Bromination of 1-ethyl-3,3,4,4-tetrafluorocyclobutene. About 9.90 g. (0.0642 mole) of 1-ethyl-3,3,4,4-tetrafluorocyclobutene, 10.27 g. (0.0643 mole) of bromine, and 0.2 ml. of a saturated aqueous solution of acetamide were sealed in an air-free pyrex tube. The tube was wrapped in foil and heated for 24 hr. at 100°. The entire amount of bromine was consumed. On opening the tube a large amount of hydrogen bromide escaped and 15.5 g. of crude products were obtained. Distillation yielded 1.2 g. of recovered starting material, 5 g. of an unsaturated monobromide, and more highly brominated products. The monobromide had the following properties: b.p. 73–74° (50 mm.), n_D^{25} 1.4171, d_4^{25} 1.687. The molar refraction calculated for an unsaturated monobromocyclic compound, $C_6H_5BrF_4$, was 35.73, while that observed was 34.74.

Anal. Calcd. for $C_6H_5BrF_4$: C, 30.9; H, 2.16; Br, 34.3. Found: C, 30.4: H, 2.42; Br, 33.8.

Tribromination. Nine grams (0.058 mole) of 1-ethyl-3,3,4,4-tetrafluorocyclobutane and 16 g. (0.10 mole) of bromine were refluxed and irradiated with ultraviolet light for 1 day. All the bromine was consumed, hydrogen bromide evolved, and 17 g. of crude products obtained. Distillation revealed a complex mixture of products from which 1.9 g. of an unsaturated tribromide b.p. 88–90° (6 mm.), n_D^{25} 1.5095, was isolated.

Anal. Calcd. for $C_6H_3BrF_4$: Br, 61.34. Found: Br, 61.75.

Attempted cyclization of propargyl chloride and tetrafluoroethylene. An equimolar mixture of propargyl chloride and tetrafluoroethylene was heated in an air-free stainless steel autoclave in the presence of terpene B inhibitor. While heating, the mixture detonated at about 150°.

Debromination of 1,2-dibromohexafluorocyclobutane. About 18.6 g. of 1,2-dibromohexafluorocyclobutane from bromotrifluoroethylene cyclization was added dropwise to a stirred slurry of 24 g. of zinc dust, activated previously by 0.5 ml. concd. hydrochloric acid, in 30 ml. of dibutoxytetraethylene glycol applying no heat. In an exothermic reaction, 8.0 g. (88%) of hexafluorocyclobutene boiled from the mixture. The product was identified as hexafluorocyclobutene by comparison of its spectrum with that of an authentic sample and by gas density molecular weight determination. This product had a molecular weight of 160 while that calculated for C_4F_6 is 162.

1,2-Dibromo-3,3,4,4-tetrafluorocyclobutene. About 0.0585 mole of activated zinc dust, prepared from 5.86 g. of 93% zinc dust plus 4 ml. of concd. hydrochloric acid, was added in small portions to a stirred solution of 26 g. (0.0585 mole) of 1,1,2,2 tetrabromotetrafluorocyclobutane in 80 ml. of ether at −80°. After zinc addition was complete, the mixture was stirred for 4 hr. at −80°, then was allowed to warm slowly, and was stirred for 1 day at room temperature. Volatile materials were removed from the reaction mixture under reduced pressure and distilled to yield 4 g. (24%) of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene, b.p. 92–94° (635 mm.), n_D^{25} 1.4222, d_4^{25} 2.112. The molar refraction calculated for 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene structure was 34.14, while that observed was 34.17.

Anal. Calcd. for $C_4Br_2F_4$: C, 16.9; H, 0.0; Br, 56.3. Found: C, 16.9; H, 0.06; Br, 56.3.

Other attempted cycloadditions. Trifluoroethylene. Twenty-two grams of trifluoroethylene was treated for 30 hr. at 180° in an air-free Pyrex tube in the presence of hydroquinone and terpene B. From this reaction 86% of the trifluoroethylene was recovered and no 1,1,2,2,3,4-hexafluorocyclobutane formed. The latter is reported to boil at 27°.[11]

2-Chloro-1,1-difluoroethylene. Forty-two grams of 2-chloro-1,1-difluoroethylene was heated for 1 day at 180° and 1 day at 195° in the manner described above. No products boiling above room temperature were formed, but 86% of the starting material was recovered.

2-Bromo-1,1-difluoroethylene. Ninety-three grams of 2-bromo-1,1-difluoroethylene was heated for 1 day at 160° and 1 day at 180° as described above. No products boiling above room temperature were formed and 95% of the starting material was recovered.

Acknowledgment. We wish to express our appreciation to the Wright-Patterson Air Force Base, Ohio and to the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, for their support of this work.

BOULDER, COLO.

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(11) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 61 (1956).

[CONTRIBUTION FROM THE SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENCE]

Addition of Alcohols to Fluorinated Ethylenes

ARIEH DEMIEL[1a]

Received October 20, 1959

The sodium alkoxide-catalyzed addition of primary alcohols to 1-bromo-2,2-difluoro-, 1,1-dibromo-2,2-difluoro-, and 1-bromo-1,2,2-trifluoroethylene has been studied. Properties of the products and infrared data are reported.

This paper parallels to some extent and supplements the recent publication of Park[1b] on the addition of ethanol to fluorobromoethylenes in the presence of alcoholic potassium hydroxide. It reports the addition of methyl, ethyl, and *n*-propyl alcohol to 1-bromo-2,2-difluoro-, 1,1-dibromo-2,2-difluoro-, and 1-bromo-1,2,2-trifluoroethylene

$$F_2C{=}CHBr \qquad F_2C{=}CBr_2 \qquad F_2C{=}CFBr$$

using the respective sodium alkoxides as catalyst.[2]

$$RO{\cdot}CF_2{\cdot}CH_2Br,\ RO{\cdot}CF_2{\cdot}CHBr_2,\ RO{\cdot}CF_2{\cdot}CHBrF$$

The physical properties and the analytical data for the compounds so obtained are summarized in Table I. The three ethoxy compounds ($R = C_2H_5$)

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(1) (a) This paper forms part of the Ph.D. thesis, submitted by the author to the Hebrew University, Jerusalem.

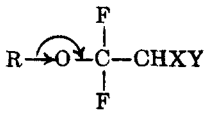
(1) (b) J. D. Park, H. J. Cummings, and J. R. Lacher, *J. Org. Chem.*, **23**, 1785 (1958).

(2) See W. T. Miller, E. W. Fager and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

have previously been described by Swarts[3,4] who prepared them from 1,2-dibromo-1,1-difluoro-, 1,2,2-tribromo-1,1-difluoro-, and 1,2-dibromo-1,1,2-trifluoroethane, respectively, with sodium ethoxide or alcoholic potassium hydroxide. In these syntheses, too, the above three ethylenes are possibly formed as intermediates (by dehydrohalogenation).

The ethers derived from 1-bromo-2,2-difluoroethylene are stable in the presence of *large* quantities of water and still more stable in the presence of alkali; in contact with *small* quantities of water or humid air they decompose quickly and liberate hydrogen fluoride which appears to catalyze the decomposition, leading to the formation of bromoacetate or free bromoacetic acid. It was, thus, not possible to obtain satisfactory analyses for these ethers. The ethers derived from 1,1-dibromo-2,2-difluoroethylene showed this tendency to decompose in a much lesser degree, those derived from bromotrifluoroethylene not at all, with the exception of the propyl ether. The latter underwent far-reaching changes upon standing at room temperature in the presence of calcium chloride. The boiling point changed from 75.2° to 55–56° (at 130 mm.) and became unsharp, the density decreased from d^{15} 1.487 to 1.02 and the refractive index from n_D^{16} 1.3848 to 1.3825. Similar observations have been reported by Rapp[5] for the stability of (1,1,2-trifluoro-2-chloroethyl) *t*-butyl ether. The thermal stability of the ethers described shows the same sequence. The lower ethers derived from bromotrifluoroethylene distill without decomposition under atmospheric pressure, the propyl ether only under reduced pressure; those derived from 1,1-dibromo-2,2-difluoroethylene can only be distilled *in vacuo* (25–30 mm.), and those obtained from 1,1-difluoro-2-bromoethylene decompose upon prolonged heating in a column even under reduced pressure.

Tarrant[6] has suggested that the tendency of ethers of the type discussed here to form fluoride ions, depends essentially on the electron-donating power of the alkyl radical; the greater this power, the less stable the ether:



$$R\rightarrow O\rightarrow \overset{F}{\underset{F}{C}}-CHXY$$

It appears that the number and negativity of electronegative elements in the [—CHXY group, too, influence the stability of the ethers. The more this group attracts electrons, the less tendency will be felt to form fluoride ions, and, therefore, the greater will be the stability of the ethers. One would thus expect the sequence

$$-CHFBr > -CHBr_2 > -CH_2Br$$

which is, indeed, the order of stability observed in the present experiments.

Table I shows that the atomic refraction of fluorine (calculated from the molecular refraction and the known equivalents of carbon, hydrogen, ether-oxygen and bromine) varies between 1.1 for the compounds containing three atoms of fluorine and 0.9 for those with only two fluorine atoms. A similar effect has been noted for the fluorobromoethanes and ethylenes.[7]

In Table II, the infrared spectra of some of the fluorinated ethers prepared, are summarized. A complete assignment of the infrared frequencies has not been successful. The CF_2 frequency is expected between 1200 and 1350 cm.$^{-1}$, in a region in which the asymmetric stretching frequency of the C—O—C group is also situated. The peak at about 1150 cm.$^{-1}$ can be ascribed to the C—F bond; the second (symmetric) C—O—C stretching frequency lies in *fluorinated* ethers at 1050 cm.$^{-1}$.[8]

EXPERIMENTAL

Starting materials. 1-Bromo-2,2-difluoro-, 1,1-dibromo-2,2-difluoro-, and *1-bromo-1,2,2-trifluoroethylene* were prepared from 1,2-dibromo-1,1-difluoroethane, 1,2,2-tribromo-1,1-difluoroethane and 1,2-dibromo-1,2,2-trifluoroethane, respectively, by treatment with aqueous potassium hydroxide. Details on these preparations will be published elsewhere.

General procedure for the addition reactions. A three necked flask, mounted with gas disperser, thermometer, stirrer and Y-tube carrying a reflux condenser and a thermometer to measure the temperature of the returning distillate, was used for the experiments; they were carried out in an atmosphere of dry and pure nitrogen. In the cases of bromotrifluoro- and bromodifluoroethylene the condenser was placed in a Dewar vessel filled with acetone–Dry Ice mixture; in the third case water was circulated through the condenser. The alcohols used were anhydrous in all experiments.

2-Bromo-1,1,2-trifluoroethyl methyl ether. The flask was cooled at −10° and a cold (−78°) solution of 18 g. of bromotrifluoroethylene in 25 ml. of methanol introduced. After adding dropwise a solution of 0.5 g. of sodium in 20 ml. of methanol, the temperature of the liquid was slowly raised to 16°. (From time to time, renewed cooling became necessary, as the reflux condenser became flooded.) The temperature of the returning distillate decreased to 3°; when it rose again to 16°, the flask was slowly heated to 60°. The product was then isolated by addition of water, dried with calcium chloride, and distilled. Thus 13.7 g. (63%) of the desired ether was obtained, b.p. 88.8°.

2-Bromo-1,1,2-trifluoroethyl ethyl ether. In the manner described above, 0.5 g. sodium in 20 ml. of ethanol was added to a solution of 21 g. of bromotrifluoroethylene in 25 ml. of ethanol at −15°. When the bath was removed, the temperature rose spontaneously to 55°, and the olefin began to boil. However, after some interval of time, the boiling

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(3) F. Swarts, *Bull. Acad. Roy. Belges*, [3], **37**, 357 (1899).

(4) F. Swarts, *Bull. Acad. Roy. Belges*, 563 (1911).

(5) J. T. Baur and K. E. Rapp, *J. Am. Chem. Soc.*, **72**, 4480 (1950); K. E. Rapp, J. T. Barr, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Am. Chem. Soc.*, **74**, 749 (1952).

(6) P. Tarrant and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 1781 (1951).

(7) Results to be published shortly.

(8) J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am Chem. Soc.*, **73**, 862 (1951).

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF ADDITION PRODUCTS

Compound	B.P. (°/mm.)	d_4^t	n_D^t	MR (found)	AR_F[b]	C Found	C Calcd.	H Found	H Calcd.	Br Found	Br Calcd.	F Found	F Calcd.
CH_3OCF_2CHFBr	88.8/760	1.721^{18}	1.3687^{18}	25.28	1.04	18.9	18.7	2.3	2.1	41.1	41.4	29.6	29.5
$C_2H_5OCF_2CHFBr$[a]	106/760	1.573^{20}	1.3744^{20}	30.08	1.10	23.5	23.2	2.9	2.9	38.9	38.6	27.6	27.5
n-$C_3H_7OCF_2CHFBr$	75.2/130	1.487^{15}	1.3848^{15}	34.81	1.13	26.7	27.2	4.0	3.7	36.6	36.2	25.8	25.8
$CH_3OCF_2CHBr_2$	55.8/130	2.101^{15}	1.4540^{15}	32.73	0.85	14.4	14.2	1.8	1.6	63.1	62.9	15.0	15.0
$C_2H_5OCF_2CHBr_2$	65/26	1.914^{15}	1.4472^{15}	37.41	0.88	17.9	17.9	2.4	2.3	60.0	59.7	14.3	14.2
n-$C_3H_7OCF_2CHBr_2$	72.2/23	1.794^{15}	1.4480^{15}	42.08	0.91	21.6	21.3	3.1	2.9	57.1	56.7	13.2	13.5
$CH_3OCF_2CH_2Br$	54.7/220	1.653^{18}	1.3898^{18}	25.08	0.91								
$C_2H_5OCF_2CH_2Br$[a]	70/175	1.527^{15}	1.3958^{15}	29.73	0.92								

[a] These compounds have been recently described by Park[1]: $C_2H_5OCF_2CH_2Br$: b.p. 55–56°/104 mm.; d_4^{25} 1.512, n_D^{25} 1.3980; $C_2H_5OCF_2CHFBr$: b.p. 62–62.5°/167 mm.; d_4^{25} 1.571; n_D^{25} 1.3710. [b] Calcd. from MR and the atomic refraction of carbon, hydrogen, bromine, and ether oxygen.

TABLE II

INFRARED SPECTRA OF THE FLUORINATED ETHERS

Substance																
CH_3OCF_2CHFBr	3015		1475		1370		1290	1220		1150	1055 (broad)	990		830	746	717
$C_2H_5OCF_2CHFBr$	3035		1460		1370		1285	1200			1055 (broad)		903	830	735 (broad)	
$C_3H_7OCF_2CHFBr$	3000		1480	1410	1370		1280	1195			1055 (broad)	980	955	848	750	727
$CH_3OCF_2CHBr_2$	3015	(3000)	1470				1282	1210		1136	1050 (broad)	990		823	741	700
$C_2H_5OCF_2CHBr_2$	3035	(3000)	1460		1390		1290	1190		1145	1030 (broad)		912	827	747	700
$C_3H_7OCF_2CHBr_2$	3000		1475	1410	1390	1360	1290	1230	1190	1150	1045 (broad)	975	955	844	746	700

ceased (no more refluxing liquid), and the desired ether could be isolated by addition of water; yield, 16.5 g. (61%); b.p. 106°.

2-Bromo-1,1,2-trifluoroethyl n-propyl ether. In the same manner, the reaction between 16 g. of bromotrifluoroethylene in 25 ml. of *n*-propyl alcohol and 0.5 g. of sodium in 20 ml. of propanol was carried out. The temperature rose spontaneously to 77°. The propanol was removed *in vacuo* and the product purified by distillation, b.p. 76° (130 mm.); yield, 16 g. (73%).

2,2-Dibromo-1,1-difluoroethyl methyl ether. In the manner described above, a few drops of a solution of 0.25 g. of sodium in 10 ml. of methanol were added to a solution of 25 g. of 1,1-dibromo-2,2-difluoroethylene in 30 ml. of methanol. A lively exothermic reaction took place. The balance of the sodium methoxide solution was added with cooling so that the temperature of the mixture did not exceed 40°. The ether was isolated by addition of water, dried and distilled, b.p. 55.8° (30 mm.); yield, 22 g. (77%).

2,2-Dibromo-1,1-difluoroethyl ethyl ether. To a solution of 24 g. of 1,1-dibromo-2,2-difluoroethylene in 30 ml. of alcohol, a solution of 0.5 g. of sodium in 20 ml. of ethanol was added, until further addition did not cause any more rise in temperature. Water was added and the ether dried over calcium chloride and distilled. It boiled at 65° (26 mm.); yield, 23 g. (79%).

2,2-Dibromo-1,1-difluoroethyl n-propyl ether. The reaction between 23 g. of 1,1-dibromo-2,2-difluoroethylene in 30 ml. of *n*-propyl alcohol and 0.5 g. of sodium in 20 ml. of the same solvent was carried out as in the foregoing case. The reaction was completed by heating the mixture at 90° for 30 min. and the excess *n*-propanol removed under reduced pressure. The product boiled at 72° (23 mm.); yield, 21 g. (72%).

With *isopropanol*, no reaction took place under the same operating conditions.

2-Bromo-1,1-difluoroethyl methyl ether. At −15°, a solution of 0.5 g. of sodium in 20 ml. of methanol was added to a solution of 20 g. of 1-bromo-2,2-difluoroethylene in 25 ml. of methanol. The mixture was slowly brought to room temperature and kept until the reflux ceased. As the product forms an azeotrope with methanol, it was precipitated by addition of water, dried and distilled; yield, 13.5 g. (61%). It boiled at 98° (760 mm.) or 58° (210 mm.). Upon standing for 4 days, it began to decompose and liberated hydrogen fluoride; at this stage, it had become impossible to distill the product without complete decomposition.

2-Bromo-1,1-difluoroethyl ethyl ether. In the same manner, the ethyl ether (b.p. 70° (175 mm.); yield, 12 g. (60%)) was obtained from 16.8 g. of 1-bromo-2,2-difluoro-ethylene in 25 ml. of alcohol and 0.5 g. of sodium in 20 ml. of ethanol. The product showed the same behavior as the methyl ether.

TEL-AVIV, ISRAEL

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY OF THE DEPARTMENT OF SURGERY,
UNIVERSITY OF WASHINGTON SCHOOL OF MEDICINE]

Derivatives of Fluorene. VIII. Fluorofluorenes. II[1]

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Further work is reported concerning ring-fluorinated 2-acetamidofluorene (a carcinogen), and related compounds. Improved preparation of the 4- and 5-fluoro isomers is described together with preparation of the new 1-fluoro and 8-fluoro-2-acetamidofluorenes. Monodemethylation of the $—N(CH_3)_2$ group is encountered in an attempted Schiemann decomposition. Some observations concerning the directive effect of substituent fluorine in nitration of the fluorene nucleus are noted.

This paper describes the preparation of further new *N*-2-(monofluorofluorenyl)acetamides[2] and related compounds, and better methods for some previously reported members of this series.

We have found the following method preferable for making *N*-2-(4-fluoro-fluorenyl)acetamide, a compound described in the previous paper in this series.[1] *m*-Nitroaniline was iodinated by modification of a known procedure.[3] The diazonium fluoborate of this substance gave the corresponding fluoro compound. The yield in this step was improved from very poor to above 40% by rapid heating (170°) in sand under aspirator vacuum. Lower temperatures and longer time, which had improved yields in some of our decompositions, led to greatly increased tar formation—perhaps because of the substituent iodine. An Ullmann reaction followed by hydrolysis, separation and cyclization gave 4-fluoro-2-nitrofluorenone. Reduction of the nitro group[1] and then of the 9-keto followed by acetylation, all as described in the Experimental section, yielded the desired product.

In an improved approach to the 2,5-isomer we began with 4-carboxyfluorenone[1] and, by way of the known acid chloride, azide and 4-aminofluorenone, obtained fluorenone-4-diazonium fluoborate. When this was decomposed in sand, 60% yields of 4-fluorofluorenone were recovered, but when heated in suspension in toluene (in this case at 60–65°), 70% yields were obtained with much greater convenience. Reduction gave the known 4-fluorofluorene.[1]

Use of a liquid medium in decomposing diazonium fluoborates is not new, but suspension in benzene, toluene, xylene,[4] chloro-, or bromo-

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(1) This work was supported in part by a grant (C-1744) from the National Cancer Institute, U. S. Public Health Service. For the preceding paper in the fluorofluorene series see *J. Am. Chem. Soc.*, **81**, 1092 (1959).

(2) These compounds are being tested for carcinogenicity and in metabolic studies by Drs. J. A. and E. C. Miller at the McArdle Memorial Laboratory, The University of Wisconsin.

(3) M. P. Brenans and M. A. Haller, *Compt. rend.*, **138**, 1503 (1904).

(4) A. Roe and G. F. Hawkins, *J. Am. Chem. Soc.*, **71**, 1785 (1949). A. Roe, *Organic Reactions*, Vol. V, John Wiley and Sons, New York, N. Y., 1949, p. 211.