_{ m D}}$	Ct F		% Cl		Molar Refractivity			
						Caled.	Found	Caled.	Found	Caled.	Found		
$CH_{4}CH_{2}CF = CH_{4}$ $CH_{4}CF = CHCH_{4}$ $CH_{4}CF_{7}CH_{2}CHF_{7}$ $CH_{4}CF_{7}CH_{2}CHCH_{7}$ $CH_{4}CF_{7}CH_{2}CHCH_{4}$ $CH_{4}CF_{7}CH_{2}CH_{6}CH_{7}$ $CH_{4}CF_{7}CFCICH_{7}$ $CH_{4}CF_{7}CH_{2}CH_{7}CH_{7}$ $CH_{4}CF_{7}CCI_{7}CH_{7}$ $CH_{4}CF_{7}CCI_{7}CH_{7}$ $CH_{4}CF_{7}CCI_{7}CH_{7}$ $CH_{6}CF_{7}CCI_{7}CH_{7}$ $CH_{6}CF_{7}CCI_{7}CH_{7}$ $CH_{7}CF_{7}CH_{7}CH_{7}$ $CH_{7}CF_{7}CH_{7}CH_{7}$ $CH_{7}CF_{7}CH_{7}CH_{7}$ $CH_{7}CF_{7}CH_{7}CH_{7}$	-19 -12	$\begin{array}{c} 23.5\\ 26\\ 56.5\\ 72\\ 108\\ 123\\ 53\\ 79-51\\ 69\\ 102\\ 140-141\\ 165-167\\ 34\\ 155-157\end{array}$	0 	$\begin{array}{c} 0.824\\ \cdot\cdot\cdot\\ 1.157\\ 1.227\\ 1.215\\ \cdot\cdot\cdot\\ 1.357\\ 1.443\\ 1.556\\ 1.497\\ 1.933\end{array}$	$1.3492^{4}$ $$ $1.3720$ $1.4163$ $1.4220$ $1.3358$ $$ $1.3758$ $1.4238$ $1.4500$ $1.28$ $1.4594$	$\begin{array}{c} 29.5\\ 13.1\\ 13.1\\ 38.9\\ 46.2\\ 31.5\\ 19.3\\ 16.4\\ 57.4\\ 15.1\end{array}$	$\begin{array}{c} 29.3\\ 12.7\\ 13.0\\ 38.4\\ 46.6\\ 31.3\\ 19.2\\ 16.4\\ 58.0\\ 13.7\end{array}$	$\begin{array}{c} 28.0\\ 48.9\\ 48.9\\ 24.2\\ 21.5\\ 39.2\\ 53.9\\ 60.2\\ 53.9\\ 60.35\end{array}$	27.6 48.2 50.1 25.1 21.5 39.2 53.8 60.7 17.6 64.2) b	$ \begin{array}{c} 19.5 \\ 24.9 \\ 30.4 \\ 30.4 \\ 25.5 \\ \\ 30.5 \\ 35.4 \\ 40.4 \\ 36.3 \\ \end{array} $	19.5  24.5 30.3 30.3 25.2  30.6 34.8 40.1 35.7		
$a_t = 15^\circ \text{ C}.$ b Bomine.	. °Sealed	tube.	••	•••				(2.5	72.4				

fluoride at 360° C. in the presence of activated carbon impregnated with antimony pentachloride. Reaction of CH<sub>3</sub>CCl== CHCH<sub>3</sub> with hydrogen fluoride (4,  $\theta$ ) was conducted with about equimolar quantities of reactants and at temperatures from  $-78^{\circ}$ to  $+23^{\circ}$  C. to obtain substantial quantities of CH<sub>3</sub>CClFCH<sub>2</sub>CH<sub>3</sub>. The product consisted of 50.8% CH<sub>3</sub>CClFCH<sub>2</sub>CH<sub>3</sub>, 13.4% CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, and 11.4% CH<sub>3</sub>CCl<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>. With 2.5 moles of hydrogen fluoride per mole of CH<sub>3</sub>CCl=CHCH<sub>3</sub>, a 62.5% yield of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> was obtained, with only 2.8% CH<sub>3</sub>-CClFCH<sub>2</sub>CH<sub>3</sub> and 1.8% CH<sub>3</sub>CCl<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

Two dichloro-olefins,  $CH_3CCl=CClCH_3$  and  $CH_2=CClCH-ClCH_3$ , were treated with hydrogen fluoride at  $-78^{\circ}$  to  $+60^{\circ}$  C. to prepare  $CH_3CClFCHClCH_3$  and  $CH_3CF_2CHClCH_5$ , but products were mostly polymerized material with only small amounts of desired compounds and traces of  $CH_3CCl_2CHClCH_3$ .

Treatment of CH<sub>3</sub>CCl<sub>2</sub>CCl<sub>2</sub>CH<sub>2</sub> with hydrogen fluoride and red mercuric oxide yielded CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CF<sub>2</sub>CClFCH<sub>3</sub>, CH<sub>3</sub>CF<sub>2</sub>CCl<sub>2</sub>CH<sub>3</sub>, and CH<sub>3</sub>CClFCCl<sub>2</sub>CH<sub>3</sub>. The technique used in this fluorination may be illustrated as follows: A 1.5-liter Monel-lined steel autoclave, chilled to  $-78^{\circ}$ C., was charged with 196 grams (1 mole) of CH<sub>3</sub>CCl<sub>2</sub>CCl<sub>2</sub>CH<sub>3</sub>. 200 grams of dry toluene, 420 grams (21 moles) of hydrogen fluoride, and 432 grams (2 moles) of red mercuric oxide. The autoclave was sealed and heated at 107–110 ° C. for 46 hours; then it was cooled and the contents bled into an aqueous alkali trap in series with a dry-ice trap. The product was washed, dried, and rectified to give 25 grams of CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub>, 15 grams of CH<sub>3</sub>CF<sub>2</sub>CClFCH<sub>3</sub>, and traces of CH<sub>3</sub>CF<sub>2</sub>CCl<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CClFCCl<sub>2</sub>CH<sub>3</sub>.

Other similar experiments showed that the degree of fluorination depended upon time and temperature of reaction. The treatment of CH<sub>3</sub>CF<sub>2</sub>CCl<sub>2</sub>CH<sub>3</sub> with antimony trifluoride in the presence of antimony pentachloride also yielded CH<sub>3</sub>CF<sub>2</sub>CClFCH<sub>4</sub> and CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub>. The fluorination of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CHCl<sub>2</sub> proved to be difficult, presumably because of ease of splitting out hydrogen chloride and subsequent polymerization of CH<sub>3</sub>CF<sub>2</sub>-CH=CHCl. However, small amounts of two compounds boiling at 56–57° and 79–81° C., believed to be CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CHF<sub>2</sub> and CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CHClF, respectively, were obtained with hydrogen fluoride and mercuric oxide (1) at 100° C. Fluorination of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CCl<sub>3</sub> with either antimony trifluoride in the presence of antimony pentachloride or mercuric oxide and hydrogen fluoride resulted in the formation of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CCl<sub>2</sub>F and CH<sub>3</sub>-



Figure 1. Synthesis of Chlorofluorobutanes

 $CF_2CH_2CClF_2$ . The pentafluorobutane,  $CH_3CF_2CH_2CF_3$ , was also produced in fluorinations with mercuric oxide and hydrogen fluoride. Techniques used in these fluorinations are illustrated as follows:

1. Fifty-three grams (0.268 mole) of  $CH_3CF_2CH_2CCl_3$  were treated with 50 grams (0.279 mole) of antimony trifluoride and 10 grams (0.033 mole) of antimony pentachloride. After heating for 2 hours on a steam cone, the mixture was steam-distilled, dried, and rectified to give 1.5 grams of  $CH_3CF_2CH_2CCIF_2$ , 4.0 grams of  $CH_3CF_2CH_2CCI_2F$ , and 18.7 grams of unreacted starting material.

2. A 1.5-liter Monel-lined steel autoclave chilled to  $-78^{\circ}$  C. was charged with 90 grams (0.455 mole) of CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CCl<sub>3</sub>, 190 grams (9.5 moles) of hydrogen fluoride, and 162 grams (0.75 mole) of red mercuric oxide. The autoclave was sealed and heated at 88–95° C. for 27 hours, after which it was cooled to 75° Products were bled into an aqueous alkali trap, washed, dried, and rectified to give 9.8 grams of  $CH_3CF_2CH_2CF_3$ , 2.0 grams of  $CH_3CF_2CH_2CFCl_2$ , traces of  $CH_3CF_2CH_2CFCl_2$ , and 2.0 grams of starting material.

The compounds prepared were identified by boiling point analogies and halogen analyses. Purification was accomplished by careful rectification in a Podbielniak type column. Table I summarizes the physical constants and halogen analyses.

#### LITERATURE CITED

- (1) Henne, A. L., J. Am. Chem. Soc., 60, 1569–71 (1938).
- (2) Henne, A. L., and Hinkamp, J. B., Ibid., 67, 1194-7 (1945).
- (3) Henne, A. L., Hinkamp, J. B., and Zimmerschied, W. J., Ibid., 67, 1906-8 (1945)
- Henne, A. L., and Plueddeman, E. P., Ibid., 65, 1271-2 (1943). (4)(5) Muskat, I. E., and Northrup, H. E., Ibid., 52, 4043-55, esp. 4051-
- 2(1930).
- (6) Renoll, M. W., Ibid., 64, 1115-16 (1942).
- Robbins, B. H., J. Pharmacol., 86, 197-204 (1946).
   Tishchenko, D. V., J. Gen. Chem. (U.S.S.R.), 8, 1232-45 (1938).

ABSTRACTED from a thesis submitted to the faculty of Purdue University by W. R. Hausch in partial fulfillment of the requirements for the degree of doctor of philosophy.

# **DIRECT BROMINATION OF FLUORINATED ALKANES**

E. T. McBee, H. B. Hass, W. G. Toland, Jr.<sup>1</sup>, and A. Truchan PURDUE UNIVERSITY AND PURDUE RESEARCH FOUNDATION, LAFAYETTE, IND.

SEVERAL new bromofluoro- and bromochlorofluoroalkanes have been prepared by thermal bromination, at 400 500° C., of the corresponding fluoro- or chlorofluoroalkane.

**NHIS** work was initiated for the purpose of making certain alkanes containing bromine and fluorine available for pharmacological tests and is an extension of the work reported previously (3-6). Bromofluoroalkanes have been prepared by replacement of a part of the bromine in a polybromoalkane with fluorine or by the addition of bromine or bromine chloride to a fluoroalkene. Recently the preparation of bromine- and fluorine-containing halocarbons by vapor-phase bromination of the corresponding fluorohydrocarbon was reported (1).

An independent investigation conducted in this laboratory resulted in the synthesis of several new bromofluoroalkanes by the substitution of bromine for hydrogen in a fluorohydrocarbon at temperatures in the range 400-500 °C. Below 400 ° the bromination rate was undesirably low, whereas carbonization of the starting material occurred at temperatures appreciably above 500 ° C.

#### THERMAL BROMINATIONS

The compound to be brominated was bubbled through liquid bromine; the mixed vapors then passed into a reactor of Pyrex tubing 120 cm. in length and 1 cm. in diameter. A Carius tube furnace was used to heat the reaction zone. Exit gases passed from the reactor into ice water, which condensed brominated

<sup>1</sup> Present address, California Research Corporation, Richmond, Calif.

products and dissolved the resultant hydrogen bromide. Unreacted bromine was seldom detected in the exit gases at reaction temperatures above 400 ° C. unless the temperature of the bromine was allowed to rise to its boiling point. Unreacted starting material containing small amounts of brominated products passed from the ice-water trap through a drying tower and condensed in a dry-ice trap. The brominated products were separated from the water, washed, dried, and rectified. All unreacted material in the dry-ice receiver was also rectified before recycling. Physical constants of new compounds prepared by the process are summarized in Table I.

1,1,1-Trifluoroethane (0.33 mole, 0.15 mole per hour) was passed through liquid bromine at 45° C., vaporizing a total of 0.14 mole of the bromine. The mixed vapors were passed into the reactor at 500 ° C. The contact time was about 25 seconds. Rectification gave CF<sub>3</sub>CH<sub>2</sub>Br, CF<sub>3</sub>CHBr<sub>2</sub>, unreacted CF<sub>3</sub>CH<sub>3</sub>, and traces of CF<sub>2</sub>BrCH<sub>2</sub>Br and CF<sub>3</sub>CBr<sub>3</sub>. Yield of CF<sub>3</sub>CH<sub>2</sub>Br was 50% and that of CF<sub>3</sub>CHBr<sub>2</sub>, 7%. Variations in reaction conditions were found to change the relative amounts of brominated products formed. Both CF<sub>3</sub>CHBr<sub>2</sub> and CF<sub>3</sub>CBr<sub>3</sub> are new compounds. As no isomers are possible without rearrangement, structures of the latter compounds are established. 1,2-Dibromo-1,1-difluoroethane was formed as a by-product, probably as a result of dehydrofluorination of CF<sub>3</sub>CH<sub>3</sub> followed by addition of bromine to  $CF_2$ =CH<sub>2</sub>. In contrast to the vapor-phase chlorination of  $CF_3CH_3$ , in which the chlorination of the first product  $(CF_3CH_2Cl)$  proceeds at a more rapid rate than the chlorination of starting CF<sub>3</sub>CH<sub>3</sub>, the rate of bromination of CF<sub>3</sub>CH<sub>2</sub>Br is apparently much lower than that of CF<sub>3</sub>CH<sub>3</sub>. This is evidenced

	B. P.,				% F		% Cl		% Br		Molar Refractivity	
Compounds	°Ĉ.'	$d'_4$	t, °C.	$n'_{\rm D}$	Caled.	Found	Calcd.	Found	Caled.	Found	Caled.	Found
$CF_{3}CHBr_{2}$ $CF_{3}CH_{2}CH_{2}Br$ $CF_{4}CH_{2}CH_{2}Br$ $CF_{5}CHBrCH_{2}Br$ $CF_{2}CICHBrCH_{3}Br$ $CF_{4}CICH_{2}CH_{3}Br$ $CF_{4}CCIBrCH_{3}$	73 62-62.5 111 115.8 90 101 69	2.224 1.653 2.086 2.121 1.662 1.726 1.708	24 25 26 24 25 24 25	$1.4029^{a} \\ 1.3572 \\ 1.4242 \\ 1.4281^{b} \\ 1.4045 \\ 1.4140 \\ 1.3790$	23.532.122.222.219.619.626.9	23.2 33.2 22.7 21.8 19.6 19.9 27.4	18.3 18.3 18.3 16.8	18.3 17.7 16.8	66.1 45.1 62.3 62.3 41.2 41.2 37.8	$\begin{array}{c} 66.2 \\ 45.4 \\ 62.3 \\ 62.5 \\ 41.2 \\ 39.8 \\ 37.9 \end{array}$	26.9 23.8 31.5 28.6 28.6 28.6 28.6	26.5 23.4 31.3 31.1 28.5 28.0 28.5