Preparation and Properties of 2-Hydroperfluoroalkyl Fluosulfonates[1]

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The hydrolytic instability of completely fluorinated carboxylic esters is well known. Haszeldine[2] has reported that these compounds (*e.g.* $CF_3CO_2CF_3$) hydrolyze on contact with water. The postulated intermediate perfluoro alcohol (CF_3OH) is unstable and immediately reacts further with water to form hydrogen fluoride and carbon dioxide. Similarly, Hauptschein and co-workers[3] found that perfluorobutyrolactone is readily hydrolyzed by water.

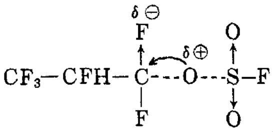
Alkyl fluosulfonate esters possess similar hydrolytic instability even though they are immiscible with water. They etch glass and are decomposed by strong acids.[4] We have found, however, that the highly fluorinated ester, 2-hydroperfluoropropyl fluosulfonate (I), is remarkedly stable to dilute acid hydrolysis. Even after refluxing with an

$$CF_3CFHCF_2{-}O{-}SO_2F$$

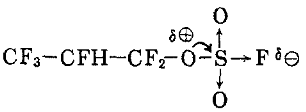
I

excess of 10% sulfuric acid for twenty-four hours, the fluosulfonate was recovered almost quantitatively.

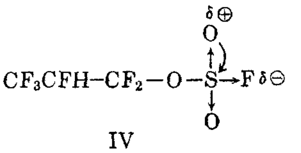
Hydrolytic stability of this compound is attributed by us to the presence of two electronegative groups; the fluorine atom on the sulfur, and the fluorocarbon moiety on the oxygen. The inductive effect of these two groups causes an electron deficiency on the oxygen atoms attached to sulfur. Since the first step in the hydrolysis reaction probably involves protonation of either the oxygen attached to carbon or the oxygen on sulfur, hydrolysis is repressed because of the partial positive charges on these atoms as shown in II, III, and IV.



II



III



IV

Fluosulfonate esters can be prepared from hydrocarbon olefins by passing the olefin through fluosulfonic acid.[4] The same method suffices for synthesis of the fluosulfonates of partially fluorinated olefins such as trifluoroethylene, vinylidene fluoride, and 1,1-difluoro-2-chloroethylene.[5] In the present work it is shown that fluosulfonate esters can also be prepared from perfluoroolefins by heating the olefin with concentrated sulfuric acid at 350° or with fluosulfonic acid at 150°.

The formation of fluosulfonates has been found to be a general reaction. The following α-olefins were used successfully: tetrafluoroethylene, hexafluoropropylene, 4-hydroperfluoro-1-butene, perfluoro-1-heptene, and 8-hydroperfluoro-1-octene. Reaction conditions, yields, and boiling points of the derived fluosulfonates are summarized in Table I.

TABLE I

2-Hydroperfluoroalkyl Fluosulfonates

Fluosulfonates	Method of Synthesis	Reaction Conditions	Yield, %	B.P.
$HCF_2CF_2{-}OSO_2F$	B	3 hr. at 200°	1	56-57
$CF_3CFHCF_2{-}OSO_2F$	A	1 hr. at 350°	32	75-76
	B	3 hr. at 150°	18	75-76
$H(CF_2)_2CFHCF_2{-}OSO_2F$	B	8 hr. at 150°	6.5	119.0-119.2
$CF_3(CF_2)_4CFHCF_2{-}OSO_2F$	B	3 hr. at 150°	5	53.5-54.5 (18 mm.)
$H(CF_2)_6CFHCF_2{-}OSO_2F$	B	3 hr. at 200°	79	80-81 (8 mm.)

EXPERIMENTAL

2-Hydroperfluoropropyl fluosulfonate from sulfuric acid. Method A. Hexafluoropropylene (150 g.) and concd. sulfuric acid (25 ml.) were charged into a platinum-lined pressure tube (330-ml. capacity). The mixture was agitated for 1 hr. at 350° under autogenous pressure. The light amber product was discharged, washed twice with water, dried over calcium sulfate, and distilled through a 30-in. platinum spinning band column. There was obtained 37.6 g. (32%) of clear, colorless liquid product, b.p. 75-76°, n_D^{25} 1.2865.

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(1) Presented at the Fluorine Symposium sponsored by the Division of Industrial and Engineering Chemistry at the 138th meeting of the American Chemical Society, New York City, September 11-16, 1960.

(2) R. N. Haszeldine, *Nature*, 168, 1028 (1951).

(3) M. Hauptschein, C. S. Stokes, and A. V. Grosse, *J. Org. Chem.*, 74, 1974 (1952).

(4) N. V. Sidgwick, *Chemical Elements and Their Composition*, Vol. II, University Press, Oxford, 1959, p. 934.

(5) J. D. Calfee and T. A. Florio, U. S. Pat. 2,628,972, February 17, 1952; R. A. Davis, U. S. Pat. 2,878,156, December 31, 1956.

Anal. Calcd. for $C_3HF_7O_3S$: C, 14.4; H, 0.4; F, 53.2; S, 12.8; mol. wt., 250. Found: C, 15.0; H, 0.6; F, 52.8, 52.9; S, 13.6, 13.8; mol. wt., 258.9, 248.0.

The infrared spectrum showed strong bands at 3.34 μ (CH stretching) and 6.75 μ (asymmetrical SO stretching). The NMR spectrum was consistent with the proposed structure.

2-Hydroperfluoropropyl fluosulfonate from fluosulfonic acid. Method B. Hexafluoropropylene (50 g.) and fluosulfonic acid (25 g.) were charged into a platinum-lined pressure vessel (330-ml. capacity). The mixture was agitated for 3 hr. at 150° under autogenous pressure. The dark amber product was poured onto ice, washed twice with water, and distilled; yield 11.3 g. (19%), b.p. 75–76°. The product was identical with that obtained by Method A.

2,4-Dihydroperfluorobutyl fluosulfonate. 4-Hydroperfluoro-1-butene (20 g.) and fluosulfonic acid (11 g.) were heated for 8 hr. at 150° in a stainless steel pressure vessel (100 ml. capacity). The product was discharged and washed with ice water. Distillation of the water-insoluble material gave 2.06 g. of 2,4-dihydroperfluorobutyl fluosulfonate, b.p. 119.0–119.2°. The infrared spectrum was consistent with the proposed structure.

2-Hydroperfluoroheptyl fluosulfonate. Perfluoro-1-heptene (70 g.) and fluosulfonic acid (15 g.) were heated in a platinum-lined pressure vessel at 150° for 3 hr. The product was discharged and shaken with water. It was then filtered through anhydrous magnesium sulfate and dried over calcium sulfate. Distillation gave 35 g. of unchanged olefin and 2.2 g. of product, b.p. 53.5–54.5° (18 mm.). The yield based on unrecovered olefin was 5%. Infrared and NMR spectra were consistent with the proposed structure.

2,8-Dihydroperfluorooctyl fluosulfonate. 8-Hydroperfluoro-1-octene (4.3 g.) was allowed to react with 1.5 g. of fluosulfonic acid in a $6 \times {}^3/_8$ in. platinum tube for 3 hr. at 200°. Distillation of the product gave 2.8 g. of unchanged olefin and 1.5 g. of fluosulfonate; b.p. 80–81° (8 mm.). Infrared and NMR spectra were consistent with the proposed structure.

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Evidence for 9-Methylene-10-acetoxy-10-methyl-9,10-dihydrophenanthrene as an Intermediate[1]

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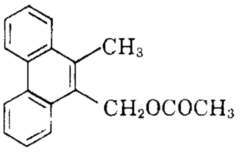
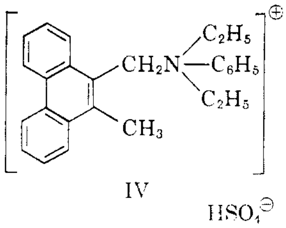
A recent report by Gardner and Sarrafizadeh R.[2] on the reaction of 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (I) with thionyl chloride and the mechanism offered by Hauptmann[3] for the formation of the product, 9-chloromethyl-10-methylphenanthrene, make it seem timely to report results obtained in this Laboratory in experiments carried out along similar lines. In the present work the diol was found to react with acetic anhydride in pyridine to give the monoacetate II in 34% yield. The structure of the monoacetate was confirmed by saponification, which regenerated the diol. At higher temperatures (150°) in diethylaniline the diol reacted with acetic anhydride to give the monoacetate in only 8% yield; the chief product (29%) was 9-acetoxymethyl-10-methylphenanthrene (III). It was accompanied by a quaternary salt, isolated in a yield of 4% as the bisulfate IV.

I II



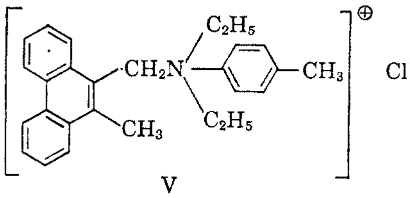
III



IV

The structure of the acetoxymethyl compound was established by hydrolysis to the corresponding alcohol, which is known.[2] Treatment of the salt IV with silver perchlorate converted it into the perchlorate.

Confirmation of the above results was obtained when the diol I was allowed to react with acetic anhydride in diethyl-*p*-toluidine. The reaction mixture was heated under reflux (150–155°); again the major product was the acetoxymethyl compound III (42.5%). A quaternary salt was isolated in a yield of 5.0% as the chloride V.



V

The ultraviolet spectra (absolute alcohol) of the dihydrophenanthrene derivatives I and II exhibited maxima at 271 mμ (ε 1.73 × 10⁴) and 272 mμ (ε 1.82 × 10⁴), respectively. The absorption spectrum of 9,10-dihydrophenanthrene has a maximum at approximately 265 mμ (ε 1 × 10⁴) and agrees in shape and intensity with that of biphenyl.[4] This similarity was also observed in the spectra of I and II. The maximum absorption of the phenanthrene derivatives III and IV was at 255 mμ (ε 2.63 × 10⁴) and 256 mμ (ε 5.66 × 10⁴), respectively. The general shape and intensity of absorption of the phenan-

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[1] This work was supported in part by a grant from the office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] P. D. Gardner and H. Sarrafizadeh R., *J. Am. Chem. Soc.*, **82**, 4287 (1960).

[3] S. Hauptmann, *Chem. Ber.*, **93**, 2604 (1960).

[4] R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941).