267. *Organic Fluorine Compounds. Part V.* The Instability of Some Sodium 1 : 1-Di-*H*-perfluoroalkoxides and its Effect on the Yields of Fluoro-ethers.*

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Sodium 2 : 2 : 2-trifluoroethoxide and 1 : 1-di-*H*-heptafluorobutoxide liberate fluoride ion in ethers and on dry pyrolysis. 1 : 1-Di-*H*-perfluoro-alcohol is also formed in the latter reaction.

Conditions have been established for the preparation of some fluoro-ethers in improved yields.

ALTHOUGH sodium 1 : 1-di-*H*-perfluoroalkoxides have been used for the synthesis of partially-fluorinated ethers,[1,2] yields have only been fair. Further, we have found no reference to the difficulty of isolating fluoroalkoxides free from fluoride ion.

We have shown that condensation of sodium fluoroalkoxides with toluene-*p*-sulphonates of unfluorinated alcohols is not straightforward. Thus, interaction of equivalent amounts of hexamethylene ditoluene-*p*-sulphonate and sodium 1 : 1-di-*H*-heptafluorobutoxide in dioxan at 80° gave the diether (I) and an appreciable amount of the monotoluene-sulphonate (II). Similar condensation with butyl toluene-*p*-sulphonate and sodium heptafluorobutoxide in diethylene glycol diethyl ether, gave butyl heptafluorobutyl ether in 55—60% yield, and nine unidentified products. Recovery of 13% of sodium as sodium fluoride indicated that the low yields of ethers were caused by loss of alkoxide through elimination of fluoride ion.

(I) $C_3F_7{\cdot}CH_2{\cdot}O{\cdot}[CH_2]_6{\cdot}O{\cdot}CH_2{\cdot}C_3F_7$ $\qquad$ $C_3F_7{\cdot}CH_2{\cdot}O{\cdot}[CH_2]_6{\cdot}OTs$ (II)

Investigation of the breakdown of 1 : 1-di-*H*-perfluoroalkoxides was hampered by difficulty in obtaining them free from fluoride ion. Indeed, pure sodium heptafluorobutoxide has not been obtained, although slightly contaminated salt was prepared by a rapid reaction with sodium and a large excess of the fluoro-alcohol in ether. Exchanges with sodium methoxide and heptafluorobutanol in methanol or ether, followed by removal of solvents or precipitation with benzene, gave products of unknown composition, free from unfluorinated alcohol but severely contaminated with fluoride ion. Sodium trifluoroethoxide is much less susceptible to degradation, and pure material was prepared by the rapid action of sodium on the alcohol in ether.

Elimination of fluoride ion from sodium trifluoroethoxide in dioxan was slow at room

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* Part IV, *J.*, 1956, 3199.

[1] Henne and Smook, *J. Amer. Chem. Soc.*, 1950, **72**, 4378.

[2] McBee and Weesner, U.S.P. 2,452,944; *Chem. Abs.*, 1949, **43**, 2219.

temperature but rapid at 100°. Analysis of the precipitate showed that the elimination was limited to 0·66 mole of sodium fluoride per mole of fluoroalkoxide (Table 1).

TABLE 1.

$CF_3{\cdot}CH_2{\cdot}ONa$ (mmole)	Time (hr.)	Temp. (° C)	Precipitate F, %	Precipitate NaF, %	NaF (mmole)	$NaF/CF_3{\cdot}CH_2{\cdot}ONa$ (mol.)
4·48	24	50	15·2	33·6	1·90	0·42
4·28	5	100	14·5	32·1	0·51	0·12
4·14	24	100	20·2	44·6	2·66	0·64
4·69	70	100	20·9	46·2	3·09	0·66
4·43 *	1 2·5	120 140	20·1	44·4	2·18	0·49

* In diethylene glycol diethyl ether.

Degradation of solid sodium trifluoroethoxide was violent at about 180° at atmospheric pressure under nitrogen, with formation of carbon and liberation of fluoride ion. Pyrolysis of sodium trifluoroethoxide and of sodium heptafluorobutoxide *in vacuo* at 140—150° gave the corresponding fluoro-alcohols, and equimolar quantities of sodium fluoride. The amount of heptafluorobutanol formed was 47% of the weight of alkoxide pyrolysed.

Formation of fluoro-alcohol during breakdown of the solid is remarkable. The reaction can best be represented by a disproportionation according to the formal equation:

$$2R_f{\cdot}CH_2{\cdot}ONa \longrightarrow R_f{\cdot}CH_2{\cdot}OH + R_f{\cdot}CH(Na){\cdot}ONa \quad (III)$$

$$(R_f = \text{perfluoroalkyl})$$

Concurrent formation of sodium fluoride may take place by ejection of fluoride ion (with the sodium) from compounds (III) which are related to the heat-sensitive metal perfluoroalkyls.[3] Thermal breakdown of unfluorinated sodium alkoxides of comparable size takes place at 250—350°, and unlike that of sodium fluoroalkoxides, appears to involve rupture of the alkyl–oxygen bond, yielding sodium hydroxide and unsaturated hydrocarbons.[4] The presence of the electronegative perfluoroalkyl group is reflected in the relative volatility and easy solubility in ethers of these sodium 1 : 1-di-*H*-perfluoroalkoxides. Their solubility is not inconsistent with the distribution, by induction, of the source of a high electric field on the fluoroalkoxide anion, and with the likely solvation of the sodium cation. Inductive effects may also explain the lability of the hydrogen atoms, the weakness of the oxygen–sodium link, and hence the low temperature of breakdown to yield fluoro-alcohol.

The easy elimination of fluoride ion in ethers, with formation of some sodium fluoride, may be accounted for by unimolecular (1) or bimolecular (2) ejection of fluoride ion, *e.g.*,

$$\begin{array}{ll}
(1) & CF_3{\cdot}CH_2{\cdot}O^- + CF_3{\cdot}CH_2{\cdot}ONa \rightleftharpoons CF_3{\cdot}CH_2{\cdot}OH + CF_3{\cdot}\bar{C}H{\cdot}ONa \\
 & CF_3{\cdot}\bar{C}H{\cdot}ONa \longrightarrow CF_2{:}CH{\cdot}ONa + F^- \\
 & CF_3{\cdot}CH_2{\cdot}O^- + CF_2{:}CH{\cdot}ONa \rightleftharpoons CF_3{\cdot}CH_2{\cdot}OH + CF_2{:}\bar{C}{\cdot}ONa \\
 & CF_2{:}\bar{C}{\cdot}ONa \longrightarrow CF{\vdots}C{\cdot}ONa + F^- \\
(2) & CF_3{\cdot}CH_2{\cdot}O^- + CF_3{\cdot}CH_2{\cdot}ONa \longrightarrow CF_3{\cdot}CH_2{\cdot}OH + F^- + CF_2{:}CH{\cdot}ONa \\
 & CF_3{\cdot}CH_2{\cdot}O^- + CF_2{:}CH{\cdot}ONa \longrightarrow CF_3{\cdot}CH_2{\cdot}OH + F^- + CF{\vdots}C{\cdot}ONa
\end{array}$$

The overall stoicheiometry of both mechanisms is identical, and the ultimate yield of sodium fluoride is 0·66 mol. of alkoxide, in agreement with the value determined experimentally. Alcoholic solutions of the fluoroalkoxides remain free from fluoride ion even at the boiling point, as do aqueous alkaline (5N) solutions of trifluoroethanol and heptafluorobutanol. This dependence of fluoride-ion elimination on solvent can be interpreted in terms of the equilibrium shown in scheme (1). In presence of excess of an alcohol or water, carbanion formation would be effectively suppressed.

The reaction of sodium fluoroalkoxides with unfluorinated toluenesulphonates in ethers is faster than that of breakdown, and provided the sodium salt is prepared rapidly

[3] Musgrave, *Quart. Reviews*, 1954, **8**, 344.

[4] Durand, *Compt. rend.*, 1921, **172**, 1504.

and used in excess (25%), good yields of fluoro-ethers can be obtained (Table 3) at 70—90°. The aqueous alkylation described by Faurote *et al.*[5] gave fluoro-ethers in only fair yield. Our failure to prepare diheptafluorobutyl ether from heptafluorobutyl toluene-*p*-sulphonate and sodium heptafluorobutoxide in non-aqueous medium can now be attributed to the accelerated decomposition of the alkoxide at 150—220° as required to activate the fluorinated toluene-*p*-sulphonate.[6] Henne and Smook[1] mentioned bis-2 : 2 : 2-trifluoroethyl ether but did not give experimental details.

EXPERIMENTAL

1 : 6-*Bis*-(1 : 1-*di*-H-*heptafluorobutoxy*)*hexane* (I).—1 : 1-Di-*H*-heptafluorobutanol (22·0 g., 0·11 mole) in dioxan (100 ml.) was treated with sodium (2·3 g., 0·1 mole), and the reaction completed at 60—70° for 5·5 hr. 1 : 6-Ditoluene-*p*-sulphonyloxyhexane (21·3 g., 0·05 mole; Table 2) was added at 50°. The stirred mixture was heated at 80° for 22 hr., and then cooled, and the precipitate was filtered off, washed thoroughly with dioxan, and dried (15·0 g.) at 110° (theoretical weight of sodium toluene-*p*-sulphonate, 19·4 g.). Excess of dioxan was removed from the filtrate by distillation *in vacuo* (b. p. 16—20°/15 mm.). The residue was treated with water, the lower layer extracted with ether, and the extract dried ($CaSO_4$). Evaporation and then distillation *in vacuo* gave: (i) essentially the desired ether (10·1 g.; 42%); and (ii) a residue (9·7 g.) of much higher boiling point. Redistillation of (i) gave pure 1 : 6-*bis*-(1 : 1-*di*-H-*heptafluorobutoxy*)*hexane*, b. p. 91°/1·4 mm., n_D^{20} 1·3395 (Found: C, 35·1; H, 3·4; F, 55·2. $C_{14}H_{16}O_2F_{14}$ requires C, 34·9; H, 3·4; F, 55·15%).

Distillation of residue (ii) gave 6-(1 : 1-*di*-H-*heptafluorobutoxy*)*hexyl toluene*-p-*sulphonate* (II) (7·2 g.), b. p. 166—169°/0·01 mm., n_D^{20} 1·4410 [Found: C, 45·4; H, 5·0; F, 29·0%; *M* (cryoscopically in benzene), 466. $C_{17}H_{21}O_4SF_7$ requires C, 44·9; H, 4·65; F, 29·3%; *M*, 454].

Butyl 1 : 1-*Di*-H-*heptafluorobutyl Ether*.—1 : 1-Di-*H*-heptafluorobutanol (36·2 g., 0·181 mole) was added dropwise during 1 hr. to finely divided sodium (3·45 g., 0·15 mole) in diethylene glycol diethyl ether (200 ml.); after 1·5 hr. fluoride ion was detected. *n*-Butyl toluene-*p*-sulphonate was then added, the mixture stirred and heated at 80° for 2 hr., and liquid (73 g.), b. p. 88—183°, distilled off. The remaining solid was washed with ether and dried (26·0 g.) at 110° [Found: F, 1·5% ≡ 0·84 g. of NaF (theoretical weight of sodium toluene-*p*-sulphonate, 28·8 g.)]. Fractionation of the distillate through a 1 ft. column (Dixon gauze cylinders, 1/16 × 1/16 in.) gave fractions: (i) (1·5 g.), b. p. 60—93°; (ii) impure heptafluorobutanol (6·2 g.), b. p. 93—97°, n_D^{20} 1·303; (iii) (5·0 g.), b. p. 97—114°; (iv) (2·1 g.), b. p. 114—120°; (v) (3·2 g.), b. p. 120—123°; (vi) *butyl* 1 : 1-*di*-H-*heptafluorobutyl ether* (16·5 g., 43%), b. p. 123—125° (mainly 124·5—125°)/770 mm., n_D^{20} 1·3263 (Found: C, 37·5; H, 4·3. $C_8H_{11}OF_7$ requires C, 37·8; H, 4·5%). Gas–liquid chromatography of this ether on dinonyl phthalate–Celite (at 109°; pressure drop 214 mm.; 0·9 l./hr. of nitrogen) gave a single sharp peak. Chromatography of fractions (i)—(v) on the same column showed that (iv) and (v) contained considerable quantities of the fluoro-ether, and also that nine unidentified components, boiling range 60—123°, were present.

In the following experiments, precautions were taken to protect alkoxides from moisture, oxygen, and carbon dioxide. When materials were handled under nitrogen, this was purified and dried. All apparatus was baked-out in nitrogen. Ether was dried by sodium and by distillation from phosphoric oxide. Sodium was cleaned and cut under ether which was then evaporated in a stream of nitrogen.

Sodium 2 : 2 : 2-*Trifluoroethoxide*.—Sodium (0·992 g., 0·043 mole, weighed under nitrogen) reacted vigorously with 2 : 2 : 2-trifluoroethanol (6·0 g., 0·06 mole; twice distilled from activated calcium sulphate) in dry ether (40 ml.). The ether was then gently distilled off under nitrogen, and the residue dried *in vacuo* (0·05—0·3 mm. of nitrogen) during 18 hr. at 50° (bath) to give *sodium* 2 : 2 : 2-*trifluoroethoxide* (4·67 g., 89%) as a fine white powder (Found: equiv., 123·8. $C_2H_2OF_3Na$ requires equiv., 122). There was no fluoride ion detectable.

Sodium 1 : 1-*Di*-H-*heptafluorobutoxide*.—1 : 1-Di-*H*-heptafluorobutanol (2·980 g., 0·0149 mole) was added rapidly to sodium (0·113 g., 4·92 mmole) under dry ether at room temperature. When the reaction was complete (10 min.), excess of ether and fluoro-alcohol were removed rapidly in a stream of nitrogen at 60—78° (bath). The residue was further dried *in vacuo* (2·5 × 10^{-3}—1·5 × 10^{-4} mm.) to the theoretical weight during 6 hr. at 50—80° (bath) to give a

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[5] Faurote, Henderson, Murphy, O'Rear, and Ravner, *Ind. Eng. Chem.*, 1956, **48**, 445.
[6] Tiers, Brown, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 5978.

white wax, essentially sodium 1 : 1-di-*H*-heptafluorobutoxide (1·096 g.) (Found: equiv., 233. Calc. for $C_4H_2OF_7Na$: equiv., 222). It contained some fluoride ion.

Action of Heat on Sodium 2 : 2 : 2-*Trifluoroethoxide in Dioxan and in Diethylene Glycol Diethyl Ether.*—The solutions of the dry salt in dioxan or diethylene glycol diethyl ether, protected from carbon dioxide and moisture, were heated for the time specified in Table 1, and then cooled. The precipitate was washed with dry ether, dried at 110°, and analysed gravimetrically for fluoride ion.

Effect of Heat on Sodium 2 : 2 : 2-*Trifluoroethoxide* in vacuo.—Sodium 2 : 2 : 2-trifluoroethoxide (0·660 g., 5·41 mmole) in a flask connected *via* a still-head to a receiver and two traps cooled in liquid nitrogen, was heated in a maintained vacuum (5×10^{-3} mm.). At 100° (bath temp.), material was evolved slowly and collected in the first trap. The temperature was raised and kept at 145—150° for 14·5 hr., and the pressure in the cooled apparatus then restored to atmospheric with nitrogen. During the heating, sodium 2 : 2 : 2-trifluoroethoxide (0·324 g., 49%) (Found: equiv., 123. $C_2H_2OF_3N$ requires equiv., 122), sublimed and 2 : 2 : 2-trifluoroethanol (0·100 g., 1·00 mmole) collected in the first trap. This alcohol, in ether, was chromatographed on dinonyl phthalate–Celite (at 76·5°; 0·95 l./hr. of nitrogen; pressure drop 164 mm.), and gave a single sharp peak which was reinforced on addition of trifluoroethanol. The brown residue in the flask was analysed gravimetrically for fluoride (Found: F, 9·5% ≡ 20·9% NaF; *i.e.* 1·14 mmoles of NaF).

Effect of Heat on Sodium 1 : 1-*Di*-H-*heptafluorobutoxide* in vacuo.—The method and apparatus were identical with those described above. Sodium 1 : 1-di-*H*-heptafluorobutoxide (0·687 g., *ca.* 3·1 mmoles) melted at 110—115° (bath)/10^{-2} mm. and volatile material condensed in the first trap. After being heated at 140° for 8 hr., the reaction vessel was cooled and the pressure in the system raise to atmospheric with nitrogen. During the decomposition, a white solid (0·194 g.) (Found: equiv., 357) sublimed and liquid (<5 mg.) condensed in the still-head and receiver. 1 : 1-Di-*H*-heptafluorobutanol (0·287 g., 1·44 mmole) collected in the first trap. The alcohol, in ether, was chromatographed on dinonyl phthalate–Celite (96°; 0·92 l./hr. of nitrogen; pressure drop 202 mm.) and gave three extremely small peaks, followed by a large peak which was reinforced on addition of heptafluorobutanol. The brown residue (0·116 g.) was analysed gravimetrically for fluoride (Found: F, 18·9% ≡ 41·8% NaF, *i.e.* 1·16 mmoles of NaF).

Ditoluene-p-*sulphonates of* αω-*Alkane- and -Oxa-alkane-diols.*—These *ditoluene*-p-*sulphonates* (Table 2) were prepared [7] by addition of toluene-*p*-sulphonyl chloride to the alcohol in pyridine.

TABLE 2. *Ditoluene*-p-*sulphonates.*

Compound	Yield (%)	M. p.	Found (%)		Reqd. (%)	
			C	H	C	H
$TsO\cdot[CH_2]_6\cdot OTs$ ……………	91	71—72°	56·6	6·3	56·3	6·15
$TsO\cdot[CH_2]_{10}\cdot OTs$ ……………	90	109—109·5	59·8	7·3	59·7	7·1
$TsO\cdot[CH_2\cdot CH_2\cdot O]_3\cdot OTs$ ……	87	81—82	52·6	5·8	52·4	5·7

Preparation of Fluoro-ethers.—The sodium 1 : 1-di-*H*-perfluoroalkoxides (25% excess) were prepared by the rapid action of sodium on the fluoro-alcohols in dioxan. The ditoluene-*p*-sulphonates were then added quickly and the stirred mixtures heated to 80—90°. After 2—5 hr. at this temperature, the mixtures were cooled, sodium toluene-*p*-sulphonate filtered off, and the fluoro-ethers (Table 3) were isolated by the usual methods.

TABLE 3. *Fluoro-ethers.*

Compound	Yield [a] (%)	B. p./mm.	Found (%)			Reqd. (%		
			C	H	F	C	H	F
$C_3F_7\cdot CH_2\cdot O\cdot[CH_2]_{10}\cdot O\cdot CH_2\cdot C_3F_7$ ……	78	98—100°/0·18	40·5	4·6	50·1	40·2	4·2	49·4
$C_3F_7\cdot CH_2\cdot O\cdot[CH_2\cdot CH_2\cdot O]_3\cdot CH_2\cdot C_3F_7$	84	92—98/0·2—0·25	32·8	3·2	—	32·7	3·1	—
$CF_3\cdot CH_2\cdot O\cdot[CH_2\cdot CH_2\cdot O]_3\cdot CH_2\cdot CF_3$ …	75	71—72/0·25	38·4	5·2	—	38·2	5·1	—
$C_3F_7\cdot CH_2\cdot O\cdot[CH_2\cdot CH_2\cdot O]_4\cdot CH_2\cdot C_3F_7$ [b]	66	102—103/0·16	34·5	3·7	47·4	34·4	3·6	47·7

[a] The yields are for ethers having single-peak gas–liquid chromatograms (dinonyl phthalate–Celite). [b] The appropriate ditoluene-*p*-sulphonate was isolated as a very high-boiling syrup (83%).

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[7] (*a*) Marvel and Sekera, *Org. Synth.*, **20**, 50; (*b*) *J. Amer. Chem. Soc.*, 1933, **55**, 345.