Acid-Catalyzed Hydrolysis of Ketene Dithioacetals and Trithioorthocarboxylates. Effects of β-Methyl Substitution

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Hydrolysis rates of β-methyl-substituted ketene dithioacetals were measured. β-Monomethyl and β,β-dimethyl substitutions reduced the reactivity of the parent acetal by factors of 26 and 6.7 × 10^5, respectively. Similar methyl substitutions of trithioorthoacetate, however, enhanced the hydrolysis reactivity by 3 and 23 times. The reversibility of protonation of ketene dithioacetal during hydrolysis was slightly increased by a β-methyl group, but dimethyl substitution seemed to inhibit reversibility by raising the potential barrier to protonation.

Recent investigations in our laboratories have demonstrated that a ketene dithioacetal undergoes acid-catalyzed hydrolysis through partially reversible protonation of the double bond[1a] (eq 1). A β-phenyl substitution of the

$$\underset{\textbf{1a}}{CH_2{=}C(SMe)_2} + H_3O^+ \rightleftharpoons \underset{\textbf{2a}}{CH_3C^+(SMe)_2} \rightleftharpoons \underset{\textbf{3a}}{CH_3C(OH)(SMe)_2} \rightarrow \underset{\textbf{4a}}{CH_3COSMe} \quad (1)$$

ketene dithioacetal enhanced greatly the reversibility of the protonation.[1b] This is caused by the stabilization of the olefinic linkage of the reactant by the phenyl conjugation, which lowers the barrier against deprotonation of the intermediate carbocation while little affecting the barrier against hydration of the cation.

In the present study, we have examined the effects of β-methyl substitution on the reversibility of the protonation. The ketene dithioacetals studied include β-methyl (**1b** and **1d**) and β,β-dimethyl (**1c**) derivatives. The di-

$R_1R_2C{=}C(SR_3)_2$

1a, $R_1 = R_2 = H; R_3 = CH_3$
b, $R_1 = H; R_2 = R_3 = CH_3$
c, $R_1 = R_2 = R_3 = CH_3$
d, $R_1 = H; R_2 = CH_3; R_3 = C_2H_5$

methylketene derivative **1c** was found to be extremely unreactive. For the sake of comparison of reactivity, hydrolysis of the corresponding trithio ortho esters **5a–c** was also investigated (Scheme I).

Results

Hydrolysis of Ketene Dithioacetals 1. Hydrolysis products obtained from the reaction of **1b** in 80 vol % CH_3CN-H_2O (0.02 M HCl) were examined by ^1H NMR spectroscopy. The spectrum was consistent with *S*-methyl thiopropionate **4b** contaminated by a small amount (~1/6) of trithioorthopropionate **5b**. The latter product must come from the reaction of the intermediate carbocation **2b** with methanethiol liberated on the formation of **4b**.

Products from the reaction of **1b** in a deuterium medium (80 vol % CH_3CN-D_2O, 0.02 M DCl) were also analyzed in the same way. The NMR spectrum showed formation of **4b** as well as **5b**. However, the methylene signal for **4b** (2.5 ppm) was only slightly perceived, and the methyl triplet collapsed into poorly separated multiplet (1.1–1.2 ppm). This indicates extensive H–D isotope exchange occurring during the reaction (eq 2). Similar examinations were also undertaken with **1d**. Although the overlap of signals for the propionyl and *S*-ethyl groups of the product thiopropionate, coupled with the contamination of ortho thio ester, made the analysis qualitative, the collapse of the methyl triplet (1.16 ppm) for the propionyl group indicates extensive isotope exchange occurring at the methylene group of the thiopropionate.

$$CH_3CH{=}C(SCH_3)_2 \xrightarrow{D_3O^+} CH_3C(D)HC^+(SCH_3)_2 \xrightarrow{-H^+} CH_3CD{=}C(SCH_3)_2 \xrightarrow{D_3O^+} \rightarrow CH_3CD_2COSCH_3 \quad (2)$$

Scheme I

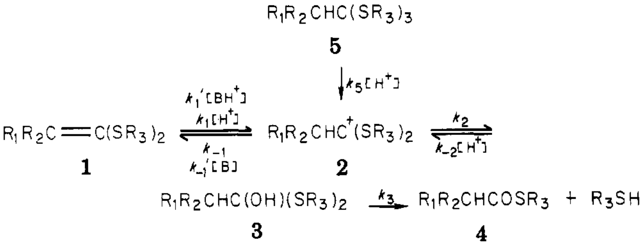

Table I. Rate Constants for the Hydrolysis of 1 and 5[a]

substrate	k_{H^+}, M^{-1} s^{-1}	rel rate	k_2/k_{-1}	k_1, M^{-1} s^{-1}
1a[b]	33.4	1.0	3.13	35.6
1b	1.28	3.8 × 10^{-2}	2.0	1.9
1c	5.01 × 10^{-5} [c]	1.5 × 10^{-6}		
1d	2.41 × 10^{-1}	7.2 × 10^{-3}	1.1	0.46
5a	6.0 × 10^{-3}	1.0		
5b	1.8 × 10^{-2}	3.0		
5c	1.4 × 10^{-1}	23		

[a] Measured at 30 °C in aqueous HCl solutions containing 10 vol % CH_3CN ($\mu = 0.45$) and 0.3–1 vol % CH_3CN ($\mu = 0.5$) for 1 and 5, respectively. [b] Reference 1a. [c] Obtained in $HClO_4$ solutions; $k_{obsd} = k_{H^+}10^{-H_0}$.

The reaction was spectrophotometrically monitored as a function of time. At low acidities (pH >0), an absorption due to **1b**,**d** (λ_{max} 250 nm) was found to disappear simultaneously with the formation of an absorption at 233 nm, which is due to the thiol ester product 4, an isosbestic point being observed at ~240 nm. In strong acid ($H_0 < -1$), however, instantaneous disappearance of **1** and simultaneous development of an absorption at 310 nm (**2**)[2] were followed by a slower decrease in this absorption, which was accompanied by formation of the thiol ester absorption (233 nm).

In the case of **1c**, the overall reaction was very slow, and accumulation of any intermediate was hardly observed even at $H_0 = -2$ ($[HClO_4] = 4.7$ M). Below H_0 −2.7 ($[HClO_4] = 5.9$ M), both formation and decay of the cation **2c** (310 nm) could be followed. Since the decay of **2c** had an isosbestic point at 263 nm, the disappearance of **1c** was

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(1) (a) Okuyama, T.; Kawao, S.; Fueno, T. *J. Am. Chem. Soc.* **1983**, *105*, 3220–3226. (b) Okuyama, T.; Fueno, T. *Ibid.* **1980**, *102*, 6590–6591; **1983**, *105*, 4390–4395.

(2) Cation **2** could be isolated as a perchlorate by the reaction of **1** or **5** with perchloric acid in acetic anhydride and had an absorption maximum at 310 nm in CH_3CN solution and ^1H and ^{13}C NMR spectra consistent with the structure.

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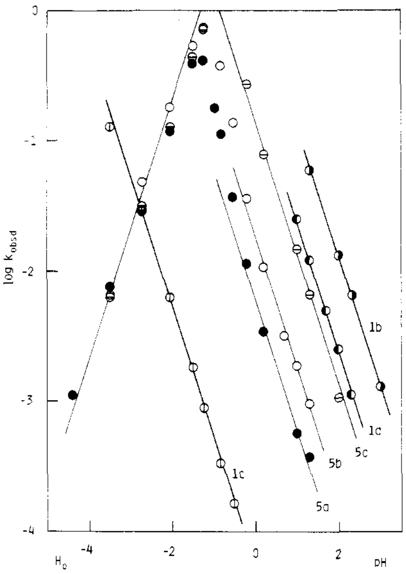

Figure 1. pH(H_0) – log k_{obsd} profiles for the hydrolyses of **1b** (◑), **1c** (circle with vertical bar), **1d** (◐), **5a** (●), **5b** (○), and **5c** (⊖).

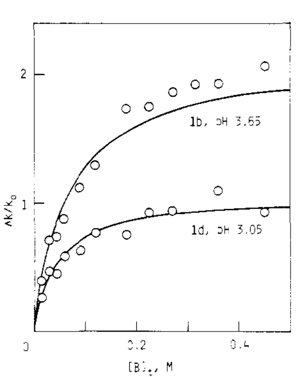

Figure 2. Buffer effects on the hydrolysis rates of **1b** (upper line, pH 3.65 ± 0.05) and **1d** (lower line, pH 3.05 ± 0.10) in formate buffer solutions. Solid curves are calculated from eq 4 by using parameters given in Table II.

monitored at this wavelength.

Pseudo-first-order rate constants k_{obsd} for the disappearance of **1b** and **1d** are proportional to the acid concentration in the range [HCl] = 0.001–0.1 M (Figure 1). Catalytic constants k_{H^+} are given in Table I. Rate constants for the disappearance of **1c** obtained in aqueous $HClO_4$ solutions (1.46–7.03 M) are logarithmically correlated with the H_0 acidity function[3] with a slope of –1. The catalytic constant k_{H^+} is calculated by eq 3. Rate constants

$$k_{obsd} = k_{H^+}10^{-H_0} \qquad (3)$$

for the decay of the carbocation **2c** in strong acid were identical with those obtained in the hydrolysis of **5c**.

In formate buffer solutions, rates of hydrolyses of **1b** and **1d** increased with buffer concentration $[B]_t$, following a saturation curve (eq 4) as shown in Figure 2. In eq 4 Δk

$$\Delta k/k_0 = (\Delta k_{max}/k_0)[B]_t/(K_{app} + [B]_t) \qquad (4)$$

$= k_{obsd} - k_0$, $\Delta k_{max} = k_{max} - k_0$, and k_0 and k_{max} are limiting rate constants at zero and infinite buffer concentrations, respectively. The parameter K_{app} is equal to $[B]_t$ when k_{obsd} attains a half-maximum increase (i.e., $\Delta k = \Delta k_{max}/2$). The curves were analyzed in the same way as before[1] on the basis of the mechanism given in Scheme I. The rate-determining step changes with buffer concentration. Kinetic parameters, which were obtained by the least-squares treatment of $k_0/\Delta k$ vs. $1/[B]_t$ using calculated values for k_0 ($=k_{H^+}[H^+]$), are summarized in Table II. The $\Delta k_{max}/k_0$ values are equal to k_2/k_{-1}[1] and are given as such in Table I.

Table II. Buffer Effects on the Hydrolysis Rates of 1b and 1d in 10 vol % CH_3CN-H_2O (μ = 0.45) at 30 °C

substrate	buffer	pH	K_{app}	$\Delta k_{max}/k_0$
1b	formate	3.07 ± 0.05	0.168 ± 0.029	1.80 ± 0.22
1b	formate	3.65 ± 0.05	0.068 ± 0.009	2.14 ± 0.17
1d	chloroacetate	2.88 ± 0.05	0.057 ± 0.021	1.16 ± 0.25
1d	formate	3.05 ± 0.10	0.045 ± 0.007	1.06 ± 0.09

Effects of added 2-mercaptoethanol on the rates of disappearance of **1b** and **1d** were also examined in HCl solutions and found to be small. The rate constants for **1b** and **1d** increased respectively about 13% and 35% in the presence of 0.5 M of the thiol, but further examinations were not undertaken.

Hydrolysis of **1b** and **1d** was also followed in deuterium media ([DCl] = 0.05 M). The first-order plots curved as in the case of a phenylketene dithioacetal.[1b] Approximate initial and ultimate slopes of the plots gave rate constants of 1.7×10^{-2} and 2.2×10^{-2} M^{-1} s^{-1} for **1b** and of 4.2×10^{-3} and 5.6×10^{-3} M^{-1} s^{-1} for **1d**, respectively. Initial rate constants give roughly the isotope effects k_{H^+}/k_{D^+} = 3.4 and 2.8 for **1b** and **1d**, respectively.

Hydrolysis of trithio ortho esters 5 leads to the thiol ester **4** through the carbocation intermediate **2**. The reaction was monitored by following formation of **4** (233 nm). The decay of **2** (310 nm) was also followed at high acidities. Both the formation of **4** and the decay of **2** gave the identical rate constants when measured. Rate constants k_{obsd} are logarithmically plotted against pH(H_0) in Figure 1. Plots are linear with a slope of –1 above pH 0 and become steeper (deviations upward from the line) with increasing acidity. At still higher acidities ($H_0 < -1.5$), the rates decrease with acidity, the slope being nearly unity. Catalytic constants k_{H^+} were evaluated from the linear plots at lower acidities and are given in Table I.

Products obtained from the reaction of **5c** in 80 vol % CH_3CN-D_2O were analyzed by ^1H NMR spectroscopy. Formation of the thiol ester **4c** was confirmed, and it was found to be contaminated only by unreacted **5c**. No sign of H–D isotope exchange at the product methyne group nor of formation of the ketene dithioacetal **1c** was detected.

Discussion

Reaction Mechanism. Hydrolysis of ketene dithioacetals **1** takes place stepwise as shown in Scheme I; the rate-determining step of the reaction depends on the structure of the substrate and the reaction conditions. A simple ketene dithioacetal, **1a**, undergoes hydrolysis through a mainly rate-determining protonation (k_2/k_{-1} = 3.13) above pH 2, but the hydration of the carbocation **2** becomes the slow step in buffer solutions as buffer concentration increases.[1a] This arises from the fact that hydration of **2** is slow and is hardly subject to buffer catalysis.

The relative rate constants k_2/k_{-1} were evaluated for **1b** and **1d** by the analyses of nonlinear dependences of rates on buffer concentrations: k_2/k_{-1} = 2.0 for **1b** and 1.1 for **1d**. Both the k_1 and k_2 steps contribute partially to the rate determination. This was also confirmed by small but definite effects of added thiol exerted on the rate. The thiol can compete with water in the nucleophilic reaction

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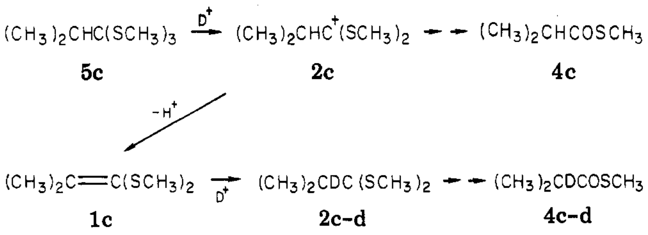
[3] (a) Rochester, C. H. "Acidity Functions"; Academic Press: London and New York, 1970. (b) Kresge, A. J.; Chen, H. J.; Capen, G. L.; Powell, M. F. Can. J. Chem. **1983**, 61, 249–256.

Scheme II



(k_2 step). Furthermore, the reversibility of the protonation was substantiated by the H-D isotope exchange found during the reaction in a deuterium medium. The curved first-order kinetics observed for the reaction in D_2O are rationalized also by the isotope exchange as before.[1b] Quantitative analysis of the isotope exchange was not attempted because the reversibility is greatly influenced by the reaction media.[1b]

The relative value k_2/k_{-1} for **1b** is somewhat smaller than that for **1a**. The β-methyl group increases slightly the reversibility of the protonation. This might be ascribed to the stabilization of the olefinic linkage by the methyl substitution,[4] which lowers the barrier against deprotonation (k_{-1}) while little affecting that against hydration (k_2) of the cation 2. This reasoning is similar to that for the effects of β-phenyl group.[1b]

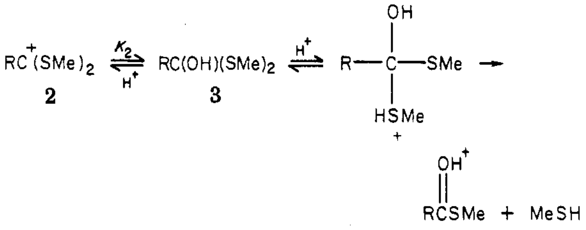
If this consideration could be extended to the β,β-dimethyl derivative **1c**, the reversibility of protonation of **1c** could have been still greater. However, the reactivity of **1c** is very small (1/6.7 × 10^5 of **1a**); that is, the barrier against protonation is large for some unknown reason. This could result in reduced reversibility of the protonation. If it were reversible, **1c** should have been found during the hydrolysis of **5c** at low acidities. Deprotonation of **2c** formed from **5c** might have afforded **1c** which is much less reactive than **5c** (1/7 × 10^3). However, **1c** has never been detected during hydrolysis of **5c**. Furthermore, NMR analysis of the hydrolysis products from **5c** in deuterium media did not show any sign of deuterium incorporation, which could have occurred if the intermediate cation **2c** could revert to **1c** during the reaction of **5c** as illustrated in Scheme II.

During the hydrolyses of **1** and **5** in strong acid, the accumulation of the carbocation **2** and its subsequent decay were monitored spectrophotometrically at 310 nm. Formation of the ultimate product **4** (233 nm) occurred simultaneously with decay of **2**, accompanied by an isosbestic point at 260–263 nm. The rates of decay of **2** and formation of **4** were identical on starting from either **1** or **5** and decreased with increasing acidity. Similar observations were made with cyclic ketene dithioacetals, 2-methylene-1,3-dithianes.[5] This behavior is accounted for in terms of a mechanism involving an equilibrium between the cation (**2**) and the hydrogen ortho thioester (**3**) followed by a subsequent slow breakdown of the latter to form a thiol ester (**4**). That is, the rate-determining step in strong acid is the k_3 step. Above pH 2, however, the rate-determining step of the carbocation decay was concluded to be the hydration of the cation **2** (k_2) for similar acyclic cations.[1] The change in rate-determining step seems to take place at $H_0 = 0$ to -1 in the present case. This changeover occurs because the k_{-2} process is catalyzed only by acid and faster than the acid-catalyzed process of the k_3 reaction. A similar change in the rate-determining step of the decay of cyclic cations (dithianyl cations) was found to occur around pH 2.[5] A C–S bond involved in the cyclic structure must be less readily cleaved.

The observation that the hydration of dithio carbocations (k_2) is rate determining at low acidities is in contrast to the previous findings that the breakdown of a hydrogen ortho ester intermediate (k_3) is the slow step of the overall reaction of dioxo carbocations in the entire acidity range studied (even near neutral pH).[6] This difference between sulfur- and oxygen-stabilized carbocations may be a result of slow reaction of the former cation with water.[7]

The change in the rate-determining step of the decay of thio carbocations corresponds to the change in the relative ease in release of hydroxy and alkylthio groups from a tetrahedral intermediate like **3**. A protonated tetrahedral intermediate loses H_2O in the k_{-2} step while it releases RSH in the k_3 step. The present observations are, in this sense, compatible with the earlier findings that alkoxy group is more easily released than alkylthio group is from a tetrahedral intermediate derived from a ketene *O,S*-acetal at higher acidities while the opposite is the case at low acidities.[8]

The decrease in log k_{obsd} with acidity follows the H_0 function with a slope of unity. This is primarily due to the decreasing fraction of **3** in equilibrium (with **2**, eq 5).



$$\overset{+}{RC}(SMe)_2 \underset{H^+}{\overset{K_2}{\rightleftharpoons}} RC(OH)(SMe)_2 \overset{H^+}{\rightleftharpoons} R-\underset{\underset{+}{HSMe}}{\overset{OH}{C}}-SMe \rightarrow R\overset{OH^+}{\overset{\|}{C}}SMe + MeSH \quad (5)$$

$$k_{obsd} = k_3^{H^+}K_2 10^{-H_0}/10^{-H_R} = k_3^{H^+}K_2/10^{-H_0} \quad (6)$$

However, the equilibrium K_2 should follow the H_R function, which decreases more rapidly than H_0 with acid concentration.[3] The breakdown of **3**, on the other hand, may be catalyzed by acid in such a strong acid and thus follow the H_0 function. It is known that $H_R \simeq 2H_0$ in a certain acidity range.[9] These result in the rate expression of eq 6. Furthermore, all the cations **2a–c** showed similar reactivity in this reaction. This might be possible because both the initial and product states are cationic and planar (the product here is a protonated thiol ester). Effects (electronic and steric) of alkyl groups on K_2 and $k_3^{H^+}$, if any, may cancel each other.

Reactivity. Relative hydrolysis rates are given in Table I. A β-methyl substitution of **1a** reduces the reactivity by 26-fold, and a further substitution lowers the reactivity of **1b** as much as 2.6 × 10^4 times. The relative rate of **1a**/**1c** is thus 6.7 × 10^5. This large reduction due to the β,β-dimethyl substitution is comparable to that observed for ketene acetals: $CH_2{=}C(OMe)_2/Me_2C{=}C(OMe)_2 \simeq 9 \times$

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[4] Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; pp 270–276. Hine, J.; Flachskam, N. W. *J. Am. Chem. Soc.* **1973**, *95*, 1179–1185.

[5] Okuyama, T.; Kawao, S.; Fujiwara, W.; Fueno, T. *J. Org. Chem.*, following paper in this issue.

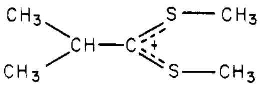
[6] Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1979**, *101*, 2669–2677. McClelland, R. A.; Ahmad, M.; Bohonek, J.; Gedge, S. *Can. J. Chem.* **1979**, *57*, 1531–1540. McClelland, R. A.; Gedge, S.; Bohonek, J. *J. Org. Chem.* **1981**, *46*, 886–891. Burt, R. A.; Chiang, Y.; Kresge, A. J.; McKinney, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 3685–3687.

[7] Okuyama, T.; Fujiwara, W.; Fueno, T. *J. Am. Chem. Soc.*, in press.

[8] Hershfield, R.; Schmir, G. L. *J. Am. Chem. Soc.* **1972**, *94*, 1263–1270. Hershfield, R.; Yeager, M. J.; Schmir, G. L. *J. Org. Chem.* **1975**, *40*, 2940–2946.

[9] Reference 3a, p 75. An approximate correlation $H_R = 2.06H_0$ is obtained for $-1 > H_0 > -4$ in $HClO_4$ solutions from the polynominal formulas given in ref 3b.

10^5.[10] These differences are much greater than those found with alkyl vinyl ethers.[11] The large effects observed with ketene acetals were rationalized by the steric interference of positive charge delocalization in the transition state.[10] If this were also the case with the sulfur analogues, acid-catalyzed hydrolysis of the corresponding trithio ortho esters **5** would have shown similar reactivity differences. Contrary to this expectation, β-methyl groups enhanced the hydrolysis rate of the ortho thio ester **5a** (Table I). The dithio carbocation intermediate **2c** formed by protonation of ketene dithioacetal **1c** or in the rate-determining step of hydrolysis of ortho thio ester **5c** may have conformational structures like **6**–**8**. For the oxygen analogue, any similar structures were considered to be sterically strained by the interference between two methyl groups.[10] Such strains may not be so serious for the sulfur analogues **6**–**8** owing to a longer C–S bond. Steric strains may be operating in the tetrahedral substrate **5c** rather than the planar intermediate **2c** or the planar substrate **1c**. This strain in the reactant, which may be relieved on reaction, would explain the enhanced reactivity of β-methyl-substituted ortho thio esters **5**. The reduced reactivity of the dithioacetal **1c** remains unexplained, but this does not seem to be particular of ketene dithioacetal **1**. A β-methyl substitution of a vinyl sulfide reduces the reactivity by a factor of 21–37,[12] the magnitude being similar to that found for **1**. Steric hindrance against the protonation and/or steric inhibition of solvation of the carbocationic transition state may be possible causes for the reduced reactivity.



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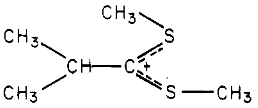

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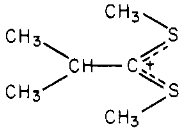

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Finally, we point out that the methylthio substrate **1b** is 5.3-fold more reactive than the ethylthio derivative **1d**. This is similar to the reactivity of alkyl vinyl sulfides,[12] but the opposite is the case for alkyl vinyl ethers.[13]

Experimental Section

Materials. Trithioorthocarboxylates **5a**–**c** were prepared from methanethiol and appropriate acid chlorides:[14] **5a**, bp 95 °C (10 mmHg) [lit.[15] bp 98.5–100 °C (11 mmHg)]; **5b**, bp 95–96.5 °C (4 mmHg); **5c**, bp 115 °C (5 mmHg). Ketene dithioacetals **1b**–**d** were synthesized from the corresponding trithio ortho esters **5** as before.[1,14] **1b**: bp 71–73 °C (15 mmHg); ^{1}H NMR (CCl_4) δ 1.86 (d, 3 H), 2.21 (s, 3 H), 2.25 (s, 3 H), 5.93 (q, 1 H). **1c**: bp 94 °C (15 mmHg); ^{1}H NMR (CCl_4) δ 2.02 (s), 2.18 (s). **1d**: bp 62–63 °C (5 mmHg) [lit.[14] bp 60–60.2 °C (4 mmHg)]; ^{1}H NMR (CCl_4) δ 1.10 (t, 6 H), 1.96 (d, 3 H), 2.70 (q, 4 H), 6.19 (q, 1 H).

Other materials were obtained as described previously.[1] Glass-distilled water was used throughout.

Product Analysis. Reactions of **1b** were carried out in 4:1 (v/v) CH_3CN–H_2O (D_2O) solutions containing 0.02 M HCl (DCl) for 20 h at 30 °C. Products were extracted with CCl_4, and the resulting solution was subjected to NMR analysis. The detailed procedure was the same as before.[1] The ^{1}H NMR spectrum of the products from CH_3CN–H_2O had signals at 1.17 (t), 2.22 (s), and 2.50 ppm (q) consistent with *S*-methyl thiopropionate **4b** as well as a singlet at 2.02 ppm (ca. half of the 2.22-ppm singlet in intensity), which is due to 1,1,1-tris(methylthio)propane (**5b**). Small signals for the ethyl group of the latter product seem to overlap partly on the 1.17-ppm triplet (at 1.08 ppm) and the 2.02-ppm singlet (at 1.83 ppm). The products from the reaction in the deuterium medium showed two singlets at 2.22 and 2.02 ppm in a relative intensity of about 2:1. However, a signal at 2.5 ppm was only slightly perceived, and the 1.2-ppm triplet was collapsed into a closely spaced multiplet.

The reaction of **1d** was also conducted in 4:1 (v/v) CH_3CN–H_2O in the same way. The product NMR spectrum showed a quartet at 2.80 ppm and a triplet at 1.24 ppm (*S*-ethyl group of **4d**) comtaminated by small peaks (byproduct **5d**); the highest field peak of the 1.24-ppm triplet was overlapped with a singlet (or poorly resolved multiplet), which is due to the propionyl methyl group of **4d**.

Hydrolysis products of **5c** were also obtained from the reaction in a deuterium medium and analyzed in the same way as above. A sample of **5c** (0.15 g) was reacted in 10 mL of 4:1 (v/v) CH_3CN–D_2O (0.07 M DCl) for 2 h. The NMR spectrum of the CCl_4 extract was consistent with a mixture of *S*-methyl thioisobutyrate **4c** [δ 1.17 (d), 2.22 (s), 2.66 (septet)] and the reactant **5c** [δ 1.15 (d), 2.09 (s)][16] in a ratio of about 2:1.

Kinetic measurements were made in the same way as before[1] at 30 °C by using a Shimadzu UV-200 spectrophotometer. Reaction of **1** at low acidities (pH >0.5) was carried out in 10 vol % aqueous acetonitrile at an ionic strength of 0.45 (KCl) while reaction of **5** was undertaken in mostly aqueous solutions (0.3–1 vol % of CH_3CN) at an ionic strength of 0.50 (KCl). Aqueous perchloric acid (0.3–1 vol % of CH_3CN) was used without added salt for reactions at higher acidities. Hydrochloric acid solutions of 0.5 and 1 M were also used.

Registry No. **1a**, 51102-74-0; **1b**, 6251-15-6; **1c**, 35329-14-7; **1d**, 13879-93-1; **5a**, 6156-22-5; **5b**, 83994-43-8; **5c**, 87711-70-4.

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