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.

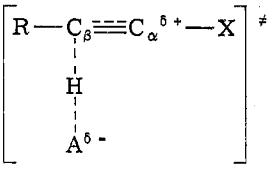
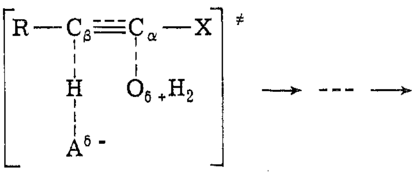


Table I
First-Order Rate Constants, k_1,[a] of Addition of Water to 1-Alkynyl Thioethers $RC{\equiv}C{-}S{-}R'$[b] in Aqueous Perchloric Acid at 25°. Ionic Strength 6.00 *M* by Addition of Sodium Perchlorate

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.



$$RCH{=}C(OH)X \longrightarrow \text{---} \longrightarrow RCH_2COX$$

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

Table II
Slopes of the Zucker–Hammett Plots, *z*, and Bunnett's *w* Parameters

Compound	*z*	*w*
$HC\equiv C{-}S{-}C_2H_5$	1.16 ± 0.04	−2.4 ± 0.3
$CH_3C\equiv C{-}S{-}C_2H_5$	1.31 ± 0.04	−3.4 ± 0.5
$C_2H_5C\equiv C{-}S{-}C_2H_5$	1.16 ± 0.04	−2.4 ± 0.5
$CH_3C\equiv C{-}S{-}C(CH_3)_3$	1.03 ± 0.03	−0.2 ± 0.5

also in the acid catalyzed hydration of acetylenic thioethers covalent bonding of water is not of much importance in the transition state of the proton transfer step.

As a matter of completeness, in Table II we have given the slopes w of plots of ($\log k + H_0$) *vs.* $\log a$ (H_2O) according to Bunnett.[8] These negative values are in the range believed to be characteristic for reactions in which water is not involved in the rate-determining step.

References and Notes

(1) Supported by the Netherlands Organization for the Advancement of Pure Research (ZWO).

(2) E. J. Stamhuis and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **82**, 394 (1963) and references therein.

(3) H. Hogeveen and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **82**, 410 (1963) and references therein.

(4) W. F. Verhelst and W. Drenth, *J. Amer. Chem. Soc.*, **96**, 6692 (1974).

(5) C. Perrin, *J. Amer. Chem. Soc.*, **86**, 256 (1964).

(6) L. Brandsma, "Preparative Acetylenic Chemistry," Elsevier, Amsterdam, 1971.

(7) D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Amer. Chem. Soc.*, **87**, 2295 (1965).

(8) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4978 (1961), and references therein.

Cuprous Trimethylsilylacetylide. Preparation and Reaction with Acid Chlorides

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The title compound, cuprous trimethylsilylacetylide (1), is of interest in that (1) trimethylsilyl protected acetylenes can be readily cleaved[1] to regenerate the terminal acetylenic function, (2) cuprous acetylide, itself, does not undergo the reactions of other cuprous acetylides, and (3) it represents the simplest Castro coupling reagent.[2] To the best of our knowledge acetylide 1 has not been prepared.[1,3]

In this paper we wish to report the preparation of 1 and its reaction with acid chlorides. Treatment of trimethylsilylacetylene in tetrahydrofuran (THF) with cuprous *tert*-butoxide[4,5] afforded a solution containing 1. Although an orange-red solid can be isolated from this solution upon dilution with ether, it is unstable and readily decomposes, even at −20°. We have tentatively assigned the structure of 1 to the orange-red solid based upon the infrared (Nujol mull) absorption bands at 1890 ($C\equiv C$), 1250 ($SiMe_3$), and 855 cm^{-1} ($SiMe_3$). The insolubility and instability of this precipitated material have precluded further characterization. The THF solutions of 1 are relatively stable at 0° provided they are not allowed to stand for extended periods of time. Thus 1 is best prepared in solution and used immediately without isolation. Furthermore, when preparing 1 it was found essential for cuprous iodide and trimethylsilylacetylene to be in excess of the lithium *tert*-butoxide, as 1 decomposed upon prolonged exposure to basic reagents. We have also prepared 1 from trimethylsilylacetylene by the butyllithium–cuprous iodide method,[6] but this method was not as satisfactory as the cuprous *tert*-butoxide procedure.

So far all attempts to obtain the Castro coupling product from 1 and the very reactive substrate methyl 2-iodobenzoate have been unsuccessful due to the instability of 1 under the reaction conditions. However, treatment of 1 with acid chlorides afforded the trimethylsilylethynyl ketones listed in Table I.

Table I
Trimethylsilylethynyl Ketones

R	Amt, mmol		$RCOC\equiv CSi(CH_3)_3$,
	RCOCl	1[a]	% yield
CH_3	15	12.8	30
CH_3	15	25.6	24
$CH_3(CH_2)_4$	8	12.8	38
$CH_3(CH_2)_4$[b]	8	12.8	62
$(CH_3)_2CH$[b]	8	12.8	48
C_6H_5	15	12.8	66
C_6H_5	15	25.6	66
p-$CH_3C_6H_4$	8	12.8	48
p-ClC_6H_4	8	12.8	61

[a] Prepared *in situ* from $CuOC(CH_3)_3$ and $HC\equiv CSi(CH_3)_3$ with the assumption of a quantitative formation of 1. [b] The solution containing 1 was evaporated to dryness under reduced pressure and the residue redissolved in THF before the addition of RCOCl.

The data in Table I show that there is no advantage in using an excess of either 1 or the acid chloride. When aliphatic acid chlorides were used, the *tert*-butyl alcohol generated in the preparation of 1 had to be removed (evaporation under reduced pressure) prior to the acid chloride addition since it competed with 1 for the acid chloride. With aryl acid chlorides the competing side reaction with *tert*-butyl alcohol was negligible.

Trimethylsilylethynyl ketones have previously been prepared by the action of trimethylsilylethynylmagnesium bromide on acid anhydrides[7] and by the aluminum chloride catalyzed reaction of acid chlorides with bis(trimethylsilyl)acetylene.[8]

The present procedure is complementary to the above methods in that it uses acid chlorides instead of the less readily available anhydrides required by the former, and the reaction conditions are essentially neutral as compared to the strongly acidic conditions of the latter.

In summary, cuprous trimethylsilylacetylide proved to be too unstable for Castro coupling; however, it does react readily with acid chlorides to give trimethylsilylethynyl ketones.[9]

Experimental Section[10]

General Procedure. To a magnetically stirred suspension of cuprous iodide in 40 ml of THF at 0° under nitrogen was added 0.9 equiv of lithium *tert*-butoxide. The mixture was stirred for 45 min at 0° and then 1 equiv of trimethylsilylacetylene[11] dissolved in 10 ml of THF was added with the temperature being maintained at 0°. After 30 min, the acid chloride was added and the cooling bath was removed. The reaction mixture was stirred for 20 hr at room temperature and the solvent was then removed on a rotary evaporator. The residue was treated with ether and filtered, and the filtrate was evaporated on a rotary evaporator. The residue was chromatographed on a small column of silica gel eluting with hexane up to 0.5% ether–hexane. The products so collected were then distilled under reduced pressure. In each chromatography run a small forefraction, ranging from 12 to 18%, of bis(trimethylsilyl)-1,4-butadiyne was obtained as a coupling product from 1.

Phenyl trimethylsilylethynyl ketone was isolated as a pale