Preparation of Tosylglycine 2-Chloroethyl Ester from the Methyl Ester in 2-Chloroethanol.—A mixture of 4.8 g. of tosylglycine methyl ester, 0.2 g. of aluminum metal shavings, catalytic amounts of carbon tetrachloride and mercuric chloride and 20 ml. of 2-chloroethanol was stirred and refluxed for 4 hr. The 2-chloroethyl ester of tosylglycine was isolated in the same manner as the isopropyl ester; yield 4.4 g. (86%). The product was recrystallized from ether, m.p. 78–80°.

Anal. Calcd. for $C_{11}H_{14}SNO_4Cl$: N, 4.80; S, 10.99. Found: N, 4.87; S, 11.05.

Preparation of Tosylglycine Methyl Ester from Tosylglycine Isopropyl Ester in Methanol.—To 50 ml. of methanol 0.2 g. (0.0066 mole + 10% excess) of aluminum shavings, 2 ml. of carbon tetrachloride and a few crystals of mercuric chloride were added. The mixture was stirred and refluxed for 6 hr. Tosylglycine isopropyl ester, 2.7 g. (0.01 mole), was added and stirring and refluxing continued for 3 days (72 hr.). This prolonged reaction time was necessary for the completion of the alkoxyl exchange since shorter reaction times led to a mixture of isopropyl and methyl esters. The methanol solution was filtered (0.3 g. insoluble) and evaporated in vacuum. The residue was dissolved in 5 ml. of fresh methanol and a mixture of 50 ml. of water and 5 ml. of concd. hydrochloric acid was added. After chilling, the crystalline precipitate was isolated and dried; yield 2 g. (82.3%) of crude product which was recrystallized from ether; yield of crystalline tosylglycine methyl ester, 1.4 g. (57.6%). The substance had the m.p. 92–94° and did not depress the melting point of tosylglycine methyl ester prepared by the esterification of tosylglycine with methanol.

Anal. Calcd. for $C_{10}H_{13}SNO_4$: N, 5.76; S, 13.18. Found: N, 5.75; S, 13.25.

Preparation of Tosylglycine Methyl Ester from Tosylglycine Benzyl Ester in Methanol.—A solution of aluminum methoxide in methanol was prepared as described above from 0.1 g. (0.0033 mole + 10% excess) of aluminum shavings. Tosylglycine benzyl ester, 3.19 g. (0.01 mole) was added and the mixture refluxed for a day (26 hr.). The methanol solution was filtered and the filtrate poured into a mixture of 400 ml. of water and 6 ml. of concd. hydrochloric acid. After chilling the crystalline product was removed by filtration. The dried substance had the m.p. 91–93° and did not depress the melting point of tosylglycine methyl ester.

Anal. Calcd. for $C_{10}H_{13}SNO_4$: N, 5.76. Found: N, 5.70.

Discussion

According to the examples described in the Experimental part, the alcoholysis of an ester with an aluminum alcoholate can be brought to completion: (a) if the aluminum alcoholate produced in the reaction has a low solubility in the solvent in which the reaction is carried out, or (b) if the alcohol corresponding to the alkoxyl group to be exchanged is used as the solvent for the reaction.

Reaction time is an important factor in the alkoxyl exchange as shown by the change of the percentage of nitrogen in the reaction product as a function of time (Table I).

The nature of the alkoxyl residue of the aluminum alcoholate determines the time necessary for the ester interchange. A complete exchange of the methoxy group for an isopropoxy group in toluene takes place in about 6 hr. while the benzoxy and the 1-methylpentoxy group replaces the methoxy group in 4 hr. in the same solvent. In methanol solution the exchange of the benzoxy group for the methoxy group takes about 26 hr., while more than 70 hr. are needed to transform the isopropyl ester into the methyl ester.

The ratio of ester to aluminum alcoholate is also a factor which influences the reaction time. Using approximately equivalent amounts of reactants, the time for complete alcohol exchange between tosylglycine methyl ester and aluminum isopropoxide in toluene solution is about 6 hr. (Table Ia). When five equivalents of aluminum isopropoxide are treated with one equivalent of tosylglycine methyl ester the reaction is completed in 7.5 minutes (Table Ib).

As demonstrated the exchange of alkoxyl groups between an ester and an aluminum alkoxide can be completed under properly chosen conditions without fractional distillation.

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CHICAGO 9, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN ONTARIO]

Toxic Fluorine Compounds. VII.[1] ω-Fluoroalkyl Thiocyanates and ω-Fluoroalkyl Mercaptans

BY W. C. HOWELL, J. E. MILLINGTON AND F. L. M. PATTISON

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Representative members of the series of ω-fluoroalkyl thiocyanates and mercaptans were synthesized and their chemical, physical and toxicological properties determined. Evidence was obtained (a) for the reductive scission *in vivo* of aliphatic thiocyanates forming cyanide ion and the corresponding mercaptans and (b) for transthiolation of mercaptans to alcohols.

The pharmacological properties of the ω-fluorine atom have been described in earlier papers in this series.[2] The preparations of the ω-fluoroalkyl thiocyanates and mercaptans were undertaken in order to obtain information regarding the detoxication mechanism of aliphatic thiocyanates and mercaptans.

2-Fluoroethyl thiocyanate[3] and 3-fluoropropyl thiocyanate[4] have been prepared previously. Of the ω-fluoroalkyl mercaptans, only the 2-fluoroethyl derivative[5] has been mentioned in the literature. The preparation of the acetyl derivative of 2-fluoro-

(1) Issued as DRB Report No. SW-23.

(2) Part VI, THIS JOURNAL, **78**, 3487 (1956).

(3) B. C. Saunders, G. J. Stacey and I. G. E. Wilding, *J. Chem. Soc.*, 773 (1949).

(4) B. C. Saunders and F. L. M. Pattison, unpublished work (1947).

(5) E. K. Ellingboe, U. S. Patent 2,439,203; April 6, 1948.

ethyl mercaptan also has been reported[5,6]; the physical constants of this material have been recorded more recently.[7]

The ω-fluoroalkyl thiocyanates were readily prepared from the corresponding ω-fluoroalkyl halides[8] or *p*-toluenesulfonates by reaction with potassium thiocyanate. Yields are shown in Table I.

TABLE I

PREPARATION AND PROPERTIES OF ω-FLUOROALKYL THIOCYANATES

Thiocyanate	Method[a]	Yield, %	B.p., °C.	Mm.	$n^{25}D$
2-Fluoroethyl[b]	II	50	78–79	20	1.4615
	III	73	83–83.5	25	
3-Fluoropropyl	II	80	78–79	10	1.4591
	III	69	75–76	9	
4-Fluorobutyl	I	66	97–98	13	1.4610
	II	60	99.5–100	13	
5-Fluoroamyl	I	55	112–113	11	1.4603
	II	89	113–114	12	
	II[c]	85[c]	116–117	14	
	III	85	109–110	9	
6-Fluorohexyl	II	95	124–125	11	1.4595

[a] Methods: I, from ω-fluoroalkyl chloride using potassium iodide as a promoter; II, from ω-fluoroalkyl bromide; III, from ω-fluoroalkyl *p*-toluenesulfonate. [b] Saunders, *et al.*,[3] report b.p. 77.5–78.5° (19 mm.). [c] Using ammonium thiocyanate.

Several of the standard methods of preparation of mercaptans proved to be unsatisfactory in this work. Thus, interaction of the corresponding bromides with thiourea followed by hydrolysis gave very low yields. Moreover, the members containing four, five and six carbon atoms tended to cyclize readily, forming tetrahydrothiophene, tetrahydrothiopyran and hexamethylene sulfide, respectively. In simulation of the biological reduction suggested below, 3-fluoropropyl, 5-fluoroamyl and 6-fluorohexyl mercaptans were conveniently prepared[9] from the corresponding ω-fluoroalkyl thiocyanates by reduction with lithium aluminum hydride; aliphatic mercaptans have not previously been prepared by this method. 4-Fluorobutyl thiocyanate under these conditions again formed tetrahydrothiophene by loss of hydrogen fluoride from the intermediate mercaptan. Accordingly, its acetate, 4-fluorobutyl thiolacetate, was synthesized[10] directly from 4-fluorobutyl *p*-toluenesulfonate by reaction with potassium thiolacetate

$$F(CH_2)_4OTs + KSCOCH_3 \longrightarrow F(CH_2)_4SCOCH_3 + TsOK$$
(Ts = *p*-$CH_3C_6H_4SO_2$–)

This method had first been shown to be satisfactory for the preparation of 2-fluoroethyl thiolacetate. Yields by the above methods are shown in Table II.

The above mentioned reduction of ω-fluoroalkyl thiocyanates to ω-fluoroalkyl mercaptans illustrates the value of lithium aluminum hydride in the preparation of ω-fluoro compounds. The need for a reducing agent which would reduce the functional groups of monofluorinated aliphatic compounds without simultaneous loss of fluorine was recognized early in the over-all work of this project. The use of standard basic reducing agents was prohibited because of the ready removal of hydrogen fluoride with concomitant unsaturation or cyclization, while high-pressure hydrogenation readily formed the corresponding non-fluorinated compound.[11] Lithium aluminum hydride has now been shown to satisfy the necessary requirements; it has been used to advantage in the reduction of ω-fluorocarboxylic acids and esters to ω-fluoroalcohols,[12] of fluorinated nitriles to amines[13] and now of ω-fluoroalkyl thiocyanates to the corresponding mercaptans.

TABLE II

PREPARATION AND PROPERTIES OF ω-FLUOROALKYL MERCAPTANS AND THIOLACETATES

Compound	Yield, %	B.p., °C.	Mm.	$n^{25}D$
2-Fluoroethyl thiolacetate[a]	75	50–51	20	1.4510
3-Fluoropropyl mercaptan	26	100–101	749	1.4355
4-Fluorobutyl thiolacetate	63.5	76.5–78	13	1.4554
5-Fluoroamyl mercaptan	77	56–56.2	17	1.4442
6-Fluorohexyl mercaptan	83	68–69	16	1.4456

[a] Gryszkiewicz-Trochimowski[6] reports b.p. 41–42° (12 mm.); Redemann, *et al.*,[7] report b.p. 58–59° (30 mm.) and $n^{20}D$ 1.4538.

The chemical properties and odor of the ω-fluoroalkyl thiocyanates and mercaptans are similar to those of the non-fluorinated materials. Thus, the ω-fluoroalkyl thiocyanates on treatment with chlorine water readily form the corresponding ω-fluoroalkanesulfonyl chlorides; this will be described in more detail in the next paper in this series. The physical properties of the new members are shown in Tables I and II.

By reference to the well-known metabolic transthiolation reaction (RSH → ROH), it was considered likely that the ω-fluoroalkyl mercaptans would exhibit the same alternation in toxicity as that of the ω-fluoroalcohols.[12] The fact that the two and four carbon members were acetylated was unimportant because of the presence of a deacetylating enzyme in the liver and kidney.[14] The toxicity results shown in Table III conform to the expected pattern and thus provide *a priori* evidence for the transthiolation *in vivo* of simple aliphatic mercaptans.

Nothing is known about the metabolic fate of aliphatic thiocyanates. It was considered likely, however, that reductive scission would occur, giving rise to cyanide and the corresponding mercaptans and that the latter would then behave as described above

$$F(CH_2)_nSCN \xrightarrow{\text{hydrogenase}} F(CH_2)_nSH + HCN$$

(6) E. Gryszkiewicz-Trochimowski, *Rec. trav. chim.*, **66**, 427 (1947).

(7) C. E. Redemann, S. W. Chaikin, R. B. Fearing, G. J. Rotariu, J. Savit and D. van Hoesen, THIS JOURNAL, **70**, 3604 (1948).

(8) F. L. M. Pattison and W. C. Howell, *J. Org. Chem.*, **21**, in press (1956).

(9) F. L. M. Pattison, Interim Reports to Defence Research Board of Canada, Nos. 3 and 4 (May and October, 1951).

(10) F. L. M. Pattison, Interim Report to Defence Research Board of Canada, No. 7 (December, 1953).

(11) F. L. M. Pattison and B. C. Saunders, *J. Chem. Soc.*, 2745 (1949).

(12) F. L. M. Pattison, W. C. Howell, A. J. McNamara, J. C. Schneider and J. F. Walker, *J. Org. Chem.*, **21**, in press (1956).

(13) F. L. M. Pattison, W. C. Howell and R. W. White, THIS JOURNAL, **78**, 3487 (1956).

(14) H. O. Michel, F. Bernheim and M. L. C. Bernheim, *J. Pharmacol. Exp. Therap.*, **61**, 321 (1937).

The pronounced alternation in toxicity of the ω-fluoroalkyl thiocyanates shown in Table III is in accord with this suggestion and thus provides evidence for this conversion *in vivo* of the thiocyanate grouping to mercaptan.

TABLE III

Compound	L.D. 50 for mice, mg./kg. (intraperitoneal)	Compound	L.D. 50 for mice, mg./kg. (intraperitoneal)
$CH_3(CH_2)_4SCN$	75	$CH_3(CH_2)_4SH$	>100
$Cl(CH_2)_4SCN$[15]	15		
$Cl(CH_2)_5SCN$[15]	24		
$F(CH_2)_2SCN$	15	$F(CH_2)_2SAc$	56
$F(CH_2)_3SCN$	18	$F(CH_2)_3SH$	>100
$F(CH_2)_4SCN$	2.6	$F(CH_2)_4SAc$	1.8
$F(CH_2)_5SCN$	30	$F(CH_2)_5SH$	>100
$F(CH_2)_6SCN$	5.0	$F(CH_2)_6SH$	1.25

Experimental[16]

2-Fluoroethyl *p*-Toluenesulfonate.—A mixture of 2-fluoroethanol (29 g., 0.45 mole) and pyridine (100 g.) was stirred in a flask immersed in an ice–HCl bath at −9°, and to it was slowly added *p*-toluenesulfonyl chloride (85 g., 0.45 mole). Stirring was continued for 6 hr., and the mixture was stored overnight in a refrigerator. Hydrochloric acid (5 *N*) was added until no pyridine odor was perceptible, and the resultant mixture was extracted several times with ether. The combined extracts were washed successively with water, aqueous sodium carbonate and finally with water again. After drying over anhydrous calcium chloride and removal of the ether, fractionation of the residue yielded 2-fluoroethyl *p*-toluenesulfonate (78.3 g., 80%), a colorless liquid of b.p. 138.5–140° (1 mm.) and $n^{25}D$ 1.5060. (Childs, *et al.*,[19] quote b.p. 135–136° (1 mm.)).

4-Fluorobutyl *p*-Toluenesulfonate.—A solution of 4-fluorobutyl iodide[8] (50 g., 0.25 mole) and silver *p*-toluenesulfonate (39 g., 0.14 mole) in acetonitrile (100 ml.) was heated under reflux for 22 hr. The precipitated silver iodide was removed by filtration and washed with a small quantity of acetonitrile. The filtrate was concentrated, and the residue on fractionation yielded 19.1 g. of recovered 4-fluorobutyl iodide and then 29.0 g. (84%) of 4-fluorobutyl *p*-toluenesulfonate, a colorless liquid of b.p. 151° (1 mm.) and $n^{25}D$ 1.4988.

Preparation of ω-Fluoroalkyl Thiocyanates.—The three methods referred to in Table I are represented by the following examples.

Method I: 4-Fluorobutyl Thiocyanate.—A mixture of 4-fluorobutyl chloride[8] (22 g., 0.2 mole), potassium thiocyanate (29.1 g., 0.3 mole) and potassium iodide (1.6 g.) in 95% ethanol (70 ml.) was heated under reflux with constant stirring for 10 hr. After cooling, water was added to dissolve the potassium chloride which had precipitated during the reaction. The aqueous solution was then extracted several times with ether. The combined extracts were dried over anhydrous sodium sulfate. After removal of the ether, the residue on fractionation yielded 17.6 g. (66.2%) of 4-fluorobutyl thiocyanate, a colorless, vile-smelling liquid.

Method II: 6-Fluorohexyl Thiocyanate.—Potassium thiocyanate (15.8 g., 0.164 mole) was mixed with 95% ethanol (37 ml.). While the mixture was being stirred and heated under reflux, 6-fluorohexyl bromide (20 g., 0.109 mole) was slowly added over 30 minutes. The mixture was heated under reflux for a further 3 hr. Bumping was minimized by vigorous stirring. After cooling, the potassium bromide was removed by filtration and washed with a small quantity of ethanol. The majority of the alcohol was then removed from the filtrate by distillation. The crude thiocyanate was diluted with water and then isolated, dried and purified as described under method I. 6-Fluorohexyl thiocyanate (16.7 g., 95%) was obtained as a colorless liquid.

Method III: 2-Fluoroethyl Thiocyanate.—A mixture of 2-fluoroethyl *p*-toluenesulfonate (30 g., 0.137 mole), potassium thiocyanate (19.9 g., 0.205 mole) and water (10 ml.) was heated under reflux for 3 hr. The product was diluted with water and extracted with ether. The combined extracts were dried over anhydrous sodium sulfate. After removal of the ether, the residue on fractionation gave 10.5 g. (73%) of 2-fluoroethyl thiocyanate, a colorless liquid.

TABLE IV

ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$F(CH_2)_3SCN$	40.33	40.14	5.04	5.05			11.77	11.59
$F(CH_2)_4SCN$	45.11	44.96	6.01	5.90			10.52	10.35
$F(CH_2)_5SCN$	48.98	48.73	6.80	6.71			9.54	9.85
$F(CH_2)_6SCN$	52.18	52.50	7.45	7.32			8.70	8.99
							F, 11.81	11.8
$F(CH_2)_3SH$	38.30	38.30	7.45	7.42	34.04	34.29		
$F(CH_2)_4SCOCH_3$	48.00	48.24	7.33	7.20	21.33	21.24		
$F(CH_2)_5SH$	49.21	49.18	8.99	9.02	26.23	25.96		
$F(CH_2)_6SH$					23.53	23.80	F, 13.97	14.0
$F(CH_2)_4OSO_2C_6H_4CH_3$	53.64	53.82	6.14	6.19				

Preparation of ω-Fluoroalkyl Mercaptans.—The following example is representative of the three reductions summarized in Table II.

6-Fluorohexyl Mercaptan.—To a solution of lithium aluminum hydride (2.36 g., 0.062 mole) in anhydrous diethyl ether (250 ml.) was slowly added, with stirring, a solution of 6-fluorohexyl thiocyanate (10 g., 0.062 mole) in anhydrous diethyl ether (100 ml.). When the addition was complete, water was added to decompose the excess hydride. The gelatinous lithium aluminum complex was hydrolyzed by the slow addition of 3 *N* hydrochloric acid until a clear solution was obtained. The ether layer was separated and the aqueous layer extracted with two 100-ml. portions of ether. The combined ethereal extracts were dried over anhydrous sodium sulfate. After removal of the ether, the residue on fractionation through a 30-cm. Vigreux column yielded 7 g. (83%) of 6-fluorohexyl mercaptan, a colorless liquid with the characteristic mercaptan odor.

Preparation of ω-Fluoroalkyl Thiolacetates.—2-Fluoroethyl and 4-fluorobutyl thiolacetates were prepared essentially by the same procedure.

4-Fluorobutyl Thiolacetate.—A mixture of 4-fluorobutyl *p*-toluenesulfonate (13 g., 0.053 mole), potassium thiolacetate (9 g., 0.08 mole) and acetone (125 ml.) was heated under reflux for 2 hr. After cooling, the solid was filtered off and washed with a little acetone. The filtrate was concentrated, diluted with water and extracted with ether. The combined extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the ether, the

(15) F. L. M. Pattison and J. E. Millington, *Can. J. Chem.*, **34**, 757 (1956).

(16) (a) The majority of the microanalyses were performed by Mr. J. F. Alicino, Metuchen, N. J. The fluorine determinations were carried out in the authors' laboratory either by the lead chlorofluoride method[17] or by the amperometric method[18] using aluminum chloride and Superchrome Garnet Y. Results are shown in Table IV. (b) The boiling points are uncorrected.

(17) N. B. Chapman, R. Heap and B. C. Saunders, *Analyst*, **73**, 434 (1948).

(18) C. R. Castor and J. H. Saylor, *Anal. Chem.*, **24**, 1369 (1952).

(19) A. F. Childs, L. J. Goldsworthy, G. F. Harding, F. E. King, A. W. Nineham, W. L. Norris, S. G. P. Plant, B. Selton and A. L. L. Tompsett, *J. Chem. Soc.*, 2174 (1948).

residue on fractionation yielded 5.0 g. (63.5%) of a colorless, vile-smelling liquid.

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LONDON, ONTARIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN ONTARIO]

Toxic Fluorine Compounds. VIII.[1] ω-Fluoroalkanesulfonyl Chlorides and Fluorides

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Representative members of the series of ω-fluoroalkanesulfonyl chlorides and fluorides were synthesized and their physical and toxicological properties determined. The toxicity figures suggested that the ω-fluoroalkanesulfonyl chlorides were metabolized by a mechanism akin to β-oxidation, whereas no clear-cut characteristics were apparent for the corresponding fluorides.

In earlier papers[2] in this series have been described the toxicological properties of various series of ω-fluoro-compounds. From the results so far presented, it seemed desirable next to examine simple analogs of the ω-fluorocarboxylic acid series, $F(CH_2)_nCOOH$. The ω-fluoroalkanesulfonic acids, $F(CH_2)_nSO_3H$, are the sulfonic acid analogs of the carboxylate series, and the two classes thus bear a superficial resemblance to one another. In order to assess the toxicological effects of these two classes, representative ω-fluoroalkanesulfonyl derivatives were prepared[3,4] for comparison with the previously described ω-fluorocarboxylates.[5] It has been reported that *n*-alkanesulfonic acids are nontoxic[6] and are excreted unchanged by the dog[7]; hence no great activity was anticipated for the ω-fluoro-derivatives.

Two members of the ω-fluoroalkanesulfonyl chloride series, $F(CH_2)_nSO_2Cl$, have been prepared previously, 2-fluoroethanesulfonyl chloride[8] and 3-fluoropropanesulfonyl chloride,[9] but toxicity determinations on these derivatives were indefinite. No member of the ω-fluoroalkanesulfonyl fluoride series, $F(CH_2)_nSO_2F$, has been previously described.

In this work, the ω-fluoroalkanesulfonyl chlorides were generally prepared by treatment of the corresponding thiocyanates[10] with chlorine water.[11] As an alternative route to 2-fluoroethanesulfonyl chloride, 2-fluoroethanol was converted to the *p*-toluenesulfonate,[10] which in turn was treated with thiourea[12] to form 2-fluoroethylisothiouronium *p*-toluenesulfonate; finally, the reaction of this salt with chlorine water[12] formed the sulfonyl chloride; yields are shown in Table I.

$$F(CH_2)_2OH \xrightarrow{TsCl} F(CH_2)_2OTs \xrightarrow{(H_2N)_2CS} [F(CH_2)_2SC(NH_2)=NH_2]^{+-}OTs \xrightarrow{Cl_2\ aq.} F(CH_2)_2SO_2Cl \quad (Ts- = p\text{-}CH_3C_6H_4SO_2-)$$

TABLE I

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALKANESULFONYL CHLORIDES

Chloride	Yield, %	B.p., °C.	Mm.	$n^{25}D$
2-Fluoroethanesulfonyl[a]	64[b]	82–83	14	1.4509
	51[c]	82–83	14	
3-Fluoropropanesulfonyl	60	95.5–96	12	1.4481
4-Fluorobutanesulfonyl	77	117–118	13	1.4512
5-Fluoropentanesulfonyl	61	134–135	13	1.4513
6-Fluorohexanesulfonyl	38	150–151	15	1.4518

[a] Saunders, *et al.*,[8] report b.p. 81.5–84.5° (13 mm.). [b] From thiocyanate. [c] From isothiouronium *p*-toluenesulfonate.

The ω-fluoroalkanesulfonyl chlorides were converted to the ω-fluoroalkanesulfonyl fluorides by treatment with aqueous potassium bifluoride. In most instances, the product was steam distilled prior to isolation and purification. Yields are shown in Table II.

TABLE II

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALKANESULFONYL FLUORIDES

Fluoride	Yield, %	B.p., °C.	Mm.	$n^{25}D$
2-Fluoroethanesulfonyl	45	62–63	14	1.3798
3-Fluoropropanesulfonyl	57	74–75	15	1.3868
4-Fluorobutanesulfonyl	56	89–90	12	1.3970
5-Fluoropentanesulfonyl	45	106–107	12	1.4040
6-Fluorohexanesulfonyl	22[a]	128–129	16	1.4092
n-Butanesulfonyl	57	60–61	17	1.3939

[a] Low yield partly due to very small scale reaction.

The ω-fluorine atom in these compounds is inert

(1) Issued as DRB Report No. SW-24.
(2) Part VII, THIS JOURNAL, **78**, 3843 (1956).
(3) F. L. M. Pattison, *Nature*, **174**, 737 (1954).
(4) F. L. M. Pattison, Interim Reports to Defence Research Board of Canada, Nos. 6 and 7 (June and December, 1953).
(5) F. J. Buckle, F. L. M. Pattison and B. C. Saunders, *J. Chem. Soc.*, 1471 (1949).
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(11) T. B. Johnson and I. B. Douglass, *ibid.*, **61**, 2548 (1939).
(12) D. Klamann and F. Drahowzal, *Monatsh.*, **83**, 463 (1952).