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AN IMPROVED METHOD FOR SYNTHESIZING DIFLUOROMETHANESULFONIC ACID

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SUMMARY

In the presence of catalytic amounts of sodium sulfate or sodium chloride, fluorosulfonyldifluoroacetic acid (**1**) was decarboxylated in CH_3CN-H_2O to give difluoromethanesulfonyl fluoride (**2**) in moderate yield. **2** can be completely hydrolyzed to the corresponding acid **3** at 80°-100°C. The overall yield of **3** from **1** was 53%.

INTRODUCTION

Difluoromethanesulfonic acid HCF_2SO_3H (**3**), as a catalyst, is more effective than trifluoromethanesulfonic acid in Friedel-Crafts reactions because of its adequate acidity, high boiling point, high degree of hydrogen-bonding and ease of separation from the products [1]. **3** also has potential application as an electrolyte (e.g. in fuel cells) [1]. Difluoromethanesulfonamides have been used as antiinflammatory, anticonvulsant, cardiovascular, antioedemic and herbicidal drugs because of their biological activities [2], for example, diflumidone (HCF_2SO_2NH-C_6H_4-COPh-m) possesses antioedemic activities enhanced by the high lipophilic character of the HCF_2SO_2- group [3]. On the other hand, we recently have shown that **3** and difluoromethanesulfonyl fluo-

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ride HCF_2SO_2F (2) are good difluorocarbene precursors [4, 5]. Therefore, difluoromethanesulfonic acid is a unique member of the fluoroalkanesulfonic acid series.

In the literature it was reported that difluoromethanesulfonic acid can be obtained by acidification of an alkali-metal difluoromethanesulfonate, prepared in low yield from chlorodifluoromethane and Na_2SO_3 [6] or K_2SO_3 [1], by heating (120°C) in a high-pressure vessel. In the laboratory, 3 is primarily prepared by the decarboxylation of fluorosulfonyldifluoroacetic acid FO_2SCF_2COOH (1) in boiling water to give HCF_2SO_2F (2) followed by saponification and acidification [8]. However, in this reaction the yield of 2 is quite low (19%) and the reaction is exothermic and difficult to control . 1 is readily available because the corresponding acid fluoride is a starting material for producing the commercial ion-exchange resin Nafion-H [9]. So we were interested in seeking an improved method for preparation of difluoromethanesulfonic acid from 1.

RESULTS AND DISCUSSION

Treatment of fluorosulfonyldifluoroacetic acid (1) with catalytic amounts (10% molar ratio) of inorganic salt (NaCl, Na_2SO_4) in a acetonitrile-water mixture gave a mixture of HCF_2SO_2F (2), HCF_2SO_3H (3), HO_3SCF_2COOH (4), HCF_3 (5) and HCF_2Cl (6).

$$\underset{\mathbf{1}}{FO_2SCF_2COOH} \xrightarrow[CH_3CN/H_2O]{NaCl} \underset{\mathbf{2}}{HCF_2SO_2F} + \underset{\mathbf{3}}{HCF_2SO_3H} + \underset{\mathbf{4}}{HO_3SCF_2COOH} + \underset{\mathbf{5}}{HCF_3} + \underset{\mathbf{6}}{HCF_2Cl}$$

Representative examples are listed in Table 1.

TABLE 1

Results of decomposition of 1 under different conditions

Entry	Additive[a]	T(°C)/t(h)	$\frac{CH_3CN}{H_2O}$(v/v)	Conversion[b]	product[c]				
					2	3	4	5	6
1	-	25/5	1/1	-	-	-	-	-	-
2	Na_2SO_4	25/5	1/1	100	50	3.5	28	18	-
3	Na_2SO_4	45/5	1/1	100	22	13	22	32	-
4	Na_2SO_4	25/5	1/0	100	-	-	-	93	-
5	Na_2SO_4	25/5	0/1	34	32	7.5	15	41	-
6	NaCl	25/4	1/1	100	47	4	27	20	trace
7	NaCl	25/4	1/0	100	-	-	-	83	trace
8	-	50/5	0/1	100	10	18	14	52	-

[a] The amount of salt is a 10% molar ratio. [b] Determined by ^{19}F NMR.
[c] Isolated yield.

Table 1 shows that an inorganic salt is effective for the decomposition of **1** (see Entry 1). If acetonitrile is used as the sole solvent, **5** is the only product (Entry 4), and if only water is used, the conversion of **1** was low (Entry 5). The optimal conditions for preparing **2** and **3** are in CH_3CN-H_2O (1:1) at room temperature for 4-5 h in the presence of additive.

The conversion of **2** into **3** in water at room temperature over several days was claimed in the literature [7] but no details were reported. In our case (25°C, 4-5 h), **3** was partially formed. It was interesting to find out whether the salt has some effect on the hydrolysis of **2**. Table 2 shows the results of conversion of **2** into **3**.

$$\underset{\mathbf{2}}{HCF_2SO_2F} \longrightarrow \underset{\mathbf{3}}{HCF_2SO_3H}$$

TABLE 2

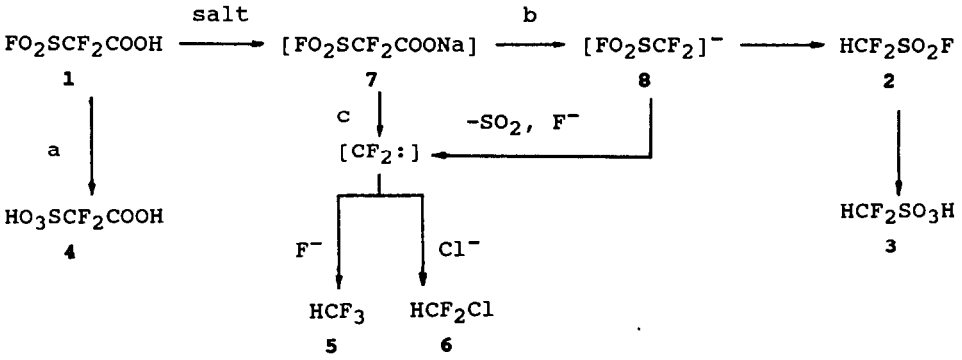
Results of conversion of 2 into 3

Entry	Additive[a]	T(°C)/t(h)	CH_3CN(v/v) / H_2O	Conversion[b]	Product[c] HCF_2SO_3H(%)
1	Na_2SO_4	25/5	0/1	-	-
2	Na_2SO_4	25/5	1/1	10	92
3	Na_2SO_4	35/5	1/1	25	96
4	Na_2SO_4	45/5	1/1	48	96.5
5	-	45/5	1/1	48	100
6[d]	-	100/6	1/1	100	98
7[d]	-	80/6	1/1[e]	100	99

[a] Catalytic amounts of salt used. [b] Determined by ^{19}F NMR.
[c] Isolated yield. [d] Carried out in a pyrex tube. [e] THF/H_2O.

It was found that 2 was partially converted into 3 in CH_3CN/H_2O mixtures and the presence of salt had little effect on the conversion However, the conversion of 2 increased as the temperature was raised When the temperature is raised to 80°-100°C, 2 can be converted into 3 completely. The overall yield of 3 from 1 was 53%.

From the products 2, 5, 6 and along with our previous work [10, 11 it is reasonable to suggest that the reaction mechanism may involve difluorocarbene intermediate .



1 can be partially hydrolyzed to 4 (pathway a), and is also converted to 7 in the presence of inorganic salt. 7 is unstable and decomposes readily, in organic solvents mainly into CF_2: (pathway c), but in an aqueous organic system into the relatively stable anion 8 [4, 10a] which then gives 2. Difluorocarbene reacts with F^- or Cl^- to give 5 or 6. 2 was hydrolyzed to 3.

EXPERIMENTAL

All boiling points are uncorrected. NMR spectra (chemical shifts in ppm from external TMS for ^1H NMR and from external TFA for ^{19}F NMR; positive values indicate upfield shifts) were recorded on an EM-360 NMR spectrometer at 60 MHz. Infrared spectra were measured on a Shimadzu IR-440 instrument. Mass spectra were recorded with a GC-MS-4021 spectrometer. **1** was prepared according to the literature [12]. Numerical yields are based on converted material.

Synthesis of difluoromethanesulfonyl fluoride and difluoromethanesulfonic acid :

Na_2SO_4, 1.4g (0.01mol), CH_3CN (50ml) and H_2O (50ml) were placed in a 250ml three-necked round-bottomed flask fitted with a magnetic stirrer a dropping funnel and a reflux condenser connected with a dry-ice trap; **1**, 17.8g (0.1mol) was then added with stirring at room temperature (25°C) After addition, the mixture was further stirred for 5 h at this temperature and separated into two layers. ^{19}F NMR analysis showed that the conversion was 100%. Sulfur dioxide was collected in the cold trap. The gas mixture was then passed into the solution of sodium hydroxide to eliminate CO_2. The remaining gas was identified as HCF_3 (400 ml,18%) by GC-MS spectroscopy. The organic layer was separated directly from the resulting mixture and **2**, 6.7g (50%) was obtained after distillation. The aqueous layer was fractionated to give **3**, 0.46g (3.5%) and **4**, 4.9g (28%).

2. b.p. 52°C. (lit [7] 52°C). ^1H NMR δ 6.35 (1H, t).
^{19}F NMR δ 42.3 (2F, d, J_{H-F}=52 Hz), -113 (1F).

3. b.p. 90-92°C/2mm. (lit [1] 90-92°C/2mm).
^1H NMR δ 6.67 (t, $\underline{H}CF_2$, J_{H-F}=52 Hz), 10.58 (t, $O\underline{H}$).
^{19}F NMR δ 44.8 (d).

4. b.p. 136-138°C/1mm. (lit [13] 145-146°C/2mm).
^1H NMR 11.40 (s). ^{19}F NMR 32.0 (s).

Conversion of **2** to **3** in the presence of Na_2SO_4 A mixture of Na_2SO_4 (0.4g, 3 mmol), **2** (4g, 0.03mol), CH_3CN (20ml) and H_2O (20ml) was stirred at 45°C for 5 h. ^{19}F NMR analysis showed that the conversion was 48%. Distillation gave **3** (1.64g, 96.5%).

Conversion of **2** into **3** in pyrex tube A mixture of **2** (4g, 0.03mol) THF (5ml) and H_2O (5ml) was placed in a 50ml pyrex tube fitted with screw cap. The contents were stirred for 6 h at 80°C. ^{19}F NMR analysis showed that the conversion was 100%. Distillation gave **3** (3.93g, 99%).

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