product which weighed 152 g. was washed with water and dried over calcium chloride. Twenty-one grams of the product was lost in the wash water. The latter gave a test for chloride ion and for fluoride ion, and was strongly acidic, perhaps because of difluoronitroacetic acid and chlorodifluoroacetyl fluoride.

Distillation of the remaining 131 g. of product gave the following fractions:

(a) 51 g. of trifluorochloroethylene. (b) 12 g. (15%) of 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane. (c) 14.5 g. (18.1%) $ClCF_2CFCl_2$ (d) 19 g. (23.8%) of 1-nitoso-1,2,2-trifluoro-1-chloro-2-nitroethane. (e) 20 g. (25%) of 1-nitro-1,1,2-trifluoro-2,2-dichloroethane. (f) 7 g. (8.75%) of 1,2-dinitro-1,1,2-trifluoro-2-chloroethane. (g) 7.5 g. (9.35%) of residue.

Acknowledgment. We wish to acknowledge support of this work by the U. S. Army Quartermaster Corps under Dr. Juan C. Montermoso as scientific officer.

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[CONTRIBUTION FROM THE RESEARCH DIVISION, JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Nucleophilic Substitution in Fluoroalkyl Sulfates, Sulfonates, and Related Compounds

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Received February 3, 1961

New chemistry based on highly fluorinated alcohols is described. The difficult nucleophilic substitution at the carbon-oxygen bond of polyfluoroalkoxy compounds takes place at appreciably lower temperatures in the chlorosulfate and sulfate esters than in the tosyl esters. Fluoroalkylamines have been prepared from the corresponding alcohols going through one intermediate step.

Fluorinated alcohols containing the grouping $-CF_2-CH_2OH$ are much more acidic than ordinary alkyl alcohols being almost as acidic as phenol.[1] Like the phenols, the fluoro alcohols are cleaved only with difficulty at the carbon-oxygen bond, so that direct exchange of the hydroxy function for halide, amino, or anilino groups has been reported only in isolated cases.[2]

Halide substitution at the carbon-oxygen bond of *p*-toluenesulfonate esters of fluorinated alcohols has been accomplished[3-5] by reaction of these esters with sodium iodide, lithium chloride, and lithium bromide in diethylene glycol at elevated temperatures, usually in excess of 200°. This method has been extended to methane-, ethane-, and benzenesulfonate esters[6] of fluoro alcohols and has given satisfactory results in the formation of 1*H*,1*H*,-ω*H*-perfluoroalkyl halides.[7]

It is rather surprising that the attempted reactions of ammonia, methylamine and diethylamine at the fluoroalkyl-oxygen bond of tosyl esters have, heretofore, been unsuccessful,[8,9] while piperidine and aniline under similar conditions have been fluoroalkylated on the nitrogen atom without apparent difficulty.[8]

Formation of fluoroalkyl halides. Selected fluoroalkyl sulfates, sulfites, chlorosulfates, methanesulfonates, and *p*-toluenesulfonates have been prepared. The properties of some of these esters are given in Tables I and II. The sulfate and chlorosulfate esters proved to be useful as fluoroalkylating agents. Thus, 1*H*,1*H*,3*H*-tetrafluoropropyl chlorosulfate (I) was converted to the chloride (II) with lithium chloride in diethylene glycol at 125°, a temperature which is unexpectedly low for the scission of the fluoroalkyl-oxygen bond. The same chloride made from the tosyl ester required a minimum temperature of 165°.

$$\underset{\text{I}}{HCF_2CF_2CH_2OSO_2Cl} \xrightarrow[125^\circ]{LiCl} \underset{\text{II}}{HCF_2CF_2CH_2Cl} \quad (61.2\%)$$

$$\underset{\text{III}}{H(CF_2CF_2)_2CH_2OSO_2Cl} \xrightarrow{KF} \underset{\text{IV}}{H(CF_2CF_2)_2CH_2F} \quad (17.1\%)$$

Similarly, the chlorosulfate ester of 1*H*,1*H*,5*H*-octafluoropentanol (III) was converted to the fluoride (IV) below 145°. The tosyl esters of this alcohol and of 1*H*,1*H*,7*H*-dodecafluoroheptanol could not be made to react with potassium fluoride in diethylene glycol at temperatures up to 245°, so that neither of the fluoroalkyl fluorides was formed. The shorter chain 1*H*,1*H*,3*H*-tetrafluoropropyl tosylate (V), however, was suitable for fluoride formation reacting readily at 170°-210° (76%). It appears that

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[1] R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1757; A. L. Henne and W. C. Francis, *J. Am. Chem. Soc.*, **75**, 991 (1953).

[2] A. M. Lovelace, W. Postelnek, and D. A. Rausch, *Aliphatic Fluorine Compounds*, Monograph-138, Reinhold, p. 46.

[3] G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

[4] W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, **77**, 4899 (1955).

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[6] P. D. Faurote and J. G. O'Rear, *Ind. & Eng. Chem.*, **49**, 189 (1957).

[7] P. D. Faurote and J. G. O'Rear, *J. Am. Chem. Soc.*, **78**, 4999 (1956).

[8] H. A. Brown and G. V. D. Tiers, *J. Org. Chem.*, **22**, 454 (1957).

[9] B. S. Marks and G. S. Schweiker, *J. Am. Chem. Soc.*, **80**, 5789 (1958).

TABLE I

FLUOROALKYL SULFITES AND SULFATES $[X(CF_2)_nCH_2O]_2SO_y$

X	n	y	Formula	Mol. Wt.	B.P.		C	H	F	S	n_D^{20}	Yield, %
H	2	1	$C_6H_6F_8SO_3$	310.18	194	Calcd.	23.2	1.9	49.0	10.3	—	—
						Found	23.1	1.8	48.1	10.1	1.3580	66.2
H	6	1	$C_{14}H_6F_{24}SO_3$	710.26	286	Calcd.	23.6	0.8	64.2	4.5	—	—
						Found	24.1	1.1	62.6	4.2	1.3341	65.1
H	2	2	$C_6H_6F_8SO_4$	326.18	90/6.8 mm.	Calcd.	22.1	1.8	46.6	9.8	—	—
						Found	22.7	2.1	45.3	9.9	1.3498	37.7
H	4	2	$C_{10}H_6F_{16}SO_4$	526.22	105/2.1 mm.	Calcd.	22.8	1.1	57.8	6.1	—	—
						Found	22.5	1.2	56.3	5.8	1.3379	12.5
H	10	2	$C_{22}H_6F_{20}SO_4$	1126.34	M.p. 123	Calcd.	23.4	0.5	67.5	2.8	—	—
						Found	23.3	0.6	63.4	2.8	—	28
F	1	2	$C_4H_4F_6SO_4$	262.14	150–154	Calcd.	18.3	1.5	43.5	—	—	—
						Found	17.8	1.8	44.2	—	1.3320	(>1.0)[a]

[a] Yield and conversion not determined.

TABLE II

FLUOROALKYL CHLORO SULFATES, TOSYLATES, AND METHANE SULFONATES $X(CF_2)_nCH_2OSO_2Y$

X	n	Y	Formula	Mol. Wt.	M.P.	B.P.		C	H	F	S	Cl	n_D^{20}	Yield, %
H	2	Cl	$C_3H_3F_4SO_3Cl$	230.58	—	142–145	Calcd.	15.6	1.3	32.9	13.9	15.4	—	—
							Found	15.4	1.4	32.6	13.4	15.4	1.3705	55.0
H	4	Cl	$C_5H_3F_8SO_3Cl$	330.60	—	67–74/6 mm.	Calcd.	18.15	0.9	46.0	9.7	10.7	—	—
							Found	18.5	1.1	45.4	9.3	10.0	1.3357	15.4[b]
F	1	Cl	$C_2H_2F_3SO_3Cl$	198.56	—	117–118	Calcd.	12.1	1.0	28.85	—	17.9	—	—
							Found	12.4	1.1	29.0	—	17.8	1.3630	24.0[b]
H	2	C_7H_7	$C_{10}H_{10}F_4SO_3$	286.25	14–16	124–126/2 mm.	Calcd.	42.0	3.5	26.6	11.2	—	—	—
							Found	41.9	3.6	26.0	11.2	—	1.4602	93.3
H	4	C_7H_7	$C_{12}H_{10}F_8SO_3$	386.27	8–12	157/5 mm.	Calcd.	37.3	2.6	39.4	8.3	—	—	—
							Found	37.0	2.8	38.7	8.3	—	1.4335	80.0
H	8	C_7H_7	$C_{16}H_{10}F_{16}SO_3$	586.31	44.5	171.5/2.3 mm.	Calcd.	32.8	1.7	51.8	5.5	—	—	—
							Found	32.8	1.7	51.1	5.5	—	—	96.8[a]
F	2	CH_3	$C_4H_5F_5SO_3$	228.15	—	112–114/70 mm.	Calcd.	21.05	2.2	41.9	14.0	—	—	—
							Found	20.8	2.3	41.7	14.0	—	1.3562	73.4
F	3	CH_3	$C_5H_5F_7SO_3$	278.16	—	78–80/6 mm.	Calcd.	21.6	1.8	47.8	—	—	—	—
							Found	21.6	1.8	47.5	—	—	1.3440	49.0

[a] Conversion 52.5%. [b] Conversion not determined.

the long chain fluoroalkyl chlorosulfates possess weaker fluoroalkyl-oxygen bonds than the corresponding *p*-toluenesulfonates.

A low reaction temperature of 120° was also sufficient in the reaction of lithium bromide with bis-1*H*,1*H*,3*H*-tetrafluoropropyl sulfate (VI) to give the fluoroalkyl bromide (VII) (94.5%).

$$\underset{\text{VI}}{HCF_2CF_2CH_2OSO_2OCH_2CF_2CF_2H} \xrightarrow[120°]{LiBr} \underset{\text{VII}}{HCF_2CF_2CH_2Br}$$

Formation of fluoroalkylamines. The method used by Brown and Tiers to make *N*-1*H*,1*H*-heptafluorobutylaniline[8] was adapted to the reaction of aniline with the tosyl ester (V) to give *N*-1*H*,1*H*,3*H*-tetrafluoropropylaniline (VIII). Substituting bis-1*H*,1*H*,3*H*-tetrafluoropropyl sulfate (VI) as the fluoroalkylating agent, an inferior yield was obtained.

$$\underset{\text{VI}}{(HCF_2CF_2CH_2O)_2SO_2 + NH_2C_6H_5}$$

$\searrow$ 27.1%

$$\underset{\text{VIII}}{HCF_2CF_2CH_2NHC_6H_5}$$

73.5% $\nearrow$

$$\underset{\text{V}}{HCF_2CF_2CH_2OSO_2C_7H_7 + NH_2C_6H_5}$$

A very small amount of product was obtained on treating anhydrous ammonia with the tosyl ester (V) in a stainless steel bomb at 175° for twenty-four hours (11%). The presence of water in the system proved to be beneficial, so that this same reaction run with 28% ammonia in the presence of an anionic dispersing agent provided a 46.5% yield. *N*-Methyl-1*H*,1*H*,3*H*-tetrafluoropropylamine and *N*,*N*-diethyl-1*H*,1*H*,3*H*-tetrafluoropropylamine were satisfactorily prepared with aqueous methyl- and diethylamine, respectively. Optimum reaction conditions were not explored, but yields of about 70% have been consistently obtained at a reaction temperature of only 145° by substitution of benzene sulfonate esters for *p*-toluenesulfonate esters. Even the long chain 1*H*,1*H*,9*H*-hexadecafluorononylamine prepared from the benzenesulfonate ester was isolated in satisfactory amount (70%).

An attempt to react aqueous trimethylamine with the tosyl ester (V) to give the quaternary salt,

TABLE III

FLUOROALKYL HALIDES $H(CF_2)_nCH_2X$

n	X	Formula	Mol. Wt.	B.P.		C	H	F	Cl	Br	I	n_D^{20}	yield, %
2	F	$C_3H_3F_5$	134.05	26	Calcd.	26.9	2.2	70.9	—	—	—	—	—
					Found	26.5	2.5	69.6	—	—	—	$<1.3000^{15}$	71.0
2	Cl	$C_3H_3F_4Cl$	150.51	54	Calcd.	23.9	—	50.5	23.6	—	—	—	—
					Found	24.2	—	50.3	23.3	—	—	1.3241	90.6
2	Br	$C_3H_3F_4Br$	194.97	74	Calcd.	18.5	1.5	39.0	—	41.0	—	—	—
					Found	18.5	1.8	38.7	—	40.4	—	1.3535^{27}	74.5
2	I	$C_3H_3F_4I$	241.97	99	Calcd.	14.9	1.2	31.4	—	—	52.4	—	—
					Found	14.8	1.3	30.1	—	—	51.1	1.4141	81.0
4	F	$C_5H_3F_9$	234.07	79	Calcd.	25.7	—	73.1	—	—	—	—	—
					Found	25.7	—	72.5	—	—	—	<1.3000	17.1^{a}
4	Cl	$C_5H_3F_8Cl$	250.53	105	Calcd.	23.9	2.0	60.6	14.2	—	—	—	—
					Found	24.6	1.4	56.4	12.9	—	—	1.3225	81.5

[a] Conversion not determined.

TABLE IV

FLUOROALKYL AMINES $HCF_2CF_2CH_2NR'R''$

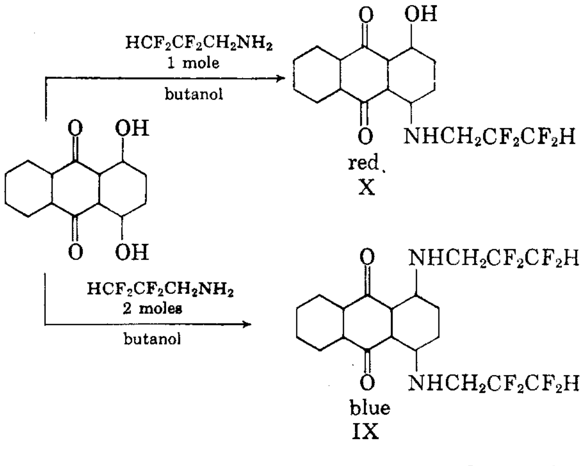
R′	R″	Formula	Mol. Wt.	B.P.		C	H	N	F	n_D^{20}	Yield, %
H	H	$C_3H_5NF_4$	131.08	84	Calcd.	27.5	3.8	10.7	58.0	—	—
					Found	27.4	3.9	10.7	57.0	1.3291	46.5
CH_3	H	$C_4H_7NF_4$	145.12	90–91	Calcd.	33.1	4.8	9.65	52.4	—	—
					Found	33.1	5.0	9.6	51.5	1.3335	29
CH_3	CH_3	$C_5H_9NF_4$	159.14	71–77	Calcd.	37.75	5.7	8.8	47.8	—	—
					Found	38.0	5.7	8.4	48.2	1.3362	11.5
C_2H_5	C_2H_5	$C_7H_{13}NF_4$	187.14	127	Calcd.	44.85	6.95	7.5	40.6	—	—
					Found	44.8	7.2	7.7	40.2	1.3620	63.5
H	C_6H_5	$C_9H_9NF_4$	207.19	91/6 mm.	Calcd.	52.2	4.35	6.8	36.7	—	—
					Found	52.6	4.5	6.7	36.8	1.4747^{27}	73.5

1*H*,1*H*,3*H* - tetrafluoropropyltrimethylammonium tosylate was unsuccessful. From the product mixture, a small amount of *N*-1*H*,1*H*,3*H*-tetrafluoropropyldimethylamine was isolated, which may have arisen by metathetical replacement of a methyl group on the alkylamine.

The reaction with aqueous ammonia is not restricted to aryl sulfonate esters or to telomer alcohols, $H(CF_2CF_2)nCH_2OH$, $n = 1$–4. The method has been used to prepare 1*H*,1*H*-pentafluoropropylamine from the 1*H*,1*H*-pentafluoropropylmethanesulfonate. More generally, conversion of fluoro alcohols to the corresponding fluoroalkylamines is now possible in a two-step sequence, where previous practice required four steps including the hazardous lithium aluminum hydride reduction of a fluorocarboxamide.[10,11]

Attempts to condense fluoro alcohols with ammonia, diethylamine, or aniline in a stainless steel shaker tube at 175°–300° for twelve to twenty-four hours has only afforded starting materials or tars. This was not improved by the use of catalysts such as zinc chloride and Raney nickel.

The fluoroalkylamines undergo typical amine reactions in spite of their low basicity. *N*-1*H*,1*H*,3*H*-Tetrafluoropropyl-*N*-benzylamine was obtained from treating *N*-tetrafluoropropylaniline (VIII) with benzyl chloride at reflux in a sodium bicarbonate slurry. The interesting acetate dyes (IX and X) resulted from oxidizing the condensation product of leuco quinizarin with one and two moles of 1*H*,1*H*,3*H*-tetrafluoropropylamine, respectively.



Properties and preparation of fluoroalkyl sulfate esters. The sulfur bond in the chlorosulfate ester of 1*H*,1*H*,3*H*-tetrafluoropropanol (I) shows the same unusual lack of reactivity as the analogous derivative of phenol.[12] This chemical similarity between fluoro alcohol and phenol derivatives was mentioned earlier. The chlorosulfate ester (I) was largely re-

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(10) J. E. Carnahan and H. J. Sampson, U. S. Pat. **2,646,449** (1953).

(11) A. L. Henne and J. J. Stewart, *J. Am. Chem. Soc.*, **77,** 1901 (1955).

(12) M. Battegay and L. Denivelle, *Compt. rend.*, **194,** 1505 (1932).

covered unchanged from reaction mixtures containing excess 1*H*,1*H*,3*H*-tetrafluoropropanol after heating at 113° for twenty hours, none of the bisfluoroalkyl sulfate ester having formed under these conditions. Even with fluoroalcoholates, the reaction of the sulfur-chlorine bond tends to be somewhat sluggish, although this proved to be the best method of preparing the bisfluoroalkyl sulfate esters. In practice, fluoroalcoholates of sodium were treated with sulfuryl chloride in the correct molar proportions to give either the bisfluoroalkyl sulfate or the intermediate fluoroalkyl chlorosulfate.

$$X(CF_2)_nCH_2ONa + SO_2Cl_2 \longrightarrow$$

$$X(CF_2)_nCH_2OSO_2Cl \xrightarrow{SO_2Cl_2} [X(CF_2)_nCH_2O]_2SO_2$$

$$X = H, F;\ n = 2\text{–}10$$

Attempts to prepare the bis-1*H*,1*H*,ω*H*-perfluoroalkyl sulfate esters from the fluoro alcohols or from the monofluoroalkyl sulfonic acid with concentrated sulfuric acid were unsuccessful. The bisfluoroalkyl sulfate esters have remarkable hydrolytic stability similar to those of 1*H*,1*H*,ω*H*-perfluoroalkyl tosylates and diphenyl sulfate.[13] Bisfluoroalkyl sulfite esters were hydrolytically less stable than sulfate esters and were not suitable as fluoroalkylating agents. They were readily prepared by the interaction of fluoro alcohols with thionyl chloride in pyridine.

EXPERIMENTAL

1H,1H,3H-Tetrafluoropropyl chlorosulfate (I). Sodium wire (23 g.; 1.0 g.-atom) was added in small pieces to 330 g. of 1*H*,1*H*,3*H*-tetrafluoropropanol (2.5 moles) at 80° with stirring. When all the sodium was dissolved, this viscous solution was slowly added to a mixture of sulfuryl chloride (168.5 g.; 1.25 moles) in 1*H*,1*H*,3*H*-tetrafluoropropanol (132 g.; 1.0 mole), adequate flow being maintained by heating the dropping funnel with a heat lamp. The reaction was maintained at 55° until it was acidic to litmus. Sodium chloride was filtered off and the product distilled at 142°-145°. The yield was 127.5 g. (55%). A somewhat lower yield was obtained on treating the fluoroalcohol with sulfuryl chloride directly at reflux.

The 1*H*,1*H*,5*H*-octafluoropentyl chlorosulfate and the 1*H*,1*H*-trifluoroethyl chlorosulfate were similarly prepared.

Bis-1H,1H,3H-tetrafluoropropyl sulfate (VI). Sodium wire (23 g.; 1.0 g.-atom) was dissolved in 1*H*,1*H*,3*H*-tetrafluoropropanol (V) (330 g.; 2.5 moles) at 80-90°. Sulfuryl chloride (67.5 g.; 0.5 mole) was mixed with 1*H*,1*H*,3*H*-tetrafluoropropanol (132 g.; 1.0 mole) and was then slowly added to the sodium solution at 70-80°. At the end of the addition, the mixture was strongly acidic. A precipitate consisting mostly of sodium chloride (83 g.) was filtered off. The filtrate, consisting of two phases, was heated to 116° at atmospheric pressure to remove unchanged reagents. The crude product was then distilled under vacuum. Pure product was collected at 90-91°/6.8 mm. The yield was 61.5 g. (37.7%), based on the sodium used. A similar reaction conducted at 20-30° resulted in a lower yield (22.4%). An attempt to prepare the bis-1*H*,1*H*,3*H*-tetrafluoropropyl sulfate (VI) from the fluoro alcohol and sulfuryl chloride in the presence of pyridine at 0-10°, analogously to the reaction of this alcohol with *p*-toluenesulfonyl chloride, was unsuccessful. The sulfate (VI), which is insoluble in water, was stable on heating in concentrated sulfuric acid at 270° for several hours.

Bis-1H,1H,5H-octafluoropentyl sulfate and bis-1H,1H-trifluoroethyl sulfate were similarly prepared.

Bis-1H,1H,11H-eicosafluoroundecyl sulfate. Sodium hydride (12 g.; 0.5 mole) was slowly added to a solution of 1*H*,1*H*,11*H*-eicosafluoroundecanol (266 g.; 0.5 mole) in 250 ml. of ether maintained at the reflux. After addition was complete, refluxing was continued for 5 hr. The mixture was cooled and xylene was added to precipitate the sodium fluoroalcoholate. The precipitated fluoroalcoholate was filtered off and then suspended in 200 ml. of dioxane. To this suspension, sulfuryl chloride (41.7 g.; 0.31 mole) was added dropwise all operations being carried out under anhydrous conditions. The temperature of the reaction mixture was gradually raised and acid gases were scrubbed out. The reaction was kept at reflux for 20 hr. After cooling, the contents of the flask were washed three times with 200-ml. portions of ethanol followed by a water wash. The insoluble material was dried, having a melting point of 123-124° and weighing 79 g. (28%).

Bis-1H,1H,3H-tetrafluoropropyl sulfite. A mixture of pyridine (176 g.; 2.22 moles), 1*H*,1*H*,3*H*-tetrafluoropropanol (264 g.; 2.0 moles), and 700 ml. of ether was added to a 1-l. flask fitted with a stirrer, reflux condenser and dropping funnel. Thionyl chloride (120 g.; 1.0 mole) was then added to another portion of ether (150 ml.) and this mixture added dropwise to the first mixture at −20°. After 1 hr., the reaction mass was allowed to warm up to room temperature. Pyridine hydrochloride was filtered off and the filtrate was distilled. The sulfite ester was collected at 194-196° (205 g.; 66.2%) as a colorless, heavy, water-insoluble liquid.

Bis-1H,1H,7H-dodecafluoroheptyl sulfite was similarly prepared. It hydrolyzes completely in 0.1*N* methanolic potassium hydroxide in 1 hr. at room temperature.

1H,1H,3H-Tetrafluoropropyl tosylate (V) *and 1H,1H,9H-hexadecafluorononyl tosylate* were prepared by the method of Tiers, Brown, and Reid[3] using aqueous base as the acid acceptor. The higher fluoroalkyl tosylates are usually prepared in better yield by the method of Faurote and O'Rear.[7]

1H,1H-Pentafluoropropyl methane sulfonate. Methanesulfonyl chloride (194 g.; 1.685 moles) was added dropwise at 5-10° to a mixture of 1*H*,1*H*-pentafluoropropanol (241 g.; 1.605 moles) and pyridine (397 ml.). After the addition, which lasted 2 hr., the mixture was stirred at room temperature overnight, then poured into ice water containing excess sodium bicarbonate. The mixture, consisting of two phases, was filtered. The lower layer was separated, dried over anhydrous magnesium sulfate, and distilled. The product was collected at 112-114°/70 mm., weighing 269 g. (73.4%).

1H,1H-Heptafluorobutylmethane sulfonate was similarly prepared.

Fluoroalkyl halides from fluoroalkyl tosylates. The method of Tiers, Brown, and Reid[3] was used to prepare the following fluoroalkyl halides: 1*H*,1*H*,3*H*-tetrafluoropropyl fluoride (71.0%), chloride (90.6%), bromide (74.5%), iodide (81.0%-slightly impure); 1*H*,1*H*,5*H*-octafluoropentyl chloride (81.5 %).

1H,1H,3H-Tetrafluoropropyl bromide (VII) *from bis-1H,1H,3H-tetrafluoropropyl sulfate* (VI). Anhydrous lithium bromide (14.5 g.; 0.167 mole), bis-1*H*,1*H*,3*H*-tetrafluoropropyl sulfate (VI) (27.5 g.; 0.844 mole), and 50 ml. of diethylene glycol were heated in a flask fitted with a water take-off tube, a stirrer, and thermometer. A condenser was placed on the take-off tube. The pot temperature was raised slowly. A liquid began to collect in the water separator when the pot temperature reached 120°. The fluoroalkyl bromide came over quickly at first, then more slowly as the temperature rose. The crude bromide (VII) was obtained in 94.5% yield (15.5 g.) calculated for the replacement of only one fluoroalkyl group, n_D^{20} 1.3541.

Anal. Calcd. for $C_3H_3F_4Br$: C, 19.0; H, 1.6; Br, 38.2. Found: C, 18.45; H, 1.54; Br, 41.0.

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(13) L. Denivelle, *Compt. rend.*, 199, 211 (1934).

1H,1H,3H-Tetrafluoropropyl chloride (II) *from 1H,1H,3H-tetrafluoropropyl chlorosulfate* (I). Lithium chloride (25.4 g.; 0.6 mole) was added to diethylene glycol (75 ml.) at 125° in a flask fitted as in the last experiment. The condenser was cooled with ice water. 1*H*,1*H*,3*H*-Tetrafluoropropyl chlorosulfate (I) (58 g.; 0.25 mole) was added dropwise over a period of 45 min. Distillation of a low boiling liquid started almost at once. When addition of the chlorosulfate ester stopped, the distillation of the product quickly came to an end. Maximum pot temperature was 170°. The crude distillate (33 g.) was washed with ice water, dried over anhydrous magnesium sulfate, and distilled. B.p. 50–51°. The yield was 23 g. (61.2%), n_D^{20} 1.3250.

1H,1H,5H-Octafluoropentyl fluoride (IV) was similarly prepared from 1*H*,1*H*,5*H*-octafluoropentyl chlorosulfate. The chlorosulfate ester (83 g.; 0.25 mole) was added to a mixture of potassium fluoride (33 g.; 0.57 mole) and diethylene glycol (100 ml.) at 110–145°. The product came over at this temperatue. After washing, drying and redistillation, the 1*H*,1*H*,5*H*-octafluoropentyl fluoride (IV) weighed 10 g. (17.1%).

Anal. Calcd. for $C_5H_3F_9$: C, 25.65; F, 73.1. Found: C, 25.7; F, 72.5.

1H,1H,3H-Tetrafluoropropylamine. To an excess of aqueous ammonia (340 ml. of 28%; 5.5 moles), 1*H*,1*H*,3*H*-tetrafluoropropyl tosylate (V) (142.8 g.; 0.5 mole), and 1.7 g. of Nacconol NR (sodium alkyl naphthalene sulfonate) were added. The reaction was carried out in a 1-l. stainless steel shaker bomb at 175° for a period of 24 hr. The charge was cooled in Dry Ice, vented, and the semisolid contents transferred to a distillation flask fitted with a 6″ Vigreux column and an ice water condenser. On warming, ammonia escaped. A crude distillate collected between 45–95°. This was diluted with ether, dried with solid sodium hydroxide, and fractionally distilled. The product boiled at 84°, n_D^{20} 1.3291. Fluoroalkylamine forms an azeotrope containing 7.8% water and boiling at 77°.

A similar reaction was carried out with anhydrous ammonia (150 g.; 8.82 moles). The dispersing agent was the ammonium salt of 9*H*-hexadecafluorononanoic acid (1.7 g.). The reaction mixture was worked up as described above. The crude amine collected at 71–78° (11%), n_D^{20} 1.3345. It could be used in preparative work without distillation.

1*H*,1*H*,3*H*-Tetrafluoropropylamine was dissolved in dry ether and gaseous hydrogen chloride passed. The precipitated hydrochloride was somewhat hygroscopic.

Anal. Calcd. for $C_3H_6NClF_4$: Cl, 21.8; F, 45.4; N, 8.36. Found: Cl, 22.3; F, 44.8; N(Kjel), 8.2.

N-Methyl-1H,1H,3H-tetrafluoropropylamine. Methylamine (33 g.; 1.0 mole) was added to a stainless steel shaker bomb cooled to Dry Ice temperature and containing a mixture of 1*H*,1*H*,3*H*-tetrafluoropropyl tosylate (V) (148 g.; 0.5 mole), water (250 ml.) and Nacconol NR (1.7 g.). The mixture was heated for 5 hr. at 175°. After cooling and venting, the reaction mixture was worked up in the same way as the unsubstituted amine above. On redistillation in a spinning band column at 90–91°, a yield of 21 g (29%) was obtained; n_D^{20} 1.3335.

N,N-Diethyl-1H,1H,3H-tetrafluoropropylamine. The method of preparation was identical with that of *N*-methyl-1*H*,1*H*,3*H*-tetrafluoropropylamine. After redistillation at 127°, the yield was 59.5 g. (63.5%), n_D^{20} 1.3607. The hydrochloride prepared by passing anhydrous hydrogen chloride into a solution of this amine was extremely hygroscopic.

1H,1H,9H-Hexadecafluorononylamine hydrochloride. 1*H*,-1*H*,9*H*-Hexadecafluorononyl tosylate (146 g.; 0.25 mole) was added to aqueous ammonia (170 ml. of 28%; 2.8 moles) containing 2.5 g. Nacconol NR. The mixture was heated at 235° in a bomb for 22 hr. Some of the charge was lost through a leak. After cooling, the mixture was discharged and filtered. The solids on the funnel were extracted with ether (300 ml.), then with methanol (300 ml.). The combined extracts were treated with concentrated hydrochloric acid until precipitation ceased. The precipitate was filtered, washed in water and dried (13 g.; 11%). The hydrochloride decomposed at 190°.

Anal. Calcd. for $C_9H_6ClF_{16}N$: F, 64.9; Cl, 7.6; N, 2.995. Found: F, 63.0; Cl, 7.98; N(Kjel), 3.3.

1H,1H-Pentafluoropropylamine. 1*H*,1*H*-Pentafluoropropyl methanesulfonate (114 g.; 0.5 mole) was added to aqueous ammonia (340 ml., 28%) containing 1.7 g. of Nacconol NR as the dispersing agent. The reaction was run in a stainless steel shaker bomb at 175° for 24 hr. Details of the work-up were similar to that of 1*H*,1*H*,3*H*-tetrafluoropropylamine. After distillation in a spinning band column, a cut boiling at 38° was collected (18 g.; 24.2%). This boiling point was somewhat low according to the literature.[14]

Anal. Calcd. for $C_3H_4F_5N$: C, 24.14; H, 2.68; F, 63.75; N, 9.39. Found: C, 23.8; H, 2.9; F, 63.55, N(Kjel), 9.0.

The hydrochloride was prepared by passing gaseous hydrogen chloride into a dry ether solution of the amine.

Anal. Calcd. for $C_3H_5F_5NCl$: C, 19.15; F, 51.2; N, 7 55. Found: C, 19.45; F, 51.4; N(Kjel), 7.45.

N-1H,1H,3H-Tetrafluoropropylaniline (VIII). The method of Brown and Tiers was used.[8]

N-Benzyl-N-1H,1H,3H-tetrafluoropropylaniline.[15] N-1*H*,1*H*,3*H*-Tetrafluoropropylaniline (VIII) (20.7 g.; 0.1 mole) was added to a slurry of sodium bicarbonate at 50°. Benzyl chloride (15.2 g.; 0.12 mole) was added and treated at reflux until carbon dioxide ceased to evolve (5 hr.). The mixture was then poured into water; the organic layer was separated, dried, and distilled. The product boiled at 128–134°/2 mm. The yield was 4.6 g. (15.5%). Most of the charge formed an azeotrope which was not worked up.

Anal. Calcd. for $C_{16}H_{15}NF_4$: C, 64.6; H, 5.2; F, 25.6; N, 4.7. Found: C, 64.5; H, 5.2; F, 24.7; N, 4.9.

N-1H,1H,3H-Tetrafluoropropylaniline (VIII) *from bis-1H,1H,3H-tetrafluoropropyl sulfate.* A mixture of bis-1*H*,-1*H*,3*H*-tetrafluoropropyl sulfate (VI) (167 g.; 0.5 mole) and aniline (98 ml.; 1.08 mole) was heated in a stainless steel shaker bomb for 10 hr. After cooling and venting the bomb, the semisolid contents were extracted by the Soxhlet technique with ether. The ether extract was washed with 5% hydrochloric acid to remove aniline. After repeated washes with water, the ether solution was dried and ether removed by distillation. The product obtained at 126°/30 mm. weighed 14 g. (27.1%).

1,4-Di-1H,1H,3H-Tetrafluoropropylaminoanthraquinone (IX). Leuco quinizarin (12 g.; 0.05 mole) was charged to a 250-ml. flask equipped with stirrer, thermometer, and reflux condenser. Butanol (40 ml.) and 1*H*,1*H*,3*H*-tetrafluoropropylamine (14.8 g.; 0.1 mole) was added to the flask and the mixture stirred at reflux for 20 hr. To the wine red solution, a solution of sodium perborate (11.8 g.) in water (15 ml.) was added to oxidize the leuco dye. Stirring was continued for 3 hr. at 90–95°. The mixture was then poured into 1500 ml. of warm water. After cooling with agitation, the solid material was filtered off and washed with water. The dried dye (8 g.) was twice recrystallized from ethanol giving shiny, blue-black crystals melting at 183°.

Anal. Calcd. for $C_{20}H_{14}O_2N_2F_8$: C, 51.5; H, 3.0; F, 32.6, N, 6.0. Found: C, 52.1; H, 3.1; F, 30.7, N(Kjel), 5.8.

1-OH,4-Di-1H,1H,3H-Tetrafluoropropylaminoanthraquinone (X). The apparatus and reaction conditions were identical with those in the last preparation. Total reflux time for the reaction of leuco quinizarin (12 g.; 0.05 mole) with 1*H*,1*H*,-3*H*-tetrafluoropropylamine (7.2 g.; 0.05 mole) in butanol (65 ml.) was 6 hr. After recrystallization of the crude dye (7.5 g.) in ethanol, the dull red product appeared to be about 80% pure. It melted at 141°.

Anal. Calcd. for $C_{17}H_{11}O_3NF_4$: C, 57.8; H, 3.115; F, 21.5; N, 3.96. Found: C, 59.8; H, 3.5; F, 17.0; N(Kjel), 3.2.

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(15) Prepared by Dr. T. E. Roberts, E. I. du Pont de Nemours and Co.

Sodium 1H,1H,ωH-fluoroalocoholates. Sodium wire dissolved readily in three to fourfold molar excess of *1H,1H,3H*-tetrafluoropropanol or *1H,1H,5H*-octafluoropentanol at 80-90° with formation of the alcoholates. When equivalent amounts of *1H,1H,5H*-octafluoropentanol and sodium were treated in ether or in dioxane at the reflux for long periods, the metal was not completely consumed. A brown film of carbonaceous material formed on the sodium particles and finally brought the reaction to a stop.

Sodium fluoroalcoholates are best prepared by the reaction of equimolar amounts of fluoro alcohol and sodium hydride in ether, and can be precipitated from ether solutions with dry xylene. The compounds should not be heated in the absence of solvents as violent decompositions may occur.[16]

Potassium 1H,1H,ωH-fluoroalcoholates. The formation of potassium fluoroalcoholates was carried out in dimethoxytetraethylene glycol at 84°. Small pieces of the metal were added to the stirred mixture under anhydrous conditions in a nitrogen atmosphere. Use of potassium in this reaction is much more dangerous than sodium, explosions having occurred even in the absence of air.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA]

Polymerization by the Diels-Alder Reaction[1,2]

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Received April 10, 1961

Polymerization reactions which utilize the Diels-Alder reaction as a propagation mechanism to produce high molecular weight polymers have been successfully accomplished. Three biscyclopentadienes, 1,6-bis(cyclopentadienyl)hexane, 1,9-bis(cyclopentadienyl)nonane and α,α′-bis(cyclopentadienyl)-*p*-xylene have been prepared. These monomers have been homopolymerized and copolymerized with the didienophiles *p*-benzoquinone and *N,N′*-hexamethylenebismaleimide. The results of the polymerization studies and the studies of polymer structure demonstrate that the homopolymerizations take place by a Diels-Alder reaction in which the monomer acts both as a diene and a dienophile while in the copolymerization reactions the biscyclopentadiene compounds serve as didienes.

A polymerization which utilizes a Diels-Alder reaction for propagation to yield high molecular weight polymers has only recently been investigated.[3-6] Cyclopentadiene readily dimerizes at room temperature, and at elevated temperatures over longer periods of time, a trimer, tetramer, pentamer, hexamer and other higher molecular weight polymers are formed.[7] Although a portion of the higher molecular weight polymer is a result of vinyl addition polymerization, the oligomers are formed through successive additions of cyclopentadiene through a Diels-Alder reaction.[8]

The fact that cyclopentadiene and methylcyclopentadiene readily dimerize by serving both as a diene and a dienophile in a Diels-Alder reaction and the fact that these dienes readily react with a wide variety of dienophiles, prompted the investigation of a series of biscyclopentadienyl compounds. Such a compound should be able to undergo not only a homopolymerization reaction but also a copolymerization reaction with a didienophile.

Substituted ferrocene derivatives have been prepared from biscyclopentadienylalkanes which were not isolated as such but used *in situ.*[9] The polymerization of α,α′-bis(cyclopentadienyl)-*p*-xylene has been reported to give an insoluble polymer by a Diels-Alder propagation,[10] but this polymer is probably the result of extensive vinyl addition polymerization.

The preparation of 1,6-bis(cyclopentadienyl)hexane (Ia), 1,9-bis(cyclopentadienyl)nonane (Ib) and α,α′-bis(cyclopentadienyl)-*p*-xylene (Ic) was carried out by the addition of cyclopentadienyl sodium to the appropriate dibromide. The products could not be suitably purified by crystallization and attempted distillation led to rapid polymerization of these monomers. The liquid monomers were partially purified by repeated slow precipitations

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(1) This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. Preliminary investigation in this research was supported by a grant from the Socony Mobile Oil Co., Inc., Paulsboro, N. J.

(2) Presented in part at the September 1959 Meeting of the American Chemical Society, Atlantic City, N. J.

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