Tetrafluorodithiosuccinyl Difluoride

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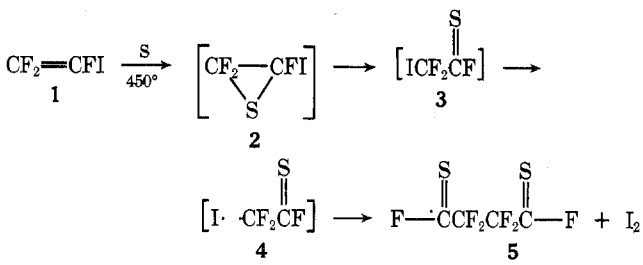
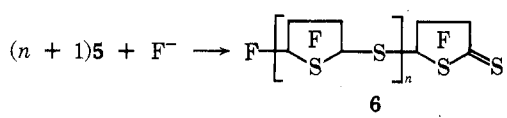
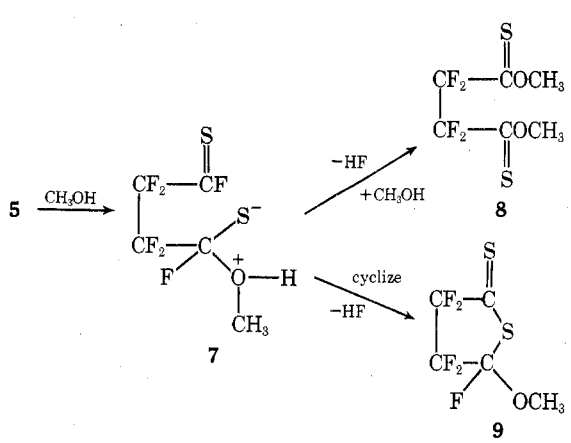
Earlier, we reported that the reactions of chlorotrifluoroethylene and bromotrifluoroethylene with sulfur vapors give high yields of chloro- and bromodifluorothioacetyl fluoride, respectively.[1] Our attempts to prepare the corresponding iododifluorothioacetyl fluoride (3) from the reaction of iodotrifluoroethylene (1) with sulfur vapors at 450° were unsuccessful. Instead, a 60% yield of tetrafluorodithiosuccinyl difluoride (5) was formed. The expected product, 3, probably does form but is unstable at the high temperature of the reaction and dissociates into an iodine radical and the resonance stabilized radical 4, which dimerizes to give 5.



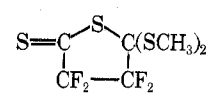
Like other thioacyl fluorides, 5 is easily polymerized at low temperatures by initiation with basic catalysts.[2] Since the polymer is not highly cross-linked and contains no reactive CSF groups, it is believed to be composed of cyclic units as illustrated by structure 6. Its slight pink color is due to the dithiolactone chromophore at the end of the chain.



Tetrafluorodithiosuccinyl difluoride (5) reacts with excess methanol to give two products, the orange-red diester 8 and the purple-red dithiolactone 9. The diester 8 was always obtained as the major product, but when the reaction was carried out at lower temperatures (−20°), appreciable amounts of 9 were also formed. The increased stability at low temperatures of an intermediate such as 7 might explain these results. At higher temperatures, 7 could eliminate HF easily and go on to the diester 8, but at lower temperatures, 7 could exist long enough to cyclize and give 9.



Reaction of 5 with ethyl and isopropyl alcohol gave only the dithio esters. An attempt to prepare the tetrathio ester by reaction of 5 with methanethiol gave instead the dimethylthiodithiolactone 10. The ester 8 reacts with piperidine to give the expected dithioamide 11.



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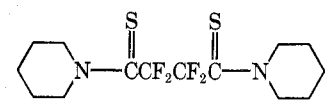

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Experimental Section[3]

Tetrafluorodithiosuccinyl Difluoride (5). A stream of nitrogen gas was bubbled into a flask containing 150 g (0.72 mol) of freshly distilled trifluoroiodoethylene, and the entrained vapors were then passed through a 500-ml flask fitted with 6 in. side arms containing 150 g of sulfur heated to reflux and then through a 12 in. horizontal wide-bore air condenser into an ice-cooled trap. Iodine crystals deposited in the air condenser, and a dark liquid condensed in the trap. The rate of nitrogen flow was adjusted so that the entire sample of trifluoroiodoethylene was added in about 2 hr. The condensate in the trap was distilled to give 41.32 g (61%) of 5 as a red-brown liquid: bp 84–85.5°; λ_{max} 428 (ϵ 46.5), 294 (ϵ 171), and 220 mμ (ϵ 11,300); ^{19}F nmr (CCl_3F) δ +66.2 (m, 2 F), −109.1 ppm (m, 4 F).

Anal. Calcd for $C_4F_6S_2$: C, 21.24; F, 50.41; S, 28.35. Found: C, 21.34; F, 50.47; S, 28.47.

Dimethyl Tetrafluorodithionosuccinate (8). A 62.5-g (0.275 mol) sample of 5 was added dropwise to 125 g of methanol cooled to 10°. The temperature of the reaction was kept between 10 and 20°. Distillation of the reaction mixture gave 51.51 g (75%) of 8 as an orange-red liquid, bp 86–88° (5 mm). Gas chromatography indicated the sample was about 95% pure. It was combined with similar samples and redistilled to give 8 as an orange-red liquid: bp 97–98° (96 mm); n^{25}D 1.4606; uv (isooctane) λ_{max} 243 (ϵ 14,000) and 399 mμ (ϵ 31); ^{19}F nmr (CCl_3F) δ −109.2 ppm (s); ^{1}H nmr (CCl_3F) δ 4.18 ppm (s).

Anal. Calcd for $C_6H_6F_4O_2S_2$: C, 28.80; H, 2.42; F, 30.37; S, 25.62. Found: C, 29.04; H, 2.44; F, 30.41; S, 25.64.

2,2,3,3,4-Pentafluoro-4-methoxydithiobutyrolactone (9) and 8. A 27.5-g (0.12 mol) sample of 5 was added dropwise to 50 ml of methanol cooled to −20°. The reaction mixture was warmed to room temperature and then distilled to give 12.66 g (42%) of 8, bp 87–88° (5.0 mm), and 5.34 g (19%) of 9 as a deep red liquid: bp 50–51° (5.0 mm); λ_{max} (isooctane) 520 (ϵ 17) and 302 mμ (ϵ 7,500); ^{19}F nmr (CCl_3F) δ −97.4 (m, $-CFOCH_3$), −110.0 and 110.9 (AB of m, $-CF_2CS-$), and 131.3 ppm (m, $-CF_2CFOCH_3$); ^{1}H nmr (CCl_3F) δ 3.78 ppm (d, J = 1.2 Hz of t, J = 0.4 Hz).

Anal. Calcd for $C_5H_3F_5OS_2$: C, 25.21; H, 1.27; F, 39.88; S, 26.92. Found: C, 24.85; H, 1.48; F, 39.86; S, 26.81.

Diethyl and Diisopropyl Tetrafluorodithionosuccinate. A 16.0-g (0.07 mol) sample of 5 was added dropwise to 50 ml of ethyl alcohol cooled to 15°. The reaction mixture was passed through a column containing 100 g of Al_2O_3 and then distilled to give 14.37 g (74%) of the ester as an orange liquid: bp 76° (0.55 mm); n^{25}D 1.4545; uv (isooctane) λ_{max} 400 (ϵ 38.6), 308 (ϵ 292), and 244 mμ (ϵ 14,100); ^{19}F nmr (CCl_3F) δ −109.2 ppm (s); ^{1}H nmr (CCl_3F) δ 1.48 (t, J = 7 Hz, 6 H) and 4.68 ppm (q, J = 7 Hz, 4 H).

Anal. Calcd for $C_8H_{10}F_4O_2S_2$: C, 34.53; H, 3.62; F, 27.31; S, 23.04. Found: C, 34.84; H, 3.63; F, 27.50; S, 23.12.

The diisopropyl ester was obtained in a similar manner and was obtained as an orange liquid: bp 77–80° (0.75 mm); uv (isooctane) λ_{max} 400 (ϵ 54.8), 302 (ϵ 410), and 248 mμ (ϵ 13,200); ^{19}F nmr (CCl_3F) δ −107.2 ppm (s); ^{1}H nmr (CCl_3F) δ 1.42 (d, J = 6 Hz, 12 H) and 5.67 ppm (septet, J = 6 Hz, 2 H).

Anal. Calcd for $C_{10}H_{14}F_4O_2S_2$: C, 39.21; H, 4.51; F, 24.81; S, 20.93. Found: C, 38.91; H, 4.21; F, 25.03; S, 20.77.

2,2,3,3-Tetrafluoro-4,4-di(methylthio)dithiobutyrolactone (10). A 16-g (0.08 mol) sample of 5 was added dropwise to 50 g of methanethiol cooled in an ice bath. Ether, 25 ml, and then 6.7 g (0.16 mol) of powdered sodium fluoride were added to the reaction mixture, and the reaction mixture was filtered and then distilled. Several products that were not cleanly separated were formed. One fraction, 4.7 g (21%) of deep purple red oil, appeared to be pure by gc and was identified as 10: bp 100–103° (0.75 mm); n^{25}D 1.5896; uv (CH_3CN) λ_{max} 513 (ϵ 13.5) and 320 mμ (ϵ 7300); ^{19}F nmr (CCl_3F) δ −103.3 (t, J = 9.5 Hz, 2 F) and −116.8 ppm (t, J = 9.5

Hz of septets, J = 0.8 Hz 2 F); ^{1}H nmr (CCl_3F) δ 2.35 ppm (t, J = 0.8 Hz).

Anal. Calcd for $C_6H_6F_4S_4$: C, 25.52; H, 2.14; F, 26.91; S, 45.42. Found: C, 25.08; H, 2.21; F, 26.45; S, 45.63.

1,1,2,2-Tetrafluoro-1,2-bis(piperidinothiocarbonyl)ethane (11). A 3.5-g (0.014 mol) sample of 8 was added dropwise to a solution of 2.55 g (0.03 mol) of piperidine in 25 ml of ether at room temperature. The reaction mixture was evaporated to dryness under nitrogen, and the yellow residue was recrystallized from hexane–benzene to give 3.0 g of the diamide as yellow crystals: mp 129–132°; uv (ethanol) λ_{max} 365 (ϵ 161) and 296 mμ (ϵ 20,900); ^{19}F nmr (CCl_3D) δ −95.0 ppm (s); ^{1}H nmr (CCl_3D) δ 1.77 (m, 18 H), 4.04 (m, 4 H), and 4.28 ppm (m, 4 H).

Anal. Calcd for $C_{14}H_{20}F_4N_2S_2$: C, 47.18; H, 5.66; F, 21.32; N, 7.86; S, 17.99. Found: C, 47.03; H, 5.89; F, 21.11; N, 7.73; S, 17.60.

Poly(tetrafluorodithiosuccinyl fluoride) (6). A solution of 4.5 g of 5 in 50 ml of ether was cooled to −78°, and 1 drop of dimethylformamide was added. Cooling was continued for 2 hr, and then the reaction mixture was warmed to room temperature. The precipitated polymer was collected on a filter, washed with ether, and dried in air. There was obtained 2.3 g of the polymer as a light pink powder, mp 242–267° (viscous melt). No solvent was found for the polymer, but an opaque, brittle pink film was pressed at 150° (10,000 lb/in.^{2}).

Anal. Calcd for $(C_4F_6S_2)_n$: C, 21.24; H, 0.0; F, 50.40; S, 28.35. Found: C, 21.31; H, 0.36; F, 50.15; S, 28.97.

Registry No.—1, 359-37-5; **5,** 53128-98-6; **6,** 53128-99-7; **8,** 53129-20-7; **9,** 53129-21-8; **10,** 53129-22-9; **11,** 53129-23-0; diethyl tetrafluorodithionosuccinate, 53129-24-1; diisopropyl tetrafluorodithionosuccinate, 53129-25-2; methanol, 67-56-1; ethyl alcohol, 64-17-5; isopropyl alcohol, 67-63-0; methanethiol, 74-93-1; piperidine, 110-89-4.

References and Notes

(1) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30,** 1375 (1965).
(2) W. J. Middleton, H. W. Jacobson, R. E. Putnam, H. C. Walter, D. G. Pye, and W. H. Sharkey, *J. Polym. Sci., Part A,* **3,** 4115 (1965).
(3) All boiling points are uncorrected.

Rôle of Water in the Proton Transfer Step of Addition of Water to 1-Alkynyl Thioethers

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Our detailed study of the acid-catalyzed hydration of 1-alkynyl ethers,[2] thioethers,[3] and amines[4] revealed that the

$$RC{\equiv}CX + H_2O \longrightarrow RCH_2{-}COX$$

$$X = OR', SR', NR_2'$$

rate-determining step involves proton transfer to carbon.

$$RC{\equiv}CX + HA \longrightarrow RCH{=}C^+X + A^- \quad \text{(slow)}$$

Since the triple bond is highly asymmetrically substituted, in the transition state the proton probably is much closer to C_β than to C_α. The proton transfer step is endothermic and its transition state will resemble the intermediate carbocation.

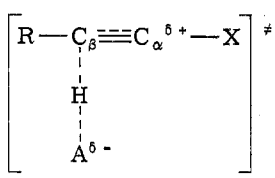
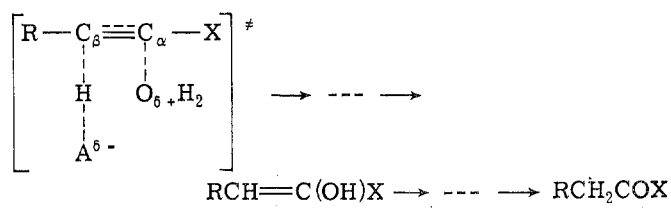


Table I
First-Order Rate Constants, k_1,[a] of Addition of Water to 1-Alkynyl Thioethers RC≡C—S—R'[b] in Aqueous Perchloric Acid at 25°. Ionic Strength 6.00 M by Addition of Sodium Perchlorate

R = H, R' = C_2H_5[c]		R = CH_3, R' = C_2H_5[d]		R = C_2H_5, R' = C_2H_5[e]		R = CH_3, R' = $C(CH_3)_3$[f]	
$HClO_4$ mol/l.	k_1 sec^{-1}	$HClO_4$ mol/l.	k_1 sec^{-1}	$HClO_4$ mol/l.	k_1 sec^{-1}	$HClO_4$ mol/l.	k_1 sec^{-1}
0.49	5.0	0.96	1.05	0.50	0.64	0.44	0.50
1.00	10.6	1.51	1.92	0.96	1.39	0.88	1.02
1.48	18.1	2.05	3.1	1.51	2.23	1.33	1.78
2.50	37	2.54	4.7	2.05	4.0	1.77	2.19
3.02	59	3.04	6.3	2.54	5.2	2.21	3.2
				3.04	7.2	2.65	3.9

[a] From spectrophotometry at 234 nm; standard deviation of the mean of at least three measurements ≤5%. Helpful assistance by Dr. R. W. Stephany is gratefully acknowledged. [b] Synthesized by Dr. J. Meijer and Mr. R. A. van der Welle following instructions by Brandsma.[6] [c] Registry no.—7299-53-8. [d] Registry no.—13597-15-4. [e] Registry no.—24298-52-0. [f] Registry no.—1595-36-4.

The question remains whether a water molecule is covalently attached to C_α already in this transition state and therefore also in the intermediate cation or later on.



Entropies of activation and rates in alcohol–water mixtures[3] indicated the absence of water in the transition state of the slow step. However, none of these arguments is very strong. Also it must be emphasized that the two possibilities, either covalently or not covalently bound, will be the extremes of a range of possibilities.

Generally, an answer to this question is sought from measurements in solutions at least 1 N in acid. Until now the fast rate of reaction of these hetero substituted acetylenes prevented us from extending our measurements to high acidity except for the relatively slow vinylthioethyne. For this compound in aqueous perchloric acid up to 3.5 N at 25°, a linear correlation was observed[3] between log k and the Hammett acidity function, $-H_0$, with a slope of 1.07.

Recently, we were able to measure the rates of 1-alkynyl thioethers in up to 3 N perchloric acid by stopped flow spectrophotometry. The results are presented in order to contribute to the complex problem of reaction kinetics in concentrated acids.

Rate constants at different perchloric acid concentrations and a constant ionic strength are given in Table I. Hammett's acidity function, H_0, and the water activity, a_w, have been determined by Perrin.[5]

When log k_1 was plotted *vs.* the acidity function $-H_0$, straight lines appeared of which the slopes, z, are given in Table II. These slopes are of the same order of magnitude or slightly higher than the slopes of 0.96–1.13 found by Noyce, *et al.*,[7] for the hydration of phenylpropiolic acids and phenylacetylenes. From a $\rho\sigma^+$ correlation for phenylpropiolic acids, it was concluded that C–OH_2 bond formation lags appreciably behind proton transfer. From a comparison of the H_0 correlation slopes, we tend to believe that