COMMUNICATIONS

Synthetic Methods and Reactions. VII[1]. Preparation of Alkyl and Haloalkyl Fluorosulfates from Alkenes (Haloalkenes) or Cyclopropanes with Fluorosulfuric Acid

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Much attention is being recently given to alkyl fluorosulfates, because the fluorosulfate anion is a good leaving group in solvolytic reactions[2], and also because of their reported good alkylating ability for *n*-donor bases (*N*- and *O*-alkylation)[3].

Several methods of preparation of alkyl (aryl) fluorosulfates are known. These include:

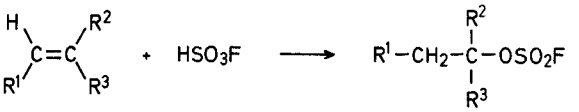
- transesterification of dialkyl sulfate[4] or trialkyl phosphate with fluorosulfuric acid,
- halogen exchange of alkyl chlorosulfates with silver fluoride[5] or tetrafluoro-2-hydroxyethane sulfonic *β*-sulton[6],
- nucleophilic displacement of fluorosulfate anion from sulfuryl chloride fluoride by phenoxy anion[7],
- reaction of RCF_2OR[8] with SO_3[8],
- aromatic nucleophilic rearrangement in fluorosulfuric acid[9], and
- thermal decomposition of aryldiazonium fluorosulfates[10].

Besides, several methods of preparation of fluoroalkyl fluorosulfates were also reported. These include:

- reaction of peroxydisulfuryl difluoride with perfluoroalkenes[11], perfluorocarboxylic anhydrides[12], and perfluoroalkyl bromides[13],
- addition of $XOSO_2F$ (X = F, Cl, Br, NF_2) to perfluoroalkenes[14],
- reaction of fluorinated alkyl halides and fluorosulfuric acid[15],
- reaction of pyrosulfuryl fluoride and fluoroacetic anhydride[16], and
- reaction of ethers with fluorosulfuric acid[17].

Despite the numerous methods of preparation reported, no simple convenient synthetic method of alkyl fluorosulfates was yet known. We wish now to report such a general method by the addition of fluorosulfuric acid to alkenes, haloalkenes and cyclopropanes, respectively. Although some alkyl and haloalkyl fluorosulfates have been prepared by the reaction of alkenes and haloalkenes with fluorosulfuric acid[17,18], the method was not yet explored for its general applicability.

In Table 1 are summarized preparative data of isolated alkyl (haloalkyl) fluorosulfates, and in Table 2 their N.M.R. parameters, including also those of alkyl fluorosulfates prepared in solution at low temperature, but not isolated. Reactions of alkenes as well as haloalkenes were usually smooth and gave isolable fluorosulfates in high yields (around 90%). However, easily polymerizable alkenes like styrene, butadiene, and isobutylene gave only polymeric materials. Others, like vinyl chloride which at −78° in solution gave a nearly quantitative yield of 1-chloroethyl fluorosulfate, afforded polymeric materials during attempted isolation at higher temperature.



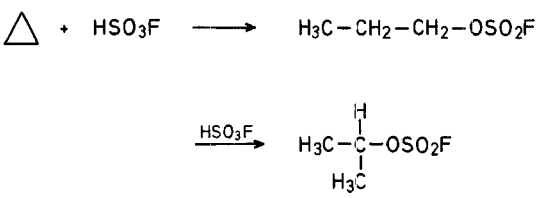
a: $R^1=R^2=R^3=H$
b: $R^1=R^2=H$, $R^3=CH_3$
c: $R^1=R^2=H$, $R^3=F$
d: $R^1=R^2=H$, $R^3=Cl$
e: $R^1=H$, $R^2=R^3=F$
f: $R^1=R^3=F$, $R^2=H$
g: $R^1=Cl$, $R^2=H$, $R^3=F$
h: $R^1=R^2=R^3=F$
i: $R^1=H$, $R^2=CH_3$, $R^3=F$

The reaction of cyclopropane with fluorosulfuric acid at −78° gave *n*-propyl fluorosulfate, with 21% isopropyl fluorosulfate (based on the starting acid) as a byproduct (total yield 94%), but distillation gives only 50% *n*-propyl and no isopropyl fluorosulfate. *n*-Propyl fluorosulfate itself is not stable in fluorosulfuric acid and readily rearranges at −40° to isopropyl fluorosulfate. It was reported that the reaction of cyclopropane and 8.43 *M* sulfuric acid gives

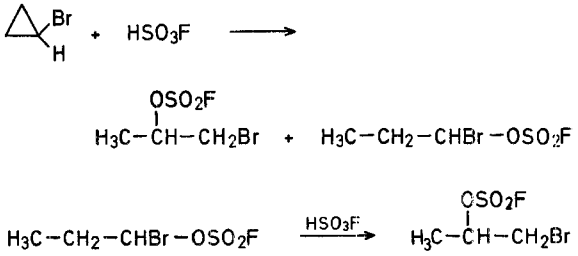
Table 1. Preparation of Alkyl Fluorosulfates from Alkenes with Fluorosulfuric Acid.

Starting Material	Reaction Temp.	Product	Yield (%)	Bp (°/torr)
$H_2C=CH_2$	0–5°	$H_3C-CH_2-OSO_2F$	80	51/81
$H_3C-CH=CH_2$	−40°	$(H_3C)_2CH-OSO_2F$	83	~20/6
$H_2C=CHF$	−78°	$H_3C-CHF-OSO_2F$	90–95	33/35
$H_2C=CF_2$	−78°	$H_3C-CF_2-OSO_2F$	90–95	25/30
△	−78°	$H_3C-CH_2-CH_2-OSO_2F$	50	43/27

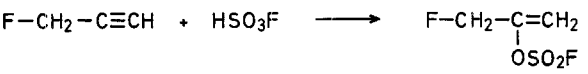
almost exclusively 1-propanol through protonated cyclopropane[19]. Thus, isopropyl fluorosulfate is probably formed in a secondary reaction.



Bromocyclopropane reacted slowly with the acid in SO_2ClF at $-70°$ and gave mainly 2-bromo-1-methylethyl fluorosulfate and 1-bromopropyl fluorosulfate[20] (in the ratio of 65:35, respectively). Raising the temperature up to $-40°$, 1-bromopropyl fluorosulfate was isomerized to 2-bromo-1-methylethyl fluorosulfate in fluorosulfuric acid.

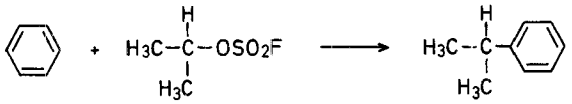


Alkynes are generally too reactive to give isolable alkenyl fluorosulfates. 3-Fluoropropyne, however, reacted with fluorosulfuric acid at $-78°$ to give 1-(fluoromethyl) vinyl fluorosulfate.



It is interesting to note that isopropyl fluorosulfate is the first example of a prepared secondary alkyl (C_nH_{2n+1}) fluorosulfate. Primary alkyl fluorosulfates[6] and those substituted alkyl fluorosulfates[11-16] containing electron-withdrawing groups are generally stable compounds, but *sec*- and *tert*-alkyl fluorosulfates without electron-withdrawing groups are much more labile. Isopropyl fluorosulfate is too unstable to be kept at room temperature, and must be kept at low temperature under carefully acid-free conditions.

It is noteworthy that the labile isopropyl fluorosulfate can readily alkylate the benzene nucleus to give isopropylbenzene derivatives in 30–60% yield. No similar *C*-alkylation of the benzene nucleus takes place with methyl and ethyl fluorosulfate.



The above reaction is exothermic and occurs spontaneously at room temperature after a short induction period. However, using diisopropylethylamine, a hindered Hünig-base, as a proton-trapping agent, the reaction is remarkably retarded. This indicates that alkylation with isopropyl fluorosulfate is acid catalyzed. Details of the alkylation of aromatic compounds with alkyl fluorosulfates will be reported separately in a forthcoming publication.

Table 2. N.M.R. Parameters of Alkyl and Haloalkyl Fluorosulfates ($ROSO_2F$) at $-50°$ in SO_2ClF

^1H Spectra (δ ppm vs TMS) R	C-1	C-2	C-3
H_3C-	4.30 (s)	–	–
H_3C-CH_2-	5.01 (q, $J_{HH}=7.0$ Hz)	1.69 (t, $J_{HH}=7.0$ Hz)	–
$H_3C-CH_2-CH_2-$	4.70 (t, $J_{HH}=6.5$ Hz)	2.02 (sex., $J_{HH}=7.0$ Hz)	1.17 (t, $J_{HH}=7.0$ Hz)
$(H_3C)_2CH-$	5.50 (hept., $J_{HH}=6.0$ Hz)	1.74 (d, $J_{HH}=6.0$ Hz)	–
$H_3C-CHF-$	6.42 (dq, $J_{HH}=4.0$ Hz, $J_{HF}=56.0$ Hz)	1.84 (dd, $J_{HH}=4.0$ Hz, $J_{HF}=21.0$ Hz)	–
$H_3C-CHCl-$	6.59 (q, $J_{HH}=6.0$ Hz)	2.16 (d, $J_{HH}=6.0$ Hz)	–
H_3C-CF_2-	–	2.17 (t, $J_{HF}=14.5$ Hz)	–
$H_2CF-CHF-$	7.78 (ddt, $J_{HF}=54.0$, 10.0 Hz, $J_{HH}=3.5$ Hz)	4.98 (ddd, $J_{HF}=47.0$, 14.0 Hz, $J_{HH}=3.5$ Hz)	–
$H_2CCl-CHF-$	6.80 (dt, $J_{HF}=54.0$ Hz, $J_{HH}=4.0$ Hz)	4.27 (dd, $J_{HH}=4.0$ Hz, $J_{HF}=13.0$ Hz)	–
H_2CF-CF_2-	–	4.96 (dt, $J_{HF}=8.5$, 45.0 Hz)	–
$H_3C-\underset{\vert}{CH}-CH_2Br$	5.57 (sex., $J_{HH}=5.5$–6.0 Hz)	3.87 (d, CH_2, $J_{HH}=5.5$ Hz) 1.92 (d, CH_3, $J_{HH}=6.0$ Hz)	–
$H_3C-CH_2-CHBr-$	6.85 (t, $J_{HH}=7.0$ Hz)	2.52 (quin., $J_{HH}=7.0$–8.0 Hz)	1.50 (t, $J_{HH}=8.0$ Hz)
$(H_3C)_2CF-$	–	2.00 (d, $J_{HF}=19.0$ Hz)	–
$H_2CF-\underset{\vert}{C}=CH_2$	–	4.16 (d, H_2CF-, $J_{HF}=47.0$ Hz) 5.80 (s, $=CH_2$)	–

Table 2, continued

^{19}F Spectra (δ ppm vs CF_3COOH) R	SO_2F	R
H_3C—	−29.36 (s)	–
H_3C—CH_2—	−33.94 (s)	–
H_3C—CH_2—CH_2—	−37.37 (s)	–
$(H_3C)_2CH$—	−37.70 (s)	–
H_3C—CHF—	−42.01 (d, J_{FF} = 10.0 Hz)	118.7 (ddq, J_{FH} = 56.0, 21.0, J_{FF} = 10 Hz)
H_3C—CHCl—	−42.12 (s)	
H_3C—CF_2—	−45.0 (t, J_{FF} = 9.0 Hz)	64.6 (dq, J_{FH} = 14.5, J_{FF} = 9.0 Hz)
H_2CF—CHF—	−45.5 (d, J_{FF} = 8.0 Hz)	139.0 (m), 241.9 (ddt, J_{H} = 47.0, 10.0 Hz, J_{FF} = 19.0 Hz)
H_2CCl—CHF—	−42.90 (d, J_{FF} = 8.0 Hz)	128.1 (dtd, J_{FH} = 54.0, 13.0 Hz, J_{FF} = 8.0 Hz)
H_2CF—CF_2—	−47.10 (t, J_{FF} = 9.0 Hz)	83.6 (sex., J_{FH} = 8.5 Hz, J_{FF} = 16.5, 9.0 Hz) 239.6 (tt, J_{FH} = 45.0 Hz, J_{FF} = 16.5 Hz)
H_3C—CH(Br)—CH_2Br	−38.81 (s)	
H_3C—CH_2—CHBr—	–	–
$(H_3C)_2CF$—	−44.70 (d, J_{FF} = 12.0 Hz)	91.60 (d. hept., J_{FH} = 19.0 Hz, J_{FF} = 12.0 Hz)
H_2CF—C(=CH_2)—	−37.73 (d, J_{FF} = 6.0 Hz)	219.50 (t.m, J_{FH} = 47.0 Hz)

Ethyl Fluorosulfate:
Fluorosulfuric acid (100.1 g, 1 mol) was put into a 200 ml three necked round flask equipped with a gas inlet tube, and a stirring bar, which was attached to a simple distillation apparatus. Ethylene was introduced into the acid at 0–5° under dry nitrogen atmosphere. After the acid was completely consumed, the reaction mixture was distilled under reduced pressure (15 torr) at room temperature and the product collected at −78°; yield: 102.3 g (80%). N.M.R. and I.R. spectra indicated that the product was pure ethyl fluorosulfate. After removing any free acid with anhydrous potassium carbonate at room temperature and filteration, the product was redistilled under reduced pressure (b.p. 51°/81 torr, lit.[6] 112–113°) to afford ethyl fluorosulfate; yield: 96.8 g; which can be stored over anhydrous potassium carbonate in a refrigerator for more than six months without any sign of decomposition.

Isopropyl fluorosulfate was prepared at −40° from propylene and fluorosulfuric acid and isolated by the same procedure as previously; yield: 83%; b.p. ~20°/6 torr. In this case, however, even traces of acid will cause vigorous decomposition. Therefore, isopropyl fluorosulfate must be kept under careful acid-free conditions. Over anhydrous potassium carbonate at −80° it was kept for weeks without decomposition.

***n*-Propyl fluorosulfate** was obtained by the reaction of cyclopropane and fluorosulfuric acid at −78°, together with isopropyl fluorosulfate, which was formed as a byproduct, by the same procedure as above; total yield: 94%. Fractional distillation of crude products under reduced pressure gave *n*-propyl fluorosulfate; yield: 50%; b.p. 43°/27 torr (lit.[6] 49°/35 torr). However, isopropyl fluorosulfate decomposed during the distillation at this temperature and could not be isolated.

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