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SHORT COMMUNICATION

FRAGMENTATION OF FLUOROSULFONYLDIFLUOROACETYL FLUORIDE INDUCED BY FLUORIDE ION [1]

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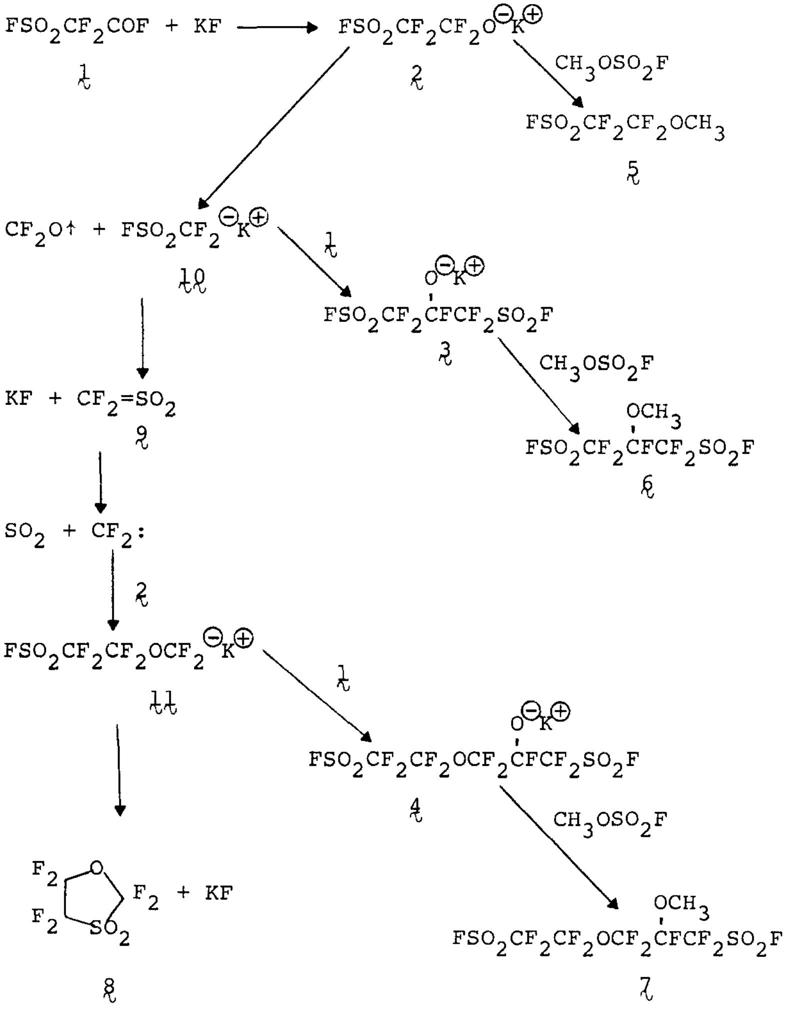
Fluorosulfonyldifluoroacetyl fluoride (**1**) is a readily accessible [2] fluorochemical of some interest because of its difunctionality. During a study of displacement reactions on 3,3-bis(bromomethyl)oxetane with fluoroalkoxides [3,4], the fluoroalkoxide **2** derived from addition of KF to **1** in diglyme was found to undergo reaction at 55-60°, but with little concomitant attack on the bis(bromomethyl)oxetane present. Treatment of **1** with a limited amount of potassium fluoride in diglyme revealed in subsequent experiments that reaction does occur readily at 40-50° with evolution of gas and the formation of several new products. Fluoroalkoxides **2**, **3** and **4** were isolated as the O-methyl derivatives **5**, **6** and **7** after treatment with methyl fluorosulfate; heterocycle **8** was also obtained.

Major product **5** is clearly derived from **2**, the initially formed adduct of KF with starting material **1**. The genesis of products **6**, **7** and **8**, however, is best rationalized by a fragmentation of **2** at 40° or higher. The fragmentation may be sequential, as depicted below, with sulfene **9** actually formed as an intermediate. Alternatively, it may proceed by a synchronous mechanism to generate difluorocarbene directly from **10**. Whichever pathway is followed, sulfene **9** is apparently unstable at 40° with respect to its components, sulfur dioxide and difluorocarbene. This instability is similar to that observed for difluoroketene, which tends to decompose at 35° in the absence of a reactive trapping agent to give carbon monoxide and tetrafluoroethylene [5]; the tetrafluoroethylene was presumed to arise from the known dimerization of difluorocarbene.



In the present case, difluorocarbene was trapped by excess fluoroalkoxide 2 to give reactive fluorocarbanion 11. Anion 11 underwent a favorable intramolecular displacement of fluoride to give the five-membered ring heterocycle 8 and, to an even greater extent, added to 1 to form the new fluoroalkoxide 4, isolated after methylation as 7. The formation of two products containing an extra difluoromethylene unit strongly supports the occurrence of difluorocarbene as an intermediate.

Elimination of carbonyl fluoride from **2** to give well-stabilized carbanion **10** as a discrete intermediate was indicated by its addition to **1** to form fluoroalkoxide **3**, isolated as its methyl derivative **6**. An analogous elimination of carbonyl fluoride from $(CF_3)_2CFCF(SO_2F)COF$ in the presence of fluoride ion was postulated to account for the product isolated by Cookson, Haszeldine, et al. [6].

Interestingly, the same study [6] reported that fluorotrifluoromethylsulfene can be generated by dehydrofluorinating CF_3CHFSO_2F. Although successfully trapped by cycloaddition with reagents such as enamines, fluorotrifluoromethylsulfene gave octafluoro-2-butene when generated with no trapping agent or free fluoride ion present. In the absence of direct evidence for formation of fluorotrifluoromethylcarbene, the authors postulate reaction of fluorotrifluoromethylsulfene with an intermediate carbanion as the source of octafluorobutene. The low yields we experienced in generating and trapping fluorotrifluoromethylketene because of its facile isomerization to trifluoroacryloyl fluoride [7], but with little or no tendency to dissociate to carbon monoxide and fluorotrifluoromethylcarbene, is in accord with these authors' proposals regarding fluorotrifluoromethylsulfene.

Thus both difluorosulfene (**9**) and difluoroketene appear to dissociate under mild conditions to form difluorocarbene. A fluoroalkylated ketene or sulfene, however, preferentially isomerizes or reacts as such rather than dissociate to its relatively energy-rich carbene counterpart.

EXPERIMENTAL

Boiling points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 21 spectrophotometer using 20% solutions in CCl_4. ^1H NMR spectra were taken on a Varian A60 spectrometer, and ^{19}F NMR spectra were taken on a Varian XL-100 spectrometer. Chemical shifts were measured with tetramethylsilane and trichlorofluoromethane as internal standards in CCl_4 solution with the downfield directions from references taken as positive.

Treatment of fluorosulfonyldifluoroacetyl fluoride with fluoride ion followed by methyl fluorosulfate

When a mixture of 11.6 g (0.20 mole) of KF, 108 g (0.60 mole) of fluorosulfonyldifluoroacetyl fluoride (**2**), and 300 ml of diglyme was stirred and heated slowly to 40°, gas evolution occurred at a moderate rate. Evolved gas which went through a -80° condenser and fumed in air was assumed to be COF_2. The mixture was kept at 40-45° for 8 h, then at 50° for 4 h, after which time gas evolution was very slow. At 55°, gas evolution remained negligible and reflux occurred. The homogeneous solution was stripped of volatiles by heating to 40° (0.5 mm). Evacuation of the lowest boiling products at 5 mm left 14.1 g of liquid in the -80° trap; distillation of this material from P_2O_5 afforded a fraction, b.p. 48-52°, 2.7 g (4%), of crude sulfone **8** (nc) which was purified by GLC. IR: 6.99 (SO_2), 8-9.5 μ (C-F, SO_2). NMR: ^1H none; ^{19}F -76.7 (p, J_{FF} 2.4 Hz, 2F, CF_2O), -83.9 (m, 2F, CF_2O), -120.6 ppm (m, 2F, SO_2CF_2).

The residue obtained after removal of volatile materials from the reaction mixture was stirred with 22.8 g (0.20 mole) of CH_3OSO_2F and allowed to stand overnight. Volatile methylation products were separated from diglyme under vacuum Fractionation afforded first a mixture of dioxane and product **5**, b.p. 50-61° (200 mm); this distillate was washed with water, dried and redistilled to give 19.5 g (46%) of **5**, b.p. 52° (200 mm). IR: 3.27, 3.34, 3.46 (CH_3O), 6.81 (SO_2F), 8-10 μ (CF, C-O, SO_2). NMR: ^1H 3.83 ppm (s, CH_3); ^{19}F 43.2 (t of t, J_{FF} 11.8, 9.7 Hz, 1F, SO_2F), -87.6 (d of t, J_{FF} 11.8, 9.6 Hz, 2F, CF_2O), -112.1 ppm (q, J_{FF} 9.7 Hz, 2F, SO_2CF_2).

Anal. Calcd. for $C_3H_3F_5O_3S$: C, 16.83; H, 1.41; S, 14.98
Found: C, 17.28; H, 1.56; S, 14.86.

The residue from distillation of **5** was washed with water, dried, and distilled to give a mixture of **6** and **7**, b.p. 57-83° (20 mm), 3.5 g, followed by 10.7 g (12%) of **7**, b.p. 83-85° (20 mm). GLC indicated that **6** was present in the mixture to the extent of 1.5 g (2%); a nearly pure sample of **6** (nc) was obtained by GLC. IR: 3.30, 3.34, 3.47 (CH_3O), 6.85 (SO_2F), 8-9.5 μ (CF, CO, SO_2). NMR: ^1H 3.94 ppm (s, CH_3O); ^{19}F 44.0 (m, 2F, SO_2F), -134.2 ppm (m, 1F, CF), with AB multiplets at -9542, -9796, -9805, and -10059 Hz (4F, CF_2).

Anal. Calcd. for $C_4H_3F_7O_5S_2$: C, 14.64; H, 0.92;
F, 40.53; S, 19.54
Found: C, 15.49; H, 1.19;
F, 40.98; S, 18.46.

For **7** (nc), IR: 3.27, 3.33, 3.45 (CH_3O), 6.81 (SO_2F), 8-10 μ (C-F, C-O, SO_2). NMR: ^1H 3.85 (m, CH_3O); ^{19}F 45.1 (m, 1F, SO_2F), 43.9 (m, 1F, SO_2F), -82.5 (m, 2F, $CF_2C\mathbf{F}_2O$), -113.0 (d of t, J_{FF} 5.0, 2.5 Hz, 2F, $SO_2C\mathbf{F}_2CF_2$), and -138.9 ppm (m, 1, CF) with AB multiplets at -7227, -7370, -7383, and -7533 Hz (2F, $CFC\mathbf{F}_2O$) and -9648, -9894, -10051, and -10296 Hz (2F, $CFC\mathbf{F}_2SO_2F$).

Anal. Calcd. for $C_6H_3F_{11}O_6S_2$: C, 16.22; H, 0.68;
F, 47.05; S, 14.44
Found: C, 16.75; H, 0.83;
F, 47.25; S, 14.19.

1 Contribution No. 2813.

2 For example, see discussion by I. L. Knunyants and G. A. Sokolski, Angew. Chem. Internat. Ed. Engl., 11 (1972) 583.

3 C. G. Krespan, J. Org. Chem., 43 (1978) 637.

4 German Patent 2116105 (Sept. 7, 1972) reports the earliest examples of such reactions.

5 D. C. England and C. G. Krespan, J. Org. Chem., 33, (1968) 816.

6 I. W. Cookson, R. N. Haszeldine, J. S. Kilburn, and W. D. Morton, Euchem Symposium, June 27-30, 1976, Menton, France.

7 D. C. England, L. Solomon, and C. G. Krespan, J. Fluorine Chem., 3 (1973/74) 63.