TABLE I

β-H-PERFLUORO ALKANESULFONIC ACIDS

Sulfonic acid	Conv.,[a] %	Yield, %	B.p. °C.	B.p. Mm.	Neut. equiv. Calcd.	Neut. equiv. Found	Anal. of sodium salt Na, % Calcd.	Na, % Found	S, % Calcd.	S, % Found
$CF_3CFHCF_2SO_3H$	93	64	111–113	20	232	228	..	..	..	..
$C_3F_7CFHCF_2SO_3H$	83	79	119–120	14	332	317	6.50	6.55	9.04	9.19
$C_5H_{11}CFHCF_2SO_3H$	74	73	119–120	3	432	415	5.07	5.25	7.05	7.21

[a] Based on olefin reacted.

ethylene has been reported by Barrick.[1] Several higher molecular weight β-H-perfluoro alkanesulfonic acids have now been prepared in good yield by the reaction of sodium bisulfite with perfluoropropene, perfluoropentene-1 and perfluoroheptene-1. A summary of the preparation and properties of these sulfonic acids is presented in Table I.

These sulfonic acids are viscous liquids, soluble in both water and diethyl ether. They are very hygroscopic and form solid hydrates when exposed to moist air. They are strong acids as indicated by their reaction with NaCl to liberate HCl. The acids as well as their sodium salts are highly surface active in aqueous media, *e.g.*, a solution containing 1% by weight of $C_5F_{11}CFHCF_2SO_3H$ gave a surface tension of 38 dynes per centimeter at 25°. A preliminary investigation was made into the thermal and hydrolytic stability of the sodium salts. The dry salts are thermally stable up to 350° but undergo extensive decomposition in aqueous base at about 250°.

Experimental

Perfluoropropene, perfluoropentene-1 and perfluoroheptene-1 were prepared by the method of Hals, Reid and Smith.[2] Preparation of the β-H-perfluoro alkanesulfonic acids was carried out according to the following typical experiment: A mixture of 90 g. (0.6 mole) of perfluoropropene, 60 g. (0.5 mole) of sodium bisulfite, 27.4 g. of borax, 120 cc. of water and 0.8 g. of benzoyl peroxide was charged to a stainless steel autoclave. The contents of the autoclave were heated with agitation at 110–120° for nine hours. Ten grams of unreacted perfluoropropene was bled from the autoclave at room temperature. The reaction mixture was then evaporated to dryness and the resulting salts extracted with hot ethanol. There was isolated 115 g. of crude ethanol-soluble $CF_3CFHCF_2SO_3Na$. About 100 g. of this vacuum-dried salt was mixed with 150 g. of 95% H_2SO_4 and 40 g. of SO_3 (Sulfan β), and distilled under reduced pressure. Fractionation of the distillate gave 68 g. of $CF_3CFHCF_2SO_3H$ boiling at 111–113° (20 mm.).

(1) P. L. Barrick, U. S. Patent 2,403,207 (July 2, 1946).

(2) L. J. Hals, T. S. Reid and G. H. Smith, THIS JOURNAL, **73**, 4054 (1951).

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A Convenient Synthesis of 2-β-Hydroxyethylaminofluorene[1]

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The literature contains a method for the preparation of 2-β-hydroxyethylaminofluorene,[2,3] but it is troublesome and gives a poor yield of product. It has now been found that the compound can be obtained readily in high yield by the decomposition of β-chloroethyl N-2-fluorenylcarbamate in alkaline solution.

The infrared spectra of β-chloroethyl N-2-fluorenylcarbamate (I), 3-(2′-fluorenyl)-2-oxazolidone (II), 2-β-hydroxyethylaminofluorene (III) have been determined. The carbonyl band of II lies at 5.76μ while that of the starting carbamate lies at 5.72μ. As II has no O–H or N–H stretching vibration bands, the structure assignment of the compound as an oxazolidone is substantiated. III has no C=O stretching vibration band but has N–H and O–H bands at 2.93 and 2.77 μ, respectively. The starting carbamate has a N–H band at 2.90μ. This substantiates the structure of III as 2-β-hydroxyethylaminofluorene.

Experimental[4]

β-Chloroethyl N-2-Fluorenylcarbamate.—To an ice-cold stirred solution of 1.81 g. of 2-aminofluorene[5] in 10 ml. of pyridine was added dropwise 1.1 ml. of β-chlorethyl chlorocarbonate. The solution was stirred an additional half hour at 0–10° and then poured into 200 ml. of cold 25% sulfuric acid. An oil was formed which solidified after two hours. Crystallization from heptane gave 2.73 g. (95% yield) of colorless microneedles, m.p. 134–134.5°.

Anal. Calcd. for $C_{16}H_{14}ClNO_2$: C, 66.67; H, 4.86. Found: C, 67.05; H, 5.09.

3-(2′-Fluorenyl)-2-oxazolidone.—A solution of 1.6 g. of potassium hydroxide in 40 ml. of ethanol was added to 2.88 g. of β-chloroethyl N-2-fluorenylcarbamate dissolved in 150 ml. of hot ethanol. The stirred solution remained clear for a short time and then a thick crystalline precipitate was formed. The stirred mixture was immediately cooled to room temperature. Stirring was continued for an additional half hour. Excess water was added and then the white crystalline precipitate was filtered. Crystallization from methyl cellosolve gave 2.38 g. (95% yield) of colorless plates, m.p. 239–240°.

Anal. Calcd. for $C_{16}H_{13}NO_2$: N, 5.58. Found: N, 5.88.

2-β-Hydroxyethylaminofluorene.—A solution of 3.2 g. of potassium hydroxide in 80 ml. of ethanol was added to a hot solution of 2.88 g. of β-chloroethyl N-2-fluorenylcarbamate in 40 ml. of ethanol. A thick crystalline precipitate of the oxazolidone was formed which dissolved with decomposition on refluxing vigorously for two hours. Three-fourths of the alcohol was distilled off. Excess water was added to the residue. Crystallization from hexane gave 2.0 g. (89% yield) of colorless plates, m.p. 148–149°. Davis, *et al.*,[3] reported yellow plates, m.p. 150°.

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(2) W. C. J. Ross, *J. Chem. Soc.*, 183 (1949).

(3) W. Davis, J. L. Everett and W. C. J. Ross, *ibid.*, 1331 (1950).

(4) All melting points are uncorrected. Infrared absorption spectra were measured with a Perkin-Elmer Model 21 Infrared Spectrophotometer.

(5) W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 448.