of these cations and in the position of the magnetic resonances of the hydrogen and carbon nuclei belonging to the ring.

With this above described new class of compounds, a promising type of organic cations, whose steric and electronic properties are quite variable, has been found. In view of their low first redox potentials they are interesting counterions in charge-transfer salts with organic or inorganic anions, for instance with $TCNQ^-$ or bis(dithiolato)–metal complex anions.[17]

Acknowledgment. I am grateful to Mrs. J. Hope for assistance with the electrochemical measurements and Professor R. L. Martin for helpful discussions.

Registry No.—**9**, 68057-87-4; **10a**, 67618-28-4; **10b**, 69461-29-6; **11b**, 69461-31-0; **12b**, 69470-08-2; 1,2-diaminobenzene, 95-54-5.

References and Notes

(1) Part 3. K. D. Franz, *Chem. Lett.*, submitted for publication; parts of this paper have been presented at the Australian Conference on Coordination and Organometallic Chemistry, Melbourne, February 1977.
(2) IBM T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598.
(3) (a) P. Beckmann, *Aust. J. Chem.*, **14**, 229 (1961); (b) S. Huenig and E. Wolf, *Chimia*, **22**, 33 (1968); (c) C. Jutz, R. Kirchlechner, and H. J. Seidel, *Chem. Ber.*, **102**, 2301 (1969); (d) J. Fabian, *J. Prakt. Chem.*, **320**, 361 (1978).
(4) R. C. Haddon, *Nature (London)*, **256**, 394 (1975).
(5) F. Gerson, E. Heilbronner, H. A. Reddock, D. H. Paskovich, and N. C. Das, *Helv. Chim. Acta*, **50**, 813 (1967).
(6) S. Huenig and E. Wolf, *Justus Liebigs Ann. Chem.*, **732**, 7 (1970); **732**, 26 (1970).
(7) K. D. Franz and R. L. Martin, *Tetrahedron*, **34**, 2147 (1978).
(8) While this work was in progress two other types of 1,9-disubstituted phenalenium ions have been reported: (a) K. Yamamoto, Y. Kayane, and I. Murata, *Bull. Chem. Soc. Jpn.*, **50**, 1964 (1977); (b) R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, and F. B. Bramwell, *J. Chem. Soc., Chem. Commun.*, 429 (1978); (c) R. C. Haddon, F. Wudl, M. L. Kaplan, and F. B. Bramwell, *J. Am. Chem. Soc.*, **100**, 7629 (1978).
(9) J. M. Leal, T. Teherani, and A. J. Bard, *J. Electroanal. Chem.*, **91**, 275 (1978).
(10) Typically, β-hydroxy ketones and their derivatives cyclize with 1,2-diaminobenzene in the absence of metal ions to 1,5-diazepines: F. D. Popp and A. Catala Noble, *Adv. Heterocycl. Chem.*, **8**, 66 (1967).
(11) This approach has been used by Neidlein and Behzadi for **4b** and **8** independently from our investigations: R. Neidlein and Z. Behzadi, *Chem. Ztg.*, **102**, 199 (1978).
(12) F. Carnovale, T. H. Gan, J. B. Peel, and K. D. Franz, *Tetrahedron*, submitted for publication. There is a good correlation between calculated and assigned values for this class of compounds, although correspondence of charge density and ^{13}C NMR shifts is generally unreliable.[13]
(13) G. L. Nelson and E. A. Williams, *Prog. Phys. Org. Chem.*, **12**, 229 (1976).
(14) K. D. Franz and R. C. Haddon, *Org. Prep. Proced. Int.*, submitted for publication.
(15) I. Murata, *Top. Nonbenzoic Arom. Chem.*, **1**, 159 (1976).
(16) This effect has been also shown for dialkylaminotropylium ions: H. Froehlisch and R. Braun, *Tetrahedron Lett.*, 2735 (1978).
(17) K. D. Franz, submitted for publication.

Fluoroalkanesulfonyl Chlorides

George G. I. Moore

Riker Laboratories, Inc., 3M Center, St. Paul, Minnesota 55101

Received November 3, 1978

A simple and effective synthesis of CH_2FSO_2Cl and CHF_2SO_2Cl has been achieved, both in 49% overall yield. The (di)fluoromethyl chlorides are converted into the (di)fluoromethyl benzyl sulfides by NaOH–benzyl mercaptan in DMF. Oxidative chlorination in cold water yields the (di)fluoromethanesulfonyl chlorides.

$$CH_xF_yCl \xrightarrow[DMF]{PhCH_2SNa} CH_xF_ySCH_2Ph \xrightarrow[H_2O]{Cl_2} CH_xF_ySO_2Cl$$

$x = 1, y = 2$

$x = 2, y = 1$

Despite identical conditions and yields, the reactions of benzyl mercaptide with CH_2FCl and CHF_2Cl proceed through S_N2 and carbene paths, respectively, as indicated by alkylation in NaOD. The oxidative chlorination of CHF_2SCH_2Ph occurs at least 50% via the sulfoxide. In situ generation of benzyl mercaptide gave a 39% overall yield of CHF_2SO_2Cl. *tert*-Butyl mercaptan proved inferior in the difluoromethylation step.

Our interest in the biological properties of various fluoroalkanesulfonamides (to date, antiinflammatory,[1] anticonvulsant,[2] cardiovascular,[3] and herbicidal[4]) has necessitated large-scale preparations of CH_2FSO_2Cl (**1**) and CHF_2SO_2Cl (**2**). Farrar's[5] original synthetic route to **2** consisted of the Strecker sequence shown in eq 1. After considerable modification, Harrington and Kaufman[6] rendered this adequate for small-scale preparations (<500 g, yields ~50%), but this route has proven complicated and inefficient (10–20% yields) for larger runs, unreliable, and hence too expensive for multigallon reactions. Specifically, the initial step required extended heating in a high-pressure kettle, resulting in extensive corrosion of the vessel. Yields in this step were particularly erratic for CHF_2Cl (several <10%). Recovery and purification of the sulfonate salts were time consuming. The final mixture of **2** (bp 96 °C) and byproduct $POCl_3$ (bp 101 °C) could not be separated by distillation, and only by competitive hydrolysis could the latter be removed. The **2** so obtained was contaminated with 5–15% of unidentified materials.

$$CH_2FCl + Na_2SO_3 \xrightarrow[\text{pressure}]{\Delta} CH_2FSO_3Na \xrightarrow{PCl_5} \underset{\mathbf{1}}{CH_2FSO_2Cl} \quad (1)$$

$$CHF_2Cl + Na_2SO_3 \rightarrow CHF_2SO_3Na \rightarrow \underset{\mathbf{2}}{CHF_2SO_2Cl} \quad (2)$$

We decided to employ the greater nucleophilicity of divalent sulfur by (di)fluoromethylating some species RSH, followed by cleavage of the protecting group R and oxidation to the tetravalent state, in either order. This approach was designed to avoid both the slow, corrosive pressure reaction with Na_2SO_3 and the difficult isolation of the sodium sulfonates. Our efforts culminated in the synthesis of benzyl sulfides **3** and **4** and subsequent direct conversion of these to **1** and **2** by cold aqueous chlorination.

0022-3263/79/1944-1708$01.00/0

Table I. Synthesis of $PhCH_2SCHF_2$ (4)

run	$PhCH_2SH$, mol	CHF_2Cl, mol	NaOH, mol	solvent, mL	conditions	yield of 4, %
1	0.2	0.75	1.75	200 dioxane–200 H_2O	*a*	56
2	0.8	1.85	4.0	400 dioxane–400 H_2O	*a*	63
3	0.8	1.9	4.0	400 THF[e]–400 H_2O	*a*	57
4	0.2	0.9	1.75	50 THF–400 H_2O	*b*	34
5	0.2	0.5	1.5	350 H_2O	*c*	13
6	0.1	0.4	(0.1 NaH)	125 DMF	*d*	68
7	0.2	0.4	(0.2 NaOMe)	200 MeOH	*c*	0
8	0.2	0.2	(0.6 Na_2CO_3)	200 DMF	*c*	0
9	1.0	1.1	(1.0 50% NaOH)	300 DMF	*d*	76

[a] Exotherm to ~60 °C, 1–2 h CHF_2Cl. [b] <40 °C. [c] Heated to 50–65 °C. [d] Exothermic; maintained at 50–65 °C. [e] THF caused less emulsification on workup than dioxane.

$$CH_2FCl + PhCH_2SNa \rightarrow CH_2FSCH_2Ph$$
$$\mathbf{3}\ (75\%)$$
$$\xrightarrow[H_2O,\ <0\ °C]{Cl_2} CH_2FSO_2Cl + ClCH_2Ph$$
$$\mathbf{1}\ (65\%)$$
$$CHF_2Cl + PhCH_2SNa \rightarrow CHF_2SCH_2Ph$$
$$\mathbf{4}\ (70\%)$$
$$\rightarrow CHF_2SO_2Cl + ClCH_2Ph$$
$$\mathbf{2}\ (70\%)$$

This process possesses many advantages over the previous one, which will become apparent as we describe this new route and its evolution.

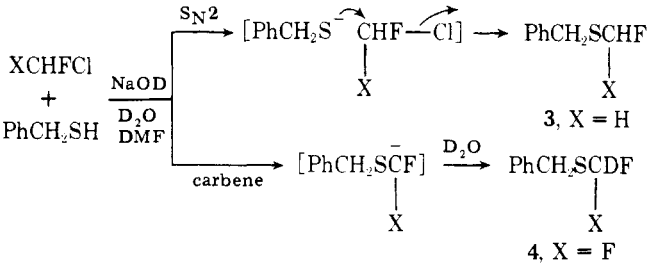
(Di)fluoromethylations. Difluoromethyl sulfides have been prepared from CHF_2Cl and both alkyl and aryl sulfides in what generally is assumed a carbene reaction,[7] while fluoromethyl sulfides have apparently received little attention. For this reason and because of its greater availability, our initial studies were made with CHF_2Cl. In Table I we illustrate conditions tested for the synthesis of **4**. Run 1 represents the conditions used by Sedova et al.[7a] in preparation of $ArSCHF_2$. We reduced the amount of base (run 2) and replaced dioxane by THF (run 3) but found the conversion still quite slow and wasteful of CHF_2Cl. The results of runs 4 and 5 suggested that water was a poor cosolvent. Anhydrous conditions were tried (run 6), with NaH in DMF giving a very rapid and exothermic conversion to **4**. Neither NaOMe nor Na_2CO_3 seemed effective (runs 7 and 8), but 50% NaOH in DMF (run 9) proved equally effective as run 6. Large-scale (100 mol) repetitions have given 70–75% yields of **4**, using only a slight excess of CHF_2Cl.[8]

The technique of run 9 also served CH_2FCl smoothly into **3**[9] (75% yield). The identical reaction conditions and yields for the syntheses of **3** and **4** led us to feel that they form by similar reaction pathways. However, CH_2FCl is unlikely under these conditions to yield the carbene :CHF and most probably serves as an S_N2 substrate, while conversely CHF_2Cl is thought to be a poor S_N2 substrate and is known to be readily converted to $:CF_2$.[10] The distinction between these alternatives lies in the necessity for C–H bond breaking in the carbene route, suggesting the use of NaOD-D_2O as base in the (di)fluoromethylation as a test of mechanism. CH_2FCl yielded **3** with essentially no incorporation of D by NMR analysis, consistent with the S_N2 path. Under these conditions, CHF_2Cl yielded 85% deuterated **4**, measured by integration of the NMR signals of the $-CH_2S-$ singlet and the $-CHF_2$ triplet (2.0–0.15). The starting material CHF_2Cl is known to be stable to base-induced D exchange; the product **4** proved stable to both NaOD and $NaSCH_2Ph$ in DMF–D_2O. Thus, the overall similarity is misleading: CH_2FCl and CHF_2Cl react through entirely different mechanisms.

Oxidative Chlorination. Chlorinative cleavage of alkyl sulfides to alkyl chlorides and sulfonyl chlorides occurs readily if the alkyl residue represents a stable cation (e.g., benzyl, *tert*-butyl).[11] Such a cleavage has recently proven useful in the synthesis of α-chloroalkanesulfenyl chlorides.[12] Oxidation of sulfenyl to sulfonyl chlorides is readily effected by Cl_2 in H_2O, and single-step cleavage and oxidation is known, as with the conversion of 4-nitrodibenzyl sulfide to 4-nitrodibenzylsulfonyl chloride and benzyl chloride.[11] We initially tried aqueous chlorination of **4** and were gratified by smooth, exothermic uptake of 3 equiv of Cl_2, resulting in **2** in passable yield (Table II, run 1). We tried to minimize the competing hydrolysis of **2** by temperature control (run 2, 3), by decreasing the solubility of the HCl byproduct (run 4, 5), and by limiting the amount of water (run 6). The low temperature of run 3 proved superior and has given **2** in 70–75% on larger trials (run 7, and later 70 mol[8]). Application of this technique to **3** was likewise successful (**1** in 65% yield). The byproduct benzyl chloride (bp 170 °C) acts as a "chaser" during distillation of **2** but interferes somewhat in distillation of **1** (bp 140 °C). Use of a ring-substituted benzyl mercaptan should minimize this.

Table II. Chlorination of $PhCH_2SCHF_2$ (4) to CHF_2SO_2Cl (2)

run	4, mol	medium	temp, °C	yield of 2, %
1	0.085	H_2O	5–25	38
2	0.11	H_2O	1–10	55
3	0.11	H_2O	−10–0	72
4	0.11	concd HCl	−10–0	33
5	0.11	satd NaCl	1–10	64
6	0.11	2 equiv H_2O–CH_2Cl_2	0–5	28
7	0.70	H_2O	−10–0	70



The relative timing of cleavage and oxidation is of interest. For **4**, the possibilities include (a) cleavage to CHF_2SCl (**5**) and oxidation, (b) oxidation to sulfoxide **6** and cleavage, or (c) oxidation to sulfone **7** and cleavage. The latter possibility was excluded by the observed stability of **7** to these conditions. Anhydrous chlorination of **4** gave sulfenyl chloride **5**, indicating that path a may contribute. However, addition of only 1 equiv of Cl_2 to an aqueous slurry of **4** gave sulfoxide **6** (50% isolated yield), arguing that the major route is path b. The

Table III. In Situ Benzyl Mercaptan[a]

$PhCH_2Cl + NH_2CSNH_2 \rightarrow PhCH_2SC(=NH)NH_2 \xrightarrow[(2)\ CHF_2Cl]{(1)\ NaOH} CHF_2SCH_2Ph$ (4)

run	solvent, mL	CHF_2Cl, mol	yield of 4, %
1	100 H_2O–300 THF	1.1	42
2	200 H_2O–400 THF	1.4	67
3	200 H_2O–400 THF	2.7	70
4	300 DMF	1.1	42

[a] All runs were 1.0-mol scale, using 3 equiv of 50% NaOH.

sulfoxide (but not the sulfone) was similarly implicated in the oxidative chlorination of *tert*-butyl sulfide to the sulfonyl chloride.[13]

(a) CHF_2SCH_2Ph (4) $\xrightarrow[\text{or } SOCl_2]{Cl_2}$ CHF_2SCl (5)

(b) $CHF_2S(O)CH_2Ph$ (6) $\xrightarrow{Cl_2}$ CHF_2SO_2Cl (2)

(c) $CHF_2SO_2CH_2Ph$ (7)

Other Modifications. We have explored in situ generation of benzyl mercaptan from thiourea in aqueous THF and in DMF (Table III) for synthesis of **4**. Again, the presence of water slowed the reaction and required excess CHF_2Cl. The resulting good yields of **4** are significant since this route allows convenient recycling of the chlorination byproduct benzyl chloride and reduces the odor problem associated with benzyl mercaptan.

Use of *tert*-butyl mercaptan gave poorer results, due to low yields of sulfide **8**, using either 50% NaOH or NaH. Oxidative chlorination was satisfactory. Preliminary trials with isopropyl mercaptan indicated satisfactory difluoromethylation but no cleavage to **2** on chlorination.

$$Me_3CSH \xrightarrow[\substack{NaH\\CHF_2Cl}]{NaOH} CHF_2SCMe_3 \rightarrow \mathbf{2}\ (60\%)$$
$$\mathbf{8}\ (12\text{–}22\%)$$

Other fluoroalkanesulfonyl chlorides have been prepared by this technique and will be discussed later.

Experimental Section

Melting points are uncorrected and were determined on a Thomas-Hoover apparatus. Distillations unless otherwise stated used a short-path (3 cm) apparatus. Microanalyses and NMR and mass spectra were performed by the Analytical Group, Central Research Laboratories, 3M Co.

Benzyl Difluoromethyl Sulfide (4). Benzyl Mercaptan–DMF (Run 9, Table I) (Preferred Method). A mixture of 80.0 g (10 mol) of 50% NaOH and 300 mL of DMF was flushed well with N_2, and 124.2 g (1.0 mol) of benzyl mercaptan was added. When homogenous, the warm solution was treated with 90 g (1.1 mol) of CHF_2Cl, introduced as a gas above the solution at such a rate as to maintain the internal temperature at 50–65 °C and to cause a gentle reflux from the dry ice cooled condenser (40 min). The tan slurry was quenched in 1000 mL of H_2O, 100 mL of CH_2Cl_2 was added, and the organic layer was washed with dilute NaOH and then with H_2O and stripped to a tan liquid. Distillation gave 132.8 g (76%) of **4** as a colorless liquid, bp 55 °C/0.06 mm. NMR ($CDCl_3$) confirmed the structure: CHF_2 at δ 6.68 (triplet, J_{HF} = 57 Hz), CH_2 at δ 3.99, and ArH at δ 7.28. Anal. Calcd for $C_8H_8F_2S$: C, 55.1; H, 4.6. Found: C, 55.2; H, 4.6.

Benzyl Mercaptan–Dioxane–H_2O (Run 2, Table I). A solution of 99.5 g (0.80 mol) of benzyl mercaptan in 400 mL of dioxane was treated under N_2 with 160 g (4.0 mol) of 50% NaOH diluted to 400 mL with H_2O. When the temperature had fallen to 50 °C, CHF_2Cl was introduced as above. The cooling effect of the condensing gas necessitated external heating to maintain an internal temperature of 50–65 °C. Aliquots were quenched in acid, and the ratio of $PhCH_2SH$/**4** was determined by GLC (5 ft 15% SE-30 column, 140 °C). By 3 h, 150 g (1.75 mol) of CHF_2Cl had been added and the GLC conversion was 88%. The mixture was quenched in H_2O, forming a milky emulsion. Addition of CH_2Cl_2, filtration of a white paste, drying over $MgSO_4$, and concentration gave a colorless liquid, distilled to a forerun of dioxane and a main cut of 57.8 g (63%) of pure **4**.

Benzyl Chloride–Thiourea–THF–H_2O. A mixture of 76.1 g (1.0 mmol) of NH_2CSNH_2, 126.6 g (1.0 mol) of $PhCH_2Cl$, 400 mL of H_2O, and 200 mL of THF was heated for 2 h and cooled, and 320 g (40 mol) of 50% NaOH was added (exotherm). The mixture was heated briefly, and CHF_2Cl was introduced above the solution maintained at 55–65 °C. After 2 h, 165 g of CHF_2Cl had been added. GLC of an acid-quenched aliquot indicated only 50% conversion of $PhCH_2SH$ to **4**. After addition of 80 g more of 50% NaOH and 70 g of CHF_2Cl over 2 h (total 2.7 mol), workup yielded 128.9 g (74% crude yield) of **4** (90% conversion). Direct chlorination gave 58.2 g of **2**, an overall yield of 39%.

A run similar to the above using DMF and 1.1 equiv CHF_2Cl gave **4** in 42% yield.

Benzyl Fluoromethyl Sulfide (3). In the same fashion and scale as in the preferred preparation of **4**, sulfide **3** was prepared from CH_2FCl and 50% NaOH in DMF in 75% yield, bp 62–65 °C/0.1 mm. NMR ($CDCl_3$) showed CHF_2 at δ 5.33 (doublet, J_{HF} = 2 Hz) and ArH at δ 7.28. Anal. Calcd for C_8H_9FS: C, 61.5; H, 5.8. Found: C, 61.4; H, 5.7.

D Exchange Using CHF_2Cl. A mixture of 5.30 g (50 mmol) of 40% NaOD in D_2O and 15 mL of DMF was treated under N_2 with 6.20 g (50 mmol) of benzyl mercaptan and then slowly with excess CHF_2Cl over 1.5 h. Little exotherm was noted. The mixture was quenched in dilute HCl, extracted with CH_2Cl_2, and dried over $MgSO_4$, and the liquid was distilled to 4.2 g of a mixture containing 15% benzyl mercaptan and 85% **4**. Integration of the NMR signals showed the $-CH_2S-/CHF_2$ ratio to be 2.0:0.15.

The stability of **4** to D exchange was proven by mixing 1.0 g each of **4** (5.7 mmol) and 40% NaOD (9.7 mmol) in 3 mL of DMF, adding 2 mL of D_2O to obtain homogeneity. Integration at 0.5 and 3 h showed the $ArH/CH_2S/CHF_2$ ratios to be 5.0:2.0:1.2 and 5.2:2.0:1.2. (The widespread nature of the CHF_2 triplet caused difficulties in precise integration.) Further, a mixture of 2.65 g (25 mmol) of 40% NaOD, 3.1 g (25 mmol) of benzyl mercaptan, and 7 mL of DMF was treated with 3.0 g (17.2 mmol) of **4**, allowed to stand for 1.5 h, and worked up with dilute HCl. (These conditions approximate the midpoint of the difluoromethylation run above.) Integration showed the CH_2S/CHF_2 ratio to be 2.0:0.97.

D Exchange Using CH_2FCl. A run on the same scale as above using CH_2FCl gave, after distillation, 6.0 g (76%) of pure **3**. Integration of the $-CH_2S-$ and CH_2F NMR signals gave a ratio of 2.0:1.9, indicating no D incorporation.

Difluoromethanesulfonyl Chloride (2). Sulfide **4** (122.6 g, 0.70 mol) was slurried in 300 mL of H_2O and the mixture chilled in a dry ice–acetone bath. At 0 °C, with ice beginning to form on the walls, Cl_2 was added as a gas above the mixture, controlling the temperature to −5 to 0 °C generally, with −10 °C reached toward the end (160 g, 2.26 mol, of Cl_2 added in 60 min). The lower layer was mixed with 20 mL of CH_2Cl_2, drained, and chilled while drying over $MgSO_4$. Distillation on a spinning band yielded 74.5 g (70%), bp 95–99 °C, identical by IR and GLC with material made earlier by the Strecker reaction sequence. Anal. Calcd for $CHClF_2O_2S$: C, 8.0; H, 0.7; F, 25.2. Found: C, 8.1; H, 0.7; F, 25.1.

Fluoromethanesulfonyl Chloride (1). In a similar fashion, sulfide **3** yielded **1** in 70% yield, bp 140 °C (contaminated with 3% of benzyl chloride), essentially identical by IR and GLC with authentic material.

Difluoromethanesulfenyl Chloride (5). Addition of 14 g (0.20 mol) of Cl_2 to 30 g (0.17 mol) of sulfide **4** at 0–5 °C gave a yellow liquid. The flask was warmed to 40 °C, causing 12.1 g of yellow liquid to distill out, bp 25–35 °C. A midcut was characterized by its IR and mass spectra [in decreasing size: *m/e* 51 (CF_2H), 118 (P), 36 (HCl), 83 (P − Cl), 99 (P − F), 82 (P − HCl)]. The crude yield was 60%. GLC showed more **5** remaining in the benzyl chloride residue.

Benzyl Difluoromethyl Sulfoxide (6). A slurry of 34.8 g (0.20 mol) of sulfide **4** in 200 mL of H_2O was chilled in a dry ice–acetone bath until ice began to form, and 14.5 g (0.205 mol) of Cl_2 was added. Extraction, drying, and stripping gave a semisolid, which was re-

crystallized from pentane to give 19.4 g (50%) of **6** as a white solid, mp 52.5–55 °C. Anal. Calcd for $C_8H_8F_2OS$: C, 50.5; H, 4.2; F, 20.0. Found: C, 50.4; H, 4.2; F, 19.9.

Benzyl Difluoromethyl Sulfone (7). A solution of 10.0 g (0.057 mol) of **4** in 75 mL of HOAc was treated with 20 g (0.176 mol) of 30% H_2O_2, resulting in an exothermic reaction. Dilution with H_2O gave **7** as a white solid, which was recrystallized twice from benzene–hexane to give 8.4 g (71%), mp 57.5–59 °C. NMR ($CDCl_3$) showed CHF_2 at δ 6.08 (triplet, J = 52 Hz), CH_2 at δ 4.37, and ArH at δ 7.4. Anal. Calcd for $C_8H_8F_2O_2S$: C, 46.5; H, 4.9. Found: C, 46.6; H, 3.8. This material failed to react with Cl_2 in H_2O at 0 and 25 °C (2.0 g gave 1.7 g recovery).

2-Fluoromethyl *tert*-Butyl Sulfide (8). A mixture of 180 g (2.0 mmol) of *tert*-butyl mercaptan, 200 mL of THF, and 480 g (6.0 mol) of 50% NaOH formed a paste. Another 600 mL of H_2O was added, and the mixture was warmed at 60–65 °C while adding 185 g (2.15 mol) of CHF_2Cl. Extraction with 200 mL of CH_2Cl_2 and fractional distillation twice yielded 21.9 g (11%) of **8**, bp 99–102 °C. The low yield was thought to be due in part to codistillation with THF. To avoid this, dimethylacetamide was used. A mixture of 21.1 g (0.50 mol) of 57% NaH–mineral oil (washed well with hexane) in 200 mL of DMAC was stirred with 50 g (0.56 mol) of *tert*-butyl mercaptan. Treatment with 70 g (0.81 mol) of CHF_2Cl and distillation under ~60 mm pressure via two dry ice cooled traps gave **8**. Redistillation gave 15.5 g (22%) of pure material, bp 106 °C. Anal. Calcd for $C_5H_{10}F_2S$: C, 42.8; H, 7.2. Found: C, 43.0; H, 7.2.

Chlorination of 8.75 g (0.062 mol) in 100 mL of H_2O at 0 °C and workup as usual yielded 5.7 g (61%) of **2**.

Registry No.—**1**, 42497-69-8; **2**, 1512-30-7; **3**, 2924-74-5; **4**, 68965-44-6; **5**, 58932-27-7; **6**, 68965-45-7; **7**, 68965-46-8; **8**, 68965-47-9; benzyl mercaptan, 100-53-8; difluorochloromethane, 75-45-6; thiourea, 62-56-6; benzyl chloride, 100-44-7; chlorofluoromethane, 593-70-4; *tert*-butyl mercaptan, 75-66-1.

References and Notes

(1) (a) G. G. I. Moore, J. K. Harrington, and K. F. Swingle, *J. Med. Chem.*, **18**, 386 (1975); (b) G. G. I. Moore in "Antiinflammatory Agents", R. A. Scherrer and M. W. Whitehouse, Eds., Academic Press, New York, 1974, p 160.
(2) G. G. I. Moore, L. R. Lappi, J. E. Bachhuber, and A. C. Conway, 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970, Abstracts, MEDI.
(3) E. H. Banitt, W. E. Coyne, K. T. McGurran, and J. E. Robertson, *J. Med. Chem.*, **17**, 116 (1974).
(4) (a) R. D. Trepka, J. K. Harrington, J. E. Robertson, and J. T. Waddington, *J. Agric. Food Chem.*, **18**, 175 (1970); (b) R. D. Trepka, J. K. Harrington, J. W. McConville, K. T. McGurran, A. Mendel, D. R. Pauly, J. E. Robertson, and J. T. Waddington, *ibid.*, **22**, 1111 (1974).
(5) M. V. Farrar, *J. Chem. Soc.*, 3058 (1960).
(6) J. K. Harrington and G. M. Kaufman, 3M Co., unpublished work.
(7) (a) L. N. Sedova, *Zh. Obshch. Khim.*, **39**, 2057 (1969); *Chem. Abstr.*, **72**, 3166q (1970); (b) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **79**, 5493 (1957); (c) J. Hine and K. Tanabe, *ibid.*, **80**, 3002 (1958); (d) L. Soboronskii, *Zh. Obshch. Khim.*, **29**, 1144 (1959); *Chem. Abstr.*, **54**, 8603 (1960); (e) W. A. Shephard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, 1969.
(8) H. R. Davis and R. J. Loer, 3M Co., unpublished work.
(9) A material claimed to be **3** was isolated by K. A. Petrov and G. A. Sokolskii, *Zh. Obshch. Khim.*, **27**, 2711 (1957) [*Chem. Abstr.*, **51**, 7198c (1957)], on treatment of $ClCH_2SCH_2Ph$ with HF. However, the low boiling point cited (25 °C at 0.1 mm vs. our 65 °C at 0.1 mm) and the instability (decomposed at 50–60 °C) argue against this.
(10) J. Hine, "Divalent Carbon", Ronald Press, New York, 1964, p 39.
(11) E. E. Gilbert, "Sulfonation and Related Reactions", Interscience, New York, 1965, p 201.
(12) W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **36**, 3145 (1971).
(13) J. S. Grossert, W. R. Hardstaff, and R. F. Langer, *J. Chem. Soc., Chem. Commun.*, 50 (1973).

Notes

Reaction of Unsaturated Compounds with Hypofluorous Acid[1a]

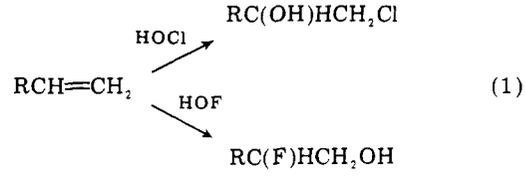
K. G. Migliorese,*[1b] E. H. Appelman, and M. N. Tsangaris[1c]

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Received December 21, 1978

The successful synthesis of hypofluorous acid by Studier and Appelman[2] has prompted the study of the reactions of this novel molecule with organic substrates. Appelman and Bonnett have recently reported the hydroxylation of aromatic compounds[3] by hypofluorous acid. The fact that hydroxylation rather than fluorination was observed in this system supports the hypothesis that HOF is polarized in the sense $HO^{\delta+}$–$F^{\delta-}$. This unique polarization was initially suggested by NMR spectral data.[4] Among the hypohalous acids, only HOF would be expected to be polarized in this way since all of the other halogen atoms are less electronegative than oxygen.[5] We would thus expect the Markownikoff addition of hypofluorous acid to alkenes to yield halohydrins of an orientation opposite to that resulting from the well-known Markownikoff addition of hypochlorous acid ($HO^{\delta-}$–$Cl^{\delta+}$).[6,7] We have therefore decided to investigate the reaction of HOF with unsaturated molecules.

The hypofluorous acid used in this work was prepared in ~50-mg quantities by the reaction of fluorine with ice at ca. −40 °C in a recirculating flow system as described by Appelman.[8] The HOF prepared in this way was invariably contaminated with substantial amounts of HF and with traces of water. The HF was present in amounts comparable to the HOF. Hypofluorous acid decomposes spontaneously to oxygen and hydrogen fluoride,[2,3] and in the course of this work several minor detonations occurred. Adequate shielding is therefore needed whenever HOF is being handled. The reactions were carried out by warming a U-tube containing the HOF to −50 °C and sweeping the HOF from the U-tube with dry nitrogen into a cold solution of the alkene or alkyne in dichloromethane or carbon tetrachloride. In general, immediate reaction was evidenced by a darkening of the solution. The reaction mixtures were concentrated by evaporation under vacuum and were analyzed by gas chromatography. The major products were characterized by gas chromatography–mass spectrometry, infrared spectrophotometry, and $^{19}F/^{1}H$ nuclear magnetic resonance spectrometry. Some volatile products may have been lost during the concentration. Our results are summarized in Table I.



(1)

Under our conditions, alkenes gave α-fluoro alcohols as the major products, while acetylenes gave mixtures of aldehydes, ketones, and acyl fluorides, which presumably resulted from

0022-3263/79/1944-1711$01.00/0