was extracted with cold benzene (three 20-ml portions). The benzene solution was washed with cold water and dried ($MgSO_4$). Removal of the solvent at reduced pressure at 20° gave a white solid. Crystallization from petroleum ether (bp 40–60°) at −20° gave (+)-perhydratropic acid (5.0 g, 75%), mp 65–67°, $[\alpha]^{18}\mathrm{D}$ +108.8° (*c* 2.27, $CHCl_3$), active oxygen content 97–98%. A sample of (±)-perhydratropic acid, prepared in the same way, had mp 44.5–45.5°.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.1; H, 6.0. Found: 64.9; H, 6.2.

(−)-2-*endo*-Pernorbornanecarboxylic Acid (3).—Application of the above procedure to (−)-2-*endo*-norbornanecarboxylic acid[7] (10.0 g), $[\alpha]^{18}\mathrm{D}$ −15° (*c* 1.0, $CHCl_3$), gave (−)-*endo*-2-pernorbornanecarboxylic acid (7.8 g, 71%), mp 64–66° after recrystallization from pentane at −80°, $[\alpha]^{18}\mathrm{D}$ −12.3°, active oxygen content *ca.* 98%.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.69; H, 7.76.

(−)-*cis*-Myrtanic Acid.—(−)-*cis*-Myrtanol[9] (15.0 g) was dispersed by means of a high-speed stirrer in a solution of concentrated sulfuric acid (50 ml) in water (400 ml). Powdered potassium permanganate (21.0 g) was added while the temperature was maintained at 20–30°. Sodium metabisulfite was added until the color was discharged and the mixture was extracted with ether. The ether extract was shaken twice with 50% aqueous sodium hydroxide and the resulting aqueous solution deposited a solid on acidification with concentrated hydrochloric acid. Crystallization from acetic acid gave (−)-*cis*-myrtanic acid (7.0 g, 43%), mp 110–111° (lit.[8] mp 111–112°), $[\alpha]^{18}\mathrm{D}$ −38.6° (*c* 2.77, $CHCl_3$). The ether solution contained unreacted *cis*-myrtanol.

(−)-*cis*-Permyrtanic Acid (4).—(−)-*cis*-Myrtanic acid (32.0 g) in methanesulfonic acid (183 g) was treated with 85% hydrogen peroxide (21.3 g) at 20–30°. The solution was stirred for an additional 2 hr at 20°. Work-up as described for perhydratropic acid gave white crystals (32.0 g), mp 45–52°. Crystallization from ether–petroleum ether (bp 40–60°) at −20° gave *cis*-permyrtanic acid (25.0 g, 70%), mp 55–56°, $[\alpha]^{18}\mathrm{D}$ −53.3° (*c* 2.72, $CHCl_3$), active oxygen content >96%.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.2; H, 8.7. Found: C, 65.5; H, 9.0.

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The Chemistry of Trifluorothiolacetic Acid and Its Derivatives. I[1]

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Trifluorothiolacetic acid (CF_3COSH) was first prepared by Sheppard and Muetterties[3] by allowing $(CF_3CO)_2O$ and H_2S to react together at 200° in 45% yield.

The chemistry of CF_3COSH has received very little attention, and only one paper[3] has appeared in the literature. The presence of the -SH group offered a way to prepare new sulfenyl halides and sulfides which contained the highly reactive trifluoroacetyl group.

CF_3COSH reacts readily with chlorine or bromine, giving the corresponding trifluoroacetylsulfenyl halide.

$$CF_3COSH + Cl_2 \xrightarrow{-78^\circ} CF_3COSCl + HCl \qquad (1)$$

$$CF_3COSH + Br_2 \xrightarrow[\text{room temperature}]{-78^\circ\text{ to}} CF_3COSBr + HBr \qquad (2)$$

With iodine monochloride, the corresponding disulfide was formed. The equations for this reaction are

$$CF_3COSH + ICl \longrightarrow [CF_3COSI] + HCl \qquad (3)$$

$$2[CF_3COSI] \longrightarrow (CF_3COS)_2 + I_2 \qquad (4)$$

Water reacts according to the following equation.

$$CF_3COSH + H_2O \longrightarrow CF_3COOH + H_2S \qquad (5)$$

After 6 days, only 88% of the thioacid had reacted. This behavior could account for the instability of the fluoroalkanethiolcarboxylic acids in water, as noted by Sheppard and Muetterties.[3] In a sodium hydroxide solution, the acid slowly evolved H_2S with the formation of sodium trifluoroacetate. Organic bases (pyridine and aniline) react to form solid complexes, with the aniline complex, being unstable, evolving H_2S as one of its decomposition products.

The trifluoroacetylsulfenyl halides react readily with mercury at room temperature, giving the white solid mercurial $(CF_3COS)_2Hg$ and the disulfide (eq 6). The mercurial is unstable at room temperature, slowly decomposing, giving quantitatively HgS. It is unstable in water, again producing HgS. The disulfide is also unstable in water and reacts according to eq 7. When heated with mercury, $(CF_3COS)_2$ formed mainly HgS and not $(CF_3COS)_2Hg$. With AgF_2 in freon-113 ($CClF_2$–$CFCl_2$) at room temperature, CF_3COF, SF_4, and SOF_2 were formed.

$$4CF_3COSX + 3Hg \longrightarrow (CF_3COS)_2Hg + 2HgX_2 + (CF_3COS)_2 \qquad (6)$$

$$X = \text{Cl or Br}$$

$$(CF_3COS)_2 + 2H_2O \longrightarrow H_2S + S + 2CF_3COOH \qquad (7)$$

The reaction of CF_3COSCl with aqueous sodium hydroxide can be represented by eq 8. The (S_3O^{2-}) represents S, S^{2-}, S_2, and $S_2O_3{}^{2-}$. Free sulfur was formed during the basic hydrolysis, and upon acidification H_2S was noted. Evaporation of the above solution left a white solid identified as sodium trifluoroacetate *via* its infrared spectrum.

$$3CF_3COSCl + 8OH^- \longrightarrow 3CF_3COO^- + 3Cl^- + 4H_2O + (S_3O^{2-}) \qquad (8)$$

The infrared spectra for these compounds are listed in Table I. All, except the aniline and pyridine salts, show characteristic carbonyl stretching frequencies at 1670–1780 cm^{-1}. The stretching vibration frequencies for the carbonyl group in thiol esters of perfluorocarboxylic acids are on the average 1695 cm^{-1}.[4] The bands at 1285–1136 cm^{-1} are due to the asymmetric and symmetric stretching vibration of the C–F bond.[5] The bands at 750–736 cm^{-1} are due to CF_3 deformation.[5]

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[2] To whom inquiries should be addressed.

[3] W. A. Sheppard and E. L. Muetterties, *J. Org. Chem.*, **25**, 180 (1960).

[4] M. Hauptschein, C. S. Stokes, and E. A. Nodiff, *J. Amer. Chem. Soc.*, **74**, 4005 (1952).

[5] S. N. Nabi and N. Sheppard, *J. Chem. Soc.*, 3439 (1959).

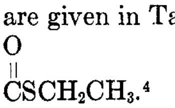
TABLE I

INFRARED ABSORPTION BANDS

Compd	Wavenumber, cm^{-1a}
CF_3COSH	3400 (vw), 2604 (vw), 1758 (s), 1285 (m), 1215 (vs), 1189 (vs), 1040 (w), 992 (s), 858 (m), 745 (m)
CF_3COSCl	1761 (s), 1279 (s), 1199 (vs), 933 (vs), 740 (s)
CF_3COSBr	1761 (s), 1278 (vs), 1207 (vs), 1200 (vs), 936 (vs), 914 (s), 739 (s)
$(CF_3COS)_2$	1754 (s), 1274 (vs), 1208 (vs), 1193 (vs), 927 (vs), 907 (s), 736 (s)
$(CF_3COS)_2Hg$	1676 (s), 1393 (vw), 1272 (s), 1210 (s), 1163 (s), 1005 (vw), 964 (vs), 939 (s), 746 (s), 696 (w)
$CF_3COSH \cdot C_5H_5N^b$	1629 (s), 1482 (vs), 1385 (m), 1319 (w), 1263 (vs), 1192 (vs), 1122 (vs), 1056 w), 1000 (m), 976 (vs), 832 (w), 800 (w), 754 (vs), 749 (vs), 721 (w), 703 (w), 682 (vs)
$CF_3COSH \cdot C_6H_7N^c$	1686 (w), 1585 (s), 1541 (s), 1493 (vs), 1460 (s), 1404 (m), 1258 (s), 1206 (w), 1183 (s), 1166 (m), 1136 (vs), 1028 (w), 989 (s), 750 (w), 742 (s), 727 (w), 702 (w), 686 (m)

[a] vw = very weak; w = weak; m = medium; s = strong; vs = very strong. [b] Broad absorption in the 3125–2381 and 2222–2000-cm^{-1} regions. [c] Broad absorption around the 2778- and 2564-cm^{-1} region.

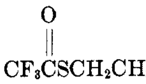
Nuclear magnetic resonance data for the compounds are given in Table II. Included for comparison is



$CF_3\overset{O}{\overset{\|}{C}}SCH_2CH_3$.[4] The proton resonance for CF_3COSH is in the region reported for $CF_3CF_2CF_2COSH$ (−5.36 ppm). The CF_3– resonance for all compounds is in the region for the CF_3– group when it is attached to a carbonyl group.[6]

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA

Compd	Chemical shift, ppm	
	Proton[a]	Fluorine[b]
CF_3COSH	5.2	77.2
 $CF_3\overset{O}{\overset{\|}{C}}SCH_2CH_3$	1.37,[c] 3.15[d]	75.8
$CF_3COSH \cdot C_5H_5N$	...	73.5
CF_3COSCl	...	74.3
CF_3COSBr	...	73.5
$(CF_3COS)_2Hg$	...	73.5
$(CF_3COS)_2$	...	74.3

[a] Downfield from TMS (internal standard). [b] Upfield from F-11 (internal standard). [c] Band center of triplet; J = 8 cps. [d] Band center of quadruplet; J = 8 cps.

The proton nmr spectrum of $CF_3COSH \cdot C_6H_5N$ is complex and shows the absence of the proton attached to the CF_3COS^- group. This would indicate that the proton has probably transferred to the nitrogen of the pyridine, forming a salt composed of $C_5H_5NH^+$ and CF_3COS^- ions. A similar behavior with the aniline salt would be expected.

The ultraviolet spectrum of CF_3COSH in cyclohexane shows λ_{max} 230 mμ. Koch[7] found, for the series of compounds CH_3COSH, $CH_2ClCOSH$, $CHCl_2COSH$, and CCl_3COSH in cyclohexane, a progressive red shift from about 220 mμ for CH_3COSH to about 238 mμ for CCl_3COSH.

The large inductive effect of the CF_3 group acting on the sulfur through the carbonyl group counteracts to some degree the raising of the ground state relative to the excited state, as is evident in the series CH_3COSH to CCl_3COSH. The inductive effect of the CF_3 group is more clearly seen in comparing organic disulfides with $(CF_3)_2S_2$.[8] Bis(trifluoromethyl) disulfide shows absorption at 235 mμ, while the organic disulfides usually absorb at slightly longer wavelengths (250 mμ). This shift is attributed to the reduction of conjugation between the nonbonding electrons on the sulfur atoms by the electronegative CF_3 groups.

CF_3COSH has a molecular weight of 130 ± 1 g/mol in the vapor state. The lack of association when compared with trifluoroacetic acid[9] is probably due to the weak hydrogen bonding present.

In a search for a better synthesis for CF_3COSH, it was found that the use of iodine not only increased the yield (up to 80%) but also allowed a lower reaction temperature than that previously reported.[1]

The role of iodine in this reaction is unclear. Possibly, a complex between iodine and the thioacid is present, because clear undistilled samples, previously shaken with mercury, slowly became colored owing to the presence of iodine (the color could be removed with mercury). This would indicate that a complex is slowly decomposing, giving I_2.

Experimental Section

The chemicals used in this study (I_2, ICl, Br_2, H_2S, Cl_2, aniline, and pyridine) were purchased and were of such purity (better than N.F. quality except for Br_2) that they were used as received. $CF_3COSCH_2CH_3$ was purchased from the Peninsular Chemresearch Co. The $(CF_3CO)_2O$ used was prepared from CF_3CO_2H and P_2O_5. The infrared spectra of the chemicals were taken where possible and agreed with the published spectra.

All handling of liquids and gases at room temperature was performed with a Pyrex vacuum system equipped with Eck & Krebs stopcocks. Solids were transferred in a dry box.

The infrared spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer. The infrared cell was made of monel metal and equipped with a Whitey-Brass valve. Path length of the cell was 8.25 cm. The infrared spectra of the solid compounds were taken neat between NaCl plates.

The proton magnetic resonance spectra were obtained with a Varian Model A-60 analytical nmr spectrometer. The fluorine spectra were obtained with a Varian Model 4311B high-resolution nmr spectrometer operating at 56.4 Mcps. Frequencies were determined using the audio side band technique.

Vapor densities were determined using a Pyrex glass bulb equipped with a Teflon stopcock having a calibrated volume of 209.6 cm^3.

X-Ray powder spectra were obtained for the solids contained in 0.5-mm Lindemann glass tubes. Exposure for 5–6 hr was made using a XRD-5 GE camera. Nickel-filtered copper radiation (Cu Kα radiation) was used. Our procedure was standardized using known compounds in which the calculated d values agreed with the published ASTM values.

The ultraviolet spectra were recorded using a Cary Model 14 recording ultraviolet spectrophotometer. The gaseous spectra were taken using a cell with a path length of 10 cm, while the liquid spectra were taken with a cell having a path length of 1.00 cm. The cyclohexane used in this work was Gas Chromatographic–Spectrophotometric quality (J. T. Baker Co.).

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(6) In CF_3COOH, the CF_3– resonance is +76.55 ppm from F-11. See J. J. Burke and T. R. Krugh, "A Table of F^{19} Chemical Shifts of a Variety of Compounds," Mellon Institute, Pittsburg 13, Pa. The CF_3– resonance in $CF_3COCF(CF_3)_2$ is +77.05 ppm from F-11. See R. D. Smith, F. S. Fawcett, and D. D. Coffman, *J. Amer. Chem. Soc.*, **84**, 4285 (1962).

(7) H. P. Koch, *J. Chem. Soc.*, 387 (1949).

(8) H. C. Clark, *Advan. Fluorine Chem.*, **3**, 26 (1963).

(9) M. D. Taylor and M. B. Templeman, *J. Amer. Chem. Soc.*, **78**, 2950 (1956).

Indices of refraction were determined using a Bausch & Lomb Abbe-3L refractometer.

Preparation and Properties of CF_3COSH.—CF_3COSH was prepared by the method of Sheppard and Muetterties[1] in a *ca.* 400-cm^3 nickel pressure vessel equipped with an autoclave space-saver valve. When 37.5 g of I_2, 3.76×10^{-1} mol of H_2S, and 4.03×10^{-1} mol of $(CF_3CO)_2O$ were heated together for 3.75 hr at 90–140°, 3.0×10^{-1} mol of CF_3COSH was produced (yield *ca.* 80%). However, with an excess of H_2S, the yield was 55–60% at 140° but dropped to *ca.* 40% at 200–210°.

The density of the acid was determined at 22° as 1.395 g/mol. The acid has a slightly yellow color. The index of refraction was 1.3563 at 7.9° and 1.3469 at 24.5°. The acid is a white solid at −195.8° and a slightly yellow liquid even at −78°. It has a vapor pressure of 517 mm at 300°K, 657 mm at 306°K, and 759 mm at 310°K. The uv spectra in the vapor phase gave two peaks: λ_{max} 281.6 mμ; λ_{min} 224.1 mμ; $\lambda_{max}^{C_6H_{12}}$ 230 mμ (ϵ 5510).

Reaction of CF_3COSH with Water.—To 6.80×10^{-3} mol of H_2O in a 0.2-l. Pyrex vessel equipped with a Teflon stopcock, 6.56×10^{-3} mol of CF_3COSH was added. After 6 days at room temperature, the mixture was analyzed. At −78°, 0.1963 g of H_2S (5.76×10^{-3} mol) was recovered. A molecular weight determination gave a value of 34.4 *vs.* the theoretical value of 34.1. The mixture also darkened lead acetate paper. An infrared spectrum of the remaining colorless liquid at room temperature showed CF_3COOH and a smaller amount of CF_3COSH to be present.

Preparation of CF_3COSCl.—In a 1-l. Pyrex vessel, 2.6×10^{-2} mol of CF_3COSH and 3.1×10^{-2} mol of Cl_2 were condensed together at −195.8°. The vessel was warmed from −195.8 to −78°, where reaction was evident and complete within 5 min. The HCl and excess Cl_2 were removed by pumping on the products cooled to −78°. The HCl was identified *via* its infrared spectrum. The product (2.56×10^{-2} mol) is a light yellow liquid (yield *ca.* 98%): bp 33° (324 mm); uv max (gas) 236 mμ; uv min (gas) 299 mμ (broad).

Anal. Calcd for C_2F_3OSCl: C, 14.6; F, 34.6; Cl, 21.6; mol wt, 164.1. Found: C, 12.8; F, 32.5; Cl, 21.2; mol wt, 164.5.

Preparation of CF_3COSBr.—In a *ca.* 1-l. Pyrex vessel equipped with a Teflon stopcock, 4.19×10^{-2} mol of Br_2 and 4.38×10^{-2} mol of CF_3COSH were condensed together at −195.8°. Warming slowly from −195.8° to room temperature resulted in the disappearance of the dark red bromine and the appearance of a yellow liquid. The HBr and excess CF_3COSH were removed by transferring at −50 to −60° the volatile products to a trap at −195.8°. The transfer was continued until a constant weight was obtained for the product. The HBr and excess CF_3COSH were identified by their respective infrared spectra. The product (4.12×10^{-2} mol, 98%) was shown to be essentially CF_3COSBr by chemical analysis and by its reaction with mercury to give $Hg(CF_3COS)_2$ and $HgBr_2$.

Anal. Calcd for C_2F_3OSBr: C, 11.5; F, 27.3; S, 15.4. Found: C, 13.9; F, 24.2; S, 17.6.

CF_3COSBr is a yellow liquid which decomposes at room temperature. No attempts were made to determine the boiling point because of the apparent instability of CF_3COSBr.

Preparation of $Hg[S(C{=}O)CF_3]_2$.—When CF_3COSCl (1.76×10^{-2} mol) and Hg (1.45×10^{-1} mol) react together at room temperature (0.5–1 hr), a gray-white product is exothermically formed. The solid product was washed and filtered with carbon disulfide. The carbon disulfide solution was evaporated, leaving a white solid (0.37×10^{-2} mol): yield 42%; mp 72 ± 1°; uv (cyclohexane) 246 mμ (ϵ 5510). The powder spectrum gave the following *d* values (in Å) with their respective intensities: 8.91 (vs), 5.03 (w), 4.88 (w), 4.47 (w), 4.08 (w), 4.07 (w), 4.01 (s), 3.79 (m), 3.70 (w), 3.02 (m), 2.98 (m), 2.58 (m), 2.50 (w), 2.47 (w), 2.40 (w), 2.34 (w), 2.33 (w), 2.28 (w), 2.24 (s), 2.14 (w), 1.965 (m), 1.897 (m), 1.828 (m), 1.823 (w), 1.796 (m), 1.645 (m), 1.585 (m), 1.535 (w), 1.408 (w), 1.356 (w), 1.227 (w), 1.157 (w), 1.128 (w), and 1.029 (w). Additional very weak lines were observed.

CF_3COSBr and mercury also react exothermically, giving $(CF_3COS)_2Hg$, yield 37%.

Anal. Calcd for $C_4F_6O_2S_2Hg$: C, 10.47; F, 24.9; S, 13.9. Found: C, 9.4; F, 25.3; S, 13.8.

Decomposition of $Hg(SCOCF_3)_2$.—For several days, 2.30×10^{-3} mol of $Hg(CF_3COS)_2$ was heated at 120–140°. A black solid formed (2.20×10^{-3} mol), which was identified as HgS *via* chemical analysis. *Anal.* Calcd for HgS: S, 13.8. Found: S, 13.6. Also, an X-ray powder photograph confirmed the material to be HgS. The other products have not been identified.

Preparation of $(CF_3COS)_2$. Method 1.—To 1.45×10^{-1} mol of mercury, 1.76×10^{-2} mol of CF_3COSCl was added in a 0.2-l. Pyrex vessel equipped with a Teflon stopcock. The reaction was warmed from −195° to room temperature. At room temperature, an exothermic reaction occurred. After 1 hr, the volatile materials at −78° were removed (*ca.* 0.1 g of CF_3COCl). The volatile materials (1.1744 g) at room temperature were removed. Weight uptake by mercury was 1.6195 g. The room temperature fraction contained $(CF_3COS)_2$, which was purified by transferring away the volatile impurities at −40° to −50°.

Method 2.—To 4.45×10^{-3} mol of ICl, 7.56×10^{-3} mol of CF_3COSH was added. Warming to room temperature produced boiling inside the flask with the formation of a brown solid. Upon standing at room temperature, the brown solid turned purple. The vessel was cooled to −78° and the volatile materials (0.2013 g) were transferred. An infrared spectrum showed the material to be HCl with some CF_3COSH.

At room temperature, the volatile materials [mainly $(CF_3COS)_2$ and some CF_3COSH] were quickly transferred, leaving behind iodine (0.5797 g), theoretical yield 0.5700 g. On the basis of the amount of iodine formed, the yield for $(CF_3COS)_2$ was nearly 100%. Difficulty was encountered in separating CF_3COSH from $(CF_3COS)_2$, and this resulted in an overall yield of less than 100%. Bis(trifluoroacetyl) disulfide is a clear colorless liquid: bp 60° (126 mm); mp 0.5 ±1°; uv max (gas) 229.8 mμ (ϵ 152,000).

Anal. Calcd for $C_4F_6O_2S_2$: C, 18.6; F, 44.2; S, 24.9. Found: C, 16.3; F, 43.3; S, 24.8.

Reaction of $(CF_3COS)_2$ with Water.—To 37.8×10^{-3} mol of water in a 0.2-l. flask equipped with a Teflon stopcock, 4.45×10^{-3} mol of $(CF_3COS)_2$ was added. After 2 days, the reaction vessel was cooled to −78° and the volatile materials were transferred into a trap cooled to −195°. Analysis of the material (wt 0.1519 g) showed it to be H_2S (calcd mol wt, 34.1; found, 35.4; darkened lead acetate paper). At room temperature, the remaining volatile materials were transferred to a trap cooled to −195.8°. Remaining in the reaction vessel was a yellow solid (0.1456 g).

An infrared spectrum of the volatile material other than H_2S showed CF_3COOH to be present. The acid was titrated with a standard base using phenolphthalein as the indicator.

Assuming that the reaction proceeded according to eq 7, 4.45×10^{-3} mol of $(CF_3COS)_2$ would give 8.90×10^{-3} mol of CF_3COOH (found: 8.72×10^{-3} mol), 4.45×10^{-3} mol of H_2S (found: 4.45×10^{-3} mol), and 4.45×10^{-3} mol of sulfur (found: 4.53×10^{-3} mol).

Preparation of $CF_3COSH \cdot C_5H_5N$.—To 1.16×10^{-2} mol of pyridine, 1.29×10^{-2} mol of CF_3COSH was added in a *ca.* 125-ml Pyrex vessel equipped with a Fischer & Porter Teflon valve, and the mixture was warmed from −195° to room temperature. After 0.5 hr, the excess acid was removed, leaving a white product (1.13×10^{-2} mol of $CF_3COSH \cdot C_5H_5N$), mp 73.5 ±1.5°.

Anal. Calcd for $C_7H_6F_3OSN$: C, 40.2; H, 2.9; F, 27.3; S, 15.3. Found: C, 39.9; H, 2.8; F, 30.5; S, 15.3.

Preparation of $CF_3COSH \cdot C_6H_5NH_2$.—An excess of CF_3COSH (5.5×10^{-3} mol) and 2.91×10^{-3} mol of $C_6H_5NH_2$ were condensed at −195.8° in a 0.2-l. Pyrex vessel equipped with a Teflon stopcock. After 4 hr at room temperature, the volatile materials were removed, leaving a white solid (2.96×10^{-3} mol of $CF_3COSH \cdot C_6H_5NH_2$). The infrared spectrum of the volatile materials showed only CF_3COSH present. The aniline was consumed, giving a product with a molar composition ratio of reactants of 1:1. Further proof for this compound was obtained *via* thermal decomposition.

Decomposition of $CF_3COSH \cdot C_6H_5NH_2$.—In a 0.2-l. Pyrex vessel, 1.0599 g of $CF_3COSH \cdot C_6H_5NH_2$ was heated to 80° for 2 hr, and then to 90° for 1.5 hr. The volatile materials (0.1569 g) were transferred to a trap cooled to −195.8°. A molecular weight of the volatile material had a value of 34.6. For H_2S, the theoretical molecular weight is 34.1. The volatile material also darkens lead acetate paper. It appears that the aniline acid complex (4.75×10^{-3} mol) decomposes to give quantitatively H_2S (4.60×10^{-3} mol) and $CF_3CONHC_6H_5$ (4.77×10^{-5} mol). The presence of $CF_3CONHC_6H_5$ was confirmed by its melting point (89.2–89.4°)[10] and by an elemental analysis.

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[10] Reported mp 89–90°. See E. J. Bourne, S. H. Henry, C. E. M. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, 4014 (1952).

Anal. Calcd for $C_8H_6F_3ON$: C, 50.8; H, 3.18; F, 30.2. Found: C, 50.2; H, 3.21; F, 30.03.

Registry No.—CF_3COSH, 2925-25-9; CF_3COSCl, 21690-85-7; CF_3COSBr, 21690-86-8; $(CF_3COS)_2$, 21690-87-9; $(CF_3COS)_2Hg$, 21690-88-0; $CF_3COSH \cdot C_5H_5N$, 21690-89-1; $CF_3COSH \cdot C_6H_7N$, 21690-90-4; $CF_3COSCH_2CH_3$, 383-64-2.

Acknowledgment.—We wish to thank Mr. B. Nist of the University of Washington for obtaining the fluorine nmr spectra and Dr. A. Levinson for obtaining the proton spectra. We are indebted to the Huffman Laboratories, Inc., for the chemical analysis. A special acknowledgment is given to Mr. L. Kegley, who first prepared CF_3COSBr and helped in preparing CF_3COSH.

Fluoronitromethane. Synthesis and Estimation of Acid Strength[1]

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The effect of α-fluorine substitution on carbon acidity has been the subject of several recent reports.[2-5] The conclusion has been accepted that the great acid strengthening effect of α-fluorine essentially disappears when effective –R substituents are also present on the same carbon atom. That is, α-F does not stabilize planar carbanions, but only pyramidal ones. We now report the first synthesis and our studies of fluoronitromethane, IV, the simplest member of the series studied by Adolph and Kamlet.[4] Understanding of IV has been delayed by its unexpected instability toward base. We find IV to have $pK_a \approx 9.55$, as compared with 10.22 for nitromethane,[6] in essential agreement with the work cited.

Fluoronitromethane (IV) was prepared by saponification and decarboxylation of diethyl fluoronitromalonate (II), eq 3, synthesis of which from diethyl malonate,

$$CH_2(CO_2Et)_2 + HNO_3,\ 90\% \xrightarrow{15^\circ} \underset{\textstyle I}{O_2N{-}CH(CO_2Et)_2} \qquad (1)$$

$$I + NaH + FClO_3 \xrightarrow{DMF} \underset{\textstyle II}{O_2N{-}CF(CO_2Et)_2} \qquad (2)$$

$$II \xrightarrow[EtOH]{NaOH} \underset{\textstyle III}{[O_2N{-}CF(CO_2Na)_2]?} \xrightarrow[H_2O]{ClCH_2CO_2H} \underset{\textstyle IV}{FCH_2NO_2} \qquad (3)$$

eq 1 and 2, has been described.[7] Yields from II ranged from 5 to 32%. The crucial step appears to be the neutralization of the difficultly characterizable III. The product was characterized by elemental analysis and spectra (*cf.* Experimental Section).

The preparation of 1-fluoro-1-nitroethane has been achieved in 5% yield, by reaction of the aqueous nitronate salt with fluorine gas.[8] Under similar conditions, the yield of IV would likely be less than 5%, since less acidic nitro compounds gave poorer yields, and nitromethane is less acidic than nitroethane.[6]

Fluoronitromethane proved sufficiently unstable to base that only an approximate determination of pK_a was feasible by titration. Spectrophotometry at low pH failed because a suitable ultraviolet absorption maximum for the conjugate base was not found. It was possible to measure the rates of base-catalyzed hydrogen–deuterium exchange of nitromethane and IV and thus to estimate a pK_a value which agreed with the titrimetric one.

Addition of more than 10% of the theoretical amount of base, pH rising above *ca.* 9.0, was accompanied by a downward drift of pH at *ca.* 0.1 unit/min. The drift ceased when the pH exceeded 10.7, roughly the equivalence value. Even if a titration was carried out rapidly, and the solution quickly neutralized, only a trace of IV was recovered. IV was quantitatively recovered from 0.1 *N* hydrochloric acid and pure water, and after titration to pH 8.7; decomposition was slight in a Borax buffer (pH 9.18) in 2 min. Excess 0.1 *N* or 1.0 *N* base decomposed IV rapidly and completely, and 60–65% yields of fluoride ion could be detected, using a fluoride electrode and standard fluoride solutions. Nitrite ion could also be detected in *ca.* 50% yield by treatment with sulfamic acid and gravimetric determination of the resulting sulfate as barium sulfate. The fate of the carbon atom of IV remains unknown: no other product was extracted into dichloromethane, carbonate was not precipitated, and formaldehyde was not detected using 2,4-dinitrophenylhydrazine. Our feeling is that base-catalyzed dimerization such as that reported for 1-chloro-1-nitroethane and -propane was taking place.[9]

A rough determination of pK_a was made by rapid titration with 0.100 *N* base. The results are shown in Table I. Only in runs 3 and 4 were clean equivalence breaks observed. Our interpretation of the titrations depends on the exchange rates reported below. Thus, it may be calculated that neutralization has $t_{1/2} = 8$ sec at pH 10 (assuming that it is the rate-determining step of hydrogen isotope exchange). The meter never reads the maximum pH, corresponding to addition of 0.5 ml of 0.1 *N* base, because of neutralization, and the maximum (runs 1 and 2) has no significance. The initial rapid drop thus reflects neutralization, and the persistent slow drop, probably decomposition. Runs 3–5 yield a pK_a value of 9.55 ± 0.1, not much less than that of nitromethane,[6] 10.22.

Results of two measurements of the rates of base-catalyzed hydrogen–deuterium exchange of IV and nitromethane are given in Table II. These were performed at pH 8.0, since a run at pH 8.5 gave nearly complete exchange in 9 min and a serious drop in pH for IV. Observed rate constants were divided by the number of exchangeable protons and the corrected constants entered in Table II. The agreement is better

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