39°); the corrosive, fuming nature of the distillate indicated SO_3 to be present in at least small amounts.

Ir analysis of the still pot contents showed it to contain not only heptafluorobutyroyl chloride (5.51 and 5.58 μ for C=O), but also heptafluorobutyroyl chlorosulfate (5.46 μ for C=O, 7.10 μ for OSO_2Cl).

Benzoyl Chlorosulfate (9). Benzoyl chloride (14.1 g, 0.10 mol) was stirred under dry N_2 while 8.0 g (0.10 mol) of SO_3 was added over 10 min with occasional cooling to keep the temperature at 30–40°. After the addition was completed, the mixture was allowed to stand for 1 hr, then distilled through a short Vigreux column to give 21.9 g (99%) of yellow oil, bp 37° (7.5 μ). ^1H NMR showed monosubstituted phenyl, nearly unchanged in chemical shift and in pattern from that of benzoyl chloride; ir 5.57 (C=O), 6.27 and 6.32 (aromatic C=C), and 7.07 μ (OSO_2Cl).

Methyl Pentafluoropropionyl Sulfate (10). To 27.0 g (0.15 mol) of methyl pentafluoropropionate stirred at 0° was added dropwise 12.0 g (0.15 mol) of SO_3. No exotherm was observed, so the reaction mixture was heated slowly to reflux (53°). Reflux was continued for 60 hr, at which time the pot temperature had leveled off at 73°. Distillation afforded 10.1 g (26%) of methyl pentafluoropropionyl sulfate: bp 38° (5 mm); ir 3.35 (saturated CH), 5.47 (C=O), 6.87 and 6.98 (SO_2), and broad 8 μ (CF); ^1H NMR δ 4.26 (OCH_3); ^{19}F NMR −83.3 (t, J_{FF} = 1.6 Hz, 3, CF_3) and −121.6 ppm (q, J_{FF} = 1.6 Hz, 2, CF_2).

Anal. Calcd for $C_4H_3F_5O_5S$: C, 18.61; H, 1.17; F, 36.80; S, 12.42. Found: C, 18.67; H, 1.33; F, 36.55; S, 13.04.

Acknowledgment. The expert technical assistance of Mr. William Nickerson is gratefully acknowledged, as is the interpretation of the ir spectra by Miss Naomi Schlichter.

Registry No.—**1**, 5762-53-8; **2**, 56114-18-2; **3**, 56114-19-3; **4**, 40416-27-1; **5**, 56114-20-6; **6**, 56114-21-7; **7**, 685-09-6; **8**, 56114-22-8; **9**, 56114-23-9; **10**, 56114-24-0; trifluoroacetyl fluoride, 354-34-7; SO_3, 7446-11-9; tetrahydrofuran, 109-99-9; polytetrahydrofuran, 24979-97-3; α-*H*-hexafluoroisobutyroyl fluoride, 382-22-9; perfluoromethacryloyl fluoride, 684-36-6; dimethyl ether, 115-10-6; α-*H*-tetrafluoropropionyl fluoride, 6065-84-5; α-fluorosulfonyltetrafluoropropionyl fluoride, 754-41-6; COF_2, 353-50-4; trisulfuryl fluoride, 13709-33-6; *m*-trifluoromethylbenzoyl fluoride, 328-99-4; heptafluorobutanoyl chloride, 375-16-6; benzoyl chloride, 98-88-4; methyl pentafluoropropionate, 378-75-6.

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Mechanism of Hydrolysis of an Unsymmetrical Ketene *O,O*-Acetal and of Ketene *O,S*-Acetals[1a]

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The hydrolyses of an unsymmetrical ketene *O,O*-acetal (2,2-dichloro-1-ethoxy-1-phenoxyethylene, **1**) and of two ketene *O,S*-acetals [2,2-dichloro-1-ethoxy-1-ethylthioethylene (**2**) and 1-ethylthio-1-phenoxyethylene (**3**)] have been studied in acidic solution at 30°. The observed catalysis by hydronium ion and acetic acid, the deuterium solvent isotope effect (k_H/k_D = 3.0 with **3**), and the nonlinear dependence of rate on buffer concentration at constant pH (with **3**) are in accord with a mechanism in which proton transfer to the olefinic bond is rate determining in HCl and $HClO_4$ solutions, and at low concentrations of acetate buffer. At high buffer concentration, the rate-limiting step is suggested to be the decomposition of a carbonium ion intermediate. The variation in the nature of the products of hydrolysis of **2** (mainly ester at $HClO_4$ < 1 *M*, and mixtures of ester and thiol ester at higher acidity) is taken as evidence for a second intermediate on the reaction pathway. The products of hydrolysis of **1** and **3** are phenol and ethyl dichloroacetate or ethyl thiolacetate, respectively, and are essentially independent of acidity in the ranges examined. The pathways of breakdown of tetrahedral addition intermediates of varying structure are discussed.

A useful approach to the study of the elusive, highly reactive, tetrahedral addition intermediates which are formed in many acyl transfer reactions consists of the generation of these or closely related substances via reactions which do not lie on the reaction pathway for acyl transfer.[2] Extensive use has been made of the hydration of imidate[3] and thioimidate[4] esters to investigate the properties of the intermediates formed in the aminolysis of esters and thiol esters, and in the alcoholysis of amides. In recent publications, the results of a study[5a] of the hydrolysis of a ketene *O,S*-acetal were employed in the assignment of the rate-limiting steps in the acid-catalyzed formation[5b] and hydrolysis[5a] of thiol esters. The present paper describes experiments with additional ketene *O,S*-acetals and with an unsymmetrical ketene *O,O*-acetal, and was designed to provide further information on the factors which control the pathways of breakdown of the intermediates formed in the hydrolysis and alcoholysis of esters and thiol esters. In the course of this research, kinetic data have been obtained which suggest the occurrence of a change in rate-determin-

ing step in the hydration of the carbon–carbon double bond of ketene *O,S*-acetals.

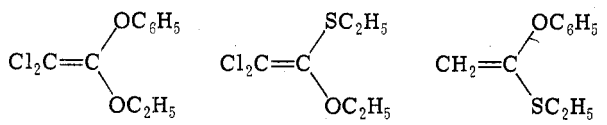
Results

Synthesis. Ketene *O,S*-acetals have been prepared by the addition of mercaptides to acetylenic ethers,[6] from ketene *O,O*-acetals,[7] by the additions of alkoxides to alkylthioacetylenes,[8] by the alkylation of thionoesters,[9] and from thiadiazoles.[10] The synthesis of **2**, by a method analogous to that used by McBee and Bolt[11] for halogenated ketene *O,O*-acetals, represents a new route, albeit of limited scope, to the preparation of certain ketene *O,S*-acetals.

$$CHCl_2CClF_2 + C_2H_5SH \longrightarrow CHCl_2CF_2SC_2H_5 \xrightarrow[C_2H_5OH]{KOH} CCl_2{=}C(OC_2H_5)SC_2H_5$$

8 2

Kinetic Studies. The rates of hydrolysis of three ketene acetals (**1–3**) under acidic conditions in predominantly



1 2 3

aqueous solutions were determined by spectrophotometric means (Table I).

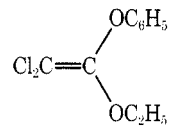
The hydrolysis of the ketene *O,O*-acetal **1** is catalyzed by acid and the rate increases linearly with acid concentration in the range of 0.08–0.8 *M* HCl. No evidence is seen for an uncatalyzed (or water-catalyzed) reaction at these acidities, although water-catalyzed reactions have been reported with reactive ketene acetals at high pH.[12–14]

The rate of hydrolysis of phenyl dichloroacetate, knowledge of which is needed to interpret the results of product analysis in the hydrolysis of **1**, was found to be essentially independent of acidity in the range of 0.83–10 *M* HCl (16.7% CH_3CN–H_2O, 30°, ionic strength equivalent to added acid) with $k_{obsd} = 1.8 \pm 0.2 \times 10^{-3}$ sec^{-1}. This observation does not necessarily mean, however, that the hydrolysis of phenyl dichloroacetate is not susceptible to acid catalysis. Under conditions of constant ionic strength, there is seen a small but definite increase of 28% in 0.96 *M* HCl over the pH-independent rate of $3.15 \pm 0.3 \times 10^{-3}$ sec^{-1} measured in the range of pH 1–5 (the latter value may be compared to that of 1.74×10^{-3} sec^{-} reported[15] for hydrolysis of phenyl dichloroacetate in H_2O, μ = 1.0, 25°). It is quite possible that a rate-decreasing effect of increasing ionic strength may mask the presence of weak acid catalysis, as was observed in the hydrolysis of, e.g., succinic[16a] and glutaric anhydrides.[16b] The detailed pH–rate profile for the hydrolysis of phenyl dichloroacetate (3.3% CH_3CN–H_2O, μ = 1.0 with added KCl, 30°, 15 pH values covering the range of pH 0–6) adheres accurately to the rate law $k_{obsd} = (8.3 \times 10^{-4}\ M^{-1}\ sec^{-1})[H^+] + 3.15 \times 10^{-3}$ sec^{-1}. For reasons set forth in the Discussion, the pH–rate profile for the hydrolysis of phenyl formate was also determined (1% CH_3CN–H_2O, μ = 1.0 with added LiCl, 30°, 23 pH values covering the range of pH 0–8) and was found to conform to the rate law $k_{obsd} = (3.8 \times 10^{-3}\ M^{-1}\ sec^{-1})[H^+] + (2.1 \times 10^{3}\ M^{-1}\ sec^{-1})[OH^-] + 4.8 \times 10^{-5}$ sec^{-1}.

The hydrolysis of the dichloroketene *O,S*-acetal **2** is subject to acid catalysis (Table I), the rate being approximately proportional to acid concentration in solutions of HCl or $HClO_4$ at < 1 *M*, and increasing much more rapidly than the stoichiometric acid concentration in more concentrated $HClO_4$ solutions. A plot of log k_{obsd} vs. the H_0 acidity function[17] is reasonably linear with a slope of 1.2, while a plot of log k_{obsd} vs. the H_c function (based on the protonation of azulenes, 1,1-diarylethylenes, and aromatic polyethers[18]) is similarly linear with a slope of 0.7. A similar dependence of rate on acidity has been reported for the hydration of styrenes,[19] where the use of the H_0 function gave slopes of 1.1–1.3, while plots using the H_R' scale (based on 1,1-diaryl olefins) had slopes of 0.59–0.68.

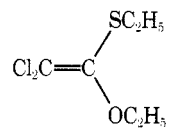
Rate measurements of the hydrolysis of **2** were not carried out at pH > 1 because the acid-catalyzed hydrolysis of

Table I
Rate Constants for Hydrolysis of Ketene Acetals at 30°



[HCl][a]	$k \times 10^3$, sec^{-1}	[HCl][a]	$k \times 10^3$, sec^{-1}
0.0833[b]	0.38	0.833[b]	3.30
0.21[b]	0.85	1.67	9.82
0.417[b]	1.63	3.33	36.5
0.624[b]	2.42		

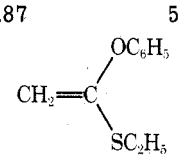
$k_H{}^c = 4.0 \times 10^{-3}\ M^{-1}$ sec^{-1}



	[HCl][d]	$k \times 10^3$, sec^{-1}
	0.097	0.127
	0.146	0.176
	0.97	1.15

$k_H{}^c = 1.22 \times 10^{-3}\ M^{-1}$ sec^{-1}

[$HClO_4$][e]	$k \times 10^3$, sec^{-1}	[$HClO_4$][e]	$k \times 10^3$, sec^{-1}
0.33	0.283	1.67	4.33
0.518	0.671	2.00	5.34
0.833	1.24	2.59	21.0
1.00	1.45	3.34	46.1
1.25	1.86	4.17	109.0
1.50	2.87	5.00	157.0



pH[f]	$k \times 10^3$, sec^{-1}	pH	$k \times 10^3$, sec^{-1}
2.32[g] (DCl)	75.9	4.48[h]	1.38
3.16 (HCl)	37.3	4.78[i]	0.791
3.36[g] (DCl)	7.03	5.04[h]	0.44
4.21[h]	2.56	5.43[h]	0.178

$k_H{}^j = 47.0\ M^{-1}$ sec^{-1}, $k_D = 16.0\ M^{-1}$ sec^{-1}

[a] 16.7% CH_3CN–H_2O. [b] μ = 0.833 (KCl). [c] Based on hydrogen ion concentration; k_H is calculated from data at [HCl] ≤ 1 *M*. [d] 3.3% CH_3CN–H_2O, μ = 0.97 (LiCl). [e] 10% CH_3CN–H_2O. [f] 10% CH_3CN–H_2O, μ = 0.9 (LiCl). [g] pD = pH meter reading + 0.40. [h] Extrapolated to zero acetate buffer concentration. [i] Constant pH maintained with pH stat [T. C. Bruice and J. R. Maley, *Anal. Biochem.*, 34, 275 (1970)]. [j] Based on hydrogen ion activity.

Table II
Rate Constants for Hydrolysis of Ethyl Dichlorothiolacetate[a,b]

[HCl], M	$k_{obsd} \times 10^5$, sec^{-1}	[HCl], M	$k_{obsd} \times 10^5$, sec^{-1}
0.005	2.99	0.20	3.28
0.01	3.07	0.40	3.10
0.02	3.02	0.50	3.09
0.05	3.13	1.0	3.71
0.10	2.94	2.0	3.74
0.15	3.21	4.0	3.74

$k_{av} = 3.25$

$[HClO_4]$	$k_{obsd} \times 10^5$, sec^{-1}
1.85	2.07
3.75	1.84
6.95	1.99

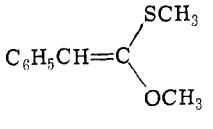
[a] 0.33% CH_3CN-H_2O, 30°. [b] Experiments in HCl solution at 0.005-1.0 M are at μ = 1.0 (LiCl).

the ketene acetal becomes slower than the further hydrolysis of both ethyl dichloroacetate ($k_{H_2O} = 5 \times 10^{-6}$ sec^{-1} at 25°)[20] and ethyl dichlorothiolacetate. The rate of hydrolysis of the latter compound is essentially constant over a wide range of acid concentration (Table II). These two esters are the expected products of the hydrolysis of **2**, and it is thus not possible to identify the initial products formed from **2** at pH > 3.

The more reactive ketene *O,S*-acetal **3** could be conveniently studied at pH 2–5. General acid catalysis is observed in acetate buffers, and the rate constants recorded in Table I are extrapolated to zero buffer concentration. At constant buffer ratio, there is a nonlinear dependence of k_{obsd} on acetate buffer concentration (Figure 1 and Table III).[21] Hydrolysis of **3** is slower in D_2O than in H_2O, with $k_H/k_D = 3.0$.

Products of Hydrolysis. Owing to the ready hydrolysis of phenyl dichloroacetate, the products of the hydrolysis of **1** were determined only in solution more acidic than 0.8 M HCl. In the range of 0.8–3.3 M HCl, the initial products of hydrolysis are phenol (and presumably ethyl dichloroacetate), formed in quantitative yield. This conclusion, based on the final absorbances at 280 nm, is supported by the observation that the hydrolysis of **1** in all cases showed no deviation from first-order kinetics. If appreciable amounts of phenyl dichloroacetate had been formed, the initially rapid hydrolysis of **1** would have been followed by the slower and easily measurable hydrolysis of phenyl dichloroacetate ($t_{1/2}$ 6.4 min).

The yield of thiol ester formed on hydrolysis of **2** rises from 4% in 0.33 N $HClO_4$ to a maximum of 34% in 3.0 N $HClO_4$, then decreases at higher acidity (Table IV). The low yields of thiol ester in dilute acid do not result from subsequent decomposition of initially formed thiol ester, since even in the least acidic solution, the ketene acetal **2** reacts ten times more rapidly than the thiol ester. The behavior of **2** is reminiscent of the hydrolysis[5a] of the phenylketene *O,S*-acetal **4** which showed increasing yields of thiol ester product as the pH was decreased from 3.0 to 1.0.



4

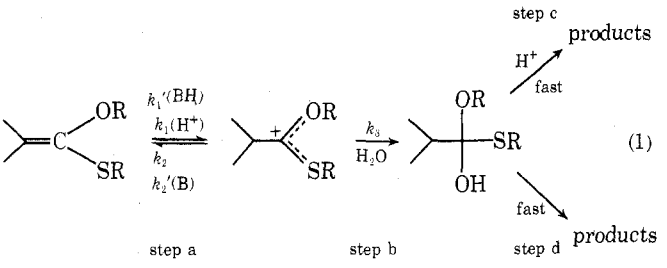
The predominant products of the hydrolysis of **3** are phenol and ethyl thiolacetate. These products, measured by uv spectroscopy, are formed in nearly 100% yield in HCl solution of pH 2–3. In dilute acetate buffers (ca. 0.02 M) at pH 4–5, the spectroscopic method indicates a small decrease in yield of the above products (to about 90%). This observation is corroborated by colorimetric assay for ethanethiol, using the Ellman procedure.[22] The formation of ethanethiol seems to be related to the presence of acetate buffer, and is under investigation.

Discussion

From previous studies, it is believed that the rate-determining step in the hydrolysis of ketene acetals is the protonation of the olefinic function by hydronium ion or general acids, including water.[5a,12-14,23,24] A similar mechanism has been ascribed to the hydrolysis of enol ethers.[25] It is probable that rate-controlling protonation also occurs in the hydrolysis of **1–3** in mineral acid solution, and in the presence of low concentrations of acetate buffers. This conclusion is supported by the observed catalysis by hydronium ion and acetic acid (see below), the sizable solvent deuterium isotope effect (with **3**), and the structural similarity of these compounds to ketene acetals studied earlier. The isotope effect ($k_H/k_D = 3.0$), which reflects the transfer of a proton in the transition state, may be compared to the values of 2.3–3.0 found for a series of ketene *O,O*-acetals.[14,23]

As expected, the hydrolysis of **1–3** follows the rate law $k_{obsd} = k_H[H^+]$ in dilute acidic solution, indicating the presence of a proton in the transition state. With **2**, the dependence of rate on acidity in perchloric acid solutions of 1–5 M is quite similar to that found in the hydration of styrenes,[19] for which the experimental evidence points strongly to a transition state which includes the hydrated proton.

The nonlinear dependence of rate on acetate buffer concentration (Figure 1) in the hydrolysis of **3** suggests that there occurs a change in rate-determining step with increasing buffer concentration, although other interpretations of the observed curvature are not ruled out by the available data.[26] It is proposed that the conversion of the ketene acetal to the carbonium ion intermediate (eq 1) is



(1)

accelerated as buffer concentration increases, until the reverse step k_2' becomes faster than the subsequent uncatalyzed hydration of the carbonium ion (step k_3). Similar nonlinear dependences of rate on buffer concentration have been frequently reported in nucleophilic addition to the carbonyl or imino group, and have been used as evidence for a change in rate-determining step.[27] Several instances are also known of nonlinear buffer catalysis in electrophilic substitution at the carbon–carbon double bond. In addition to the hydrolysis of **3** and **4**,[5b] downward curvature in plots of k_{obsd} vs. buffer concentration has been reported in the hydrolysis of a vinyl ether,[28] and in the hydrolysis[23] and methanolysis[29] of ketene *O,O*-acetals, and may result from a change in rate-determining step.

If the nonlinear buffer effect on the hydrolysis of **3** is

Table IV
Effect of Acidity on Yield of Thiol Ester Formed in Hydrolysis of 2[a]

$[HClO_4]$	% thiol ester	$[HClO_4]$	% thiol ester
0.333	4.1	3.34	28.8
0.517	8.2	4.17	22.1
0.833	12.1	5.00	20.9
1.00	15.8	6.26	17.7
1.25	19.5	0.313[b]	26.1
1.50	25.8	0.626[b]	25.5
1.67	29.4	1.25[b]	24.8
2.00	33.0	1.88[b]	23.6
2.50	33.4	2.50[b]	22.2
3.00	34.2	3.13[b]	20.9

[a] 10% CH_3CN-H_2O, 30°. [b] μ = 6.26 ($NaClO_4$).

taken as evidence for the existence of a carbonium ion intermediate whose formation is rate limiting at low acetate buffer concentration, and whose hydration becomes rate determining at high buffer concentration, the rate data may be analyzed further. In what follows, some quantitative conclusions concerning the partitioning of the carbonium ion intermediate are presented, keeping in mind the tentative nature of this analysis.

Application of the steady-state approximation to the carbonium ion (eq 1) leads to eq 2 for the dependence of k_{obsd} on buffer concentration ($[B_t] = [BH] + [B]$; $K_a = [B][H^+]/[BH]$). Both at zero buffer concentration (eq 3) and at infinitely high buffer concentration (eq 4), k_{obsd} is proportional to $[H^+]$. The initial slopes of plots of k_{obsd} vs. B_T depend on the mole fraction of buffer in the acidic form (eq 5), and the effectiveness of the buffer may be described by a constant, K_{app}, which is equal to the concentration of buffer required to produce half the maximum possible rate increase (eq 6).

$$k_{obsd} = \frac{\left(k_1[H^+] + \frac{k_1'[H^+]B_T}{[H^+] + K_a}\right)\frac{k_3}{k_2'}\left(\frac{[H^+] + K_a}{K_a}\right)}{\left(\frac{k_2 + k_3}{k_2'}\right)\left(\frac{[H^+] + K_a}{K_a}\right) + B_T} \quad (2)$$

$$k_{obsd} = \frac{k_1k_3[H^+]}{k_2 + k_3} \quad (3)$$

$$k_{max} = \frac{k_1k_3[H^+]}{k_2} \quad (4)$$

$$k_{obsd} = \left(\frac{k_1'k_3}{k_2 + k_3}\right)\left(\frac{[H^+]}{[H^+] + K_a}\right)B_T = \left(\frac{k_1'k_3(1 - \alpha)}{k_2 + k_3}\right)B_T \quad (5)$$

$$K_{app} = \left(\frac{k_2 + k_3}{k_2'}\right)\left(\frac{[H^+] + K_a}{K_a}\right) = \frac{k_2 + k_3}{k_2'\alpha} \quad (6)$$

Values of k_{max} and K_{app} were obtained at four buffer ratios by computer fitting of the data of Figure 1 to the equation for the two-parameter rectangular hyperbola (Table V).[31] The calculations given in Table V sugggest that the effect of acetate buffer in the hydrolysis of **3** conforms approximately to eq 1 and 2. The reason for the lack of constancy of the terms listed in columns 4, 6, and 8 is not clear, and may result from the gradual variation in pH observed on serial dilution of acetate buffers of constant buffer ratios. Taking the average value of $k_{max}/[H^+]$ as 5200 M^{-1} sec^{-1} and $k_1k_3/(k_2 + k_3)$ = 47 M^{-1} sec^{-1} (Table I) leads to a value of 110 for k_3/k_2, which describes the partitioning of the carbonium ion between hydration and proton abstraction. Using previously obtained[5] data on the effect of formate buffer in the hydrolysis of **4** (k_{max} = ca. 0.136 sec^{-1} at pH 3.0) gives an estimate of k_3/k_2 = 11 for that compound. The lower value of k_3/k_2 with **4** (uncorrected for a statistical factor of 2) may reflect (a) the increased driving force for proton abstraction in the case where the developing double bond is conjugated with the β-phenyl substituent, and (b) the greater steric requirements for proton abstraction from **3**.

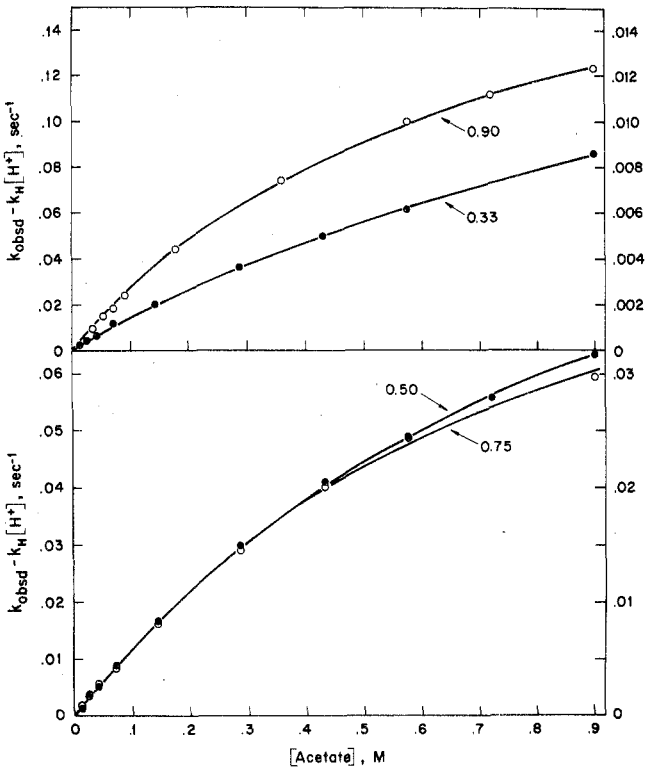


Figure 1. Effect of acetate buffer on the rate of hydrolysis of **3**: ●, left ordinate; ○, right ordinate. The mole fraction of buffer in the free base form is shown. The solid lines are calculated from the expression $k_{obsd} - k_H[H^+] = (k_{max} - k_H[H^+])[buffer]/([buffer] + K_{app})$, using the values of k_{max} and K_{app} in Table V and k_H = 47 M^{-1} sec^{-1}.

Where comparison to other compounds can be made, the observed reactivities of **1**–**3** and **4** (k_H = 12 and 36 M^{-1} sec^{-1} for the two geometric isomers) are reasonable. For example, replacement of the ethoxy group of ethyl vinyl ether by phenoxy reduces the rate of hydrolysis by 530.[25] Similarly, the reactivities of dichloroketene diethyl acetal[14] (25°) and **1** (30°) are in the ratio of 850:1. Also, comparison of the reactivities of ethyl vinyl ether and ethyl styryl ether (both in 80% dioxane) shows that β-phenylation causes a decrease in rate of about 500-fold,[32] while β-dichlorination reduces the rate of hydrolysis by 10^8.[14,25] It follows that replacement of the β-phenyl substituent in vinyl ethers by the dichloro group inhibits reaction by a factor of about 2 × 10^5. This effect may be compared to the relative reactivities of **4** and **2**, which are in the ratio of 1–3 × 10^4. Finally, the similar reactivities of **1** and **2** suggest that replacement of an alkoxy group of a ketene dialkyl acetal by either a phenoxy or an alkylthio function would result in an equivalent decrease in hydrolytic rate of about 10^3, presumably as a result of decreased stabilization of the carbonium ion-like transition state by the electron-withdrawing substituents.

Partitioning of Tetrahedral Intermediates. The products of hydrolysis of the ketene O,S-acetal **2** vary with acidity in a manner reminiscent of the behavior of **4**,[5a] though the change in products takes place in more acid solutions (Figure 2). The absence of a correlation between the

Table V
Summary of Parameters for Acetate-Catalyzed Hydrolysis of 3[a]

pH	Intercept $\times 10^3$,[b] sec^{-1}	Initial slope[b] M^{-1} sec^{-1}	Initial slope[c] $(1-\alpha)$	k_{max},[d] sec^{-1}	$10^{-3}\ k_{max}/[H^+]$, M^{-1} sec^{-1}	K_{app},[e] M	$K_{app}\ \alpha$,[c] M
4.21	2.56	0.146	0.22	0.24	3.9	1.65	0.54
4.48	1.38	0.130	0.26	0.14	4.2	1.05	0.52
5.04	0.44	0.070	0.28	0.06	6.6	0.85	0.64
5.43	0.178	0.030	0.30	0.023	6.2	0.77	0.69

[a] 10% CH_3CN-H_2O, μ = 0.90 (LiCl), 30°. [b] Intercept and initial slope of plots of k_{obsd} vs. total buffer concentration (Figure 1). [c] α = mole fraction acetate ion. [d] Extrapolated rate constant at infinite buffer concentration. [e] See eq 6.

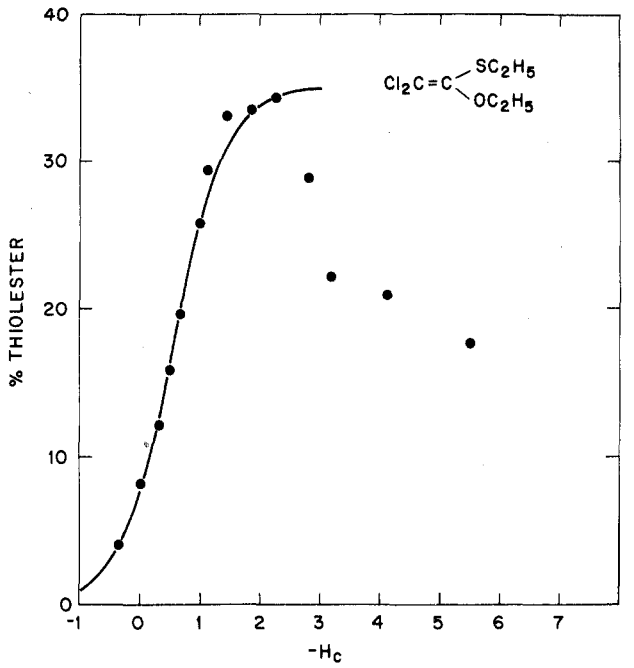
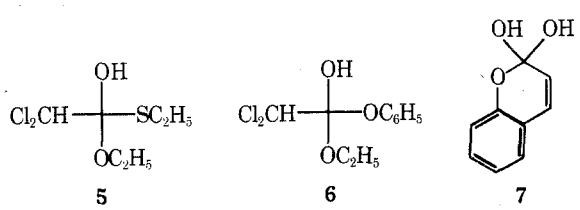


Figure 2. Effect of perchloric acid concentration on the yield of thiol ester formed on hydrolysis of **2**. The line is the calculated titration curve of an acid of pK −0.55, with asymptotes at 0 and 35%.

effect of changing acidity on products and on reaction rate (the plot, not shown, of log k_{obsd} vs. H_c is linear) is evidence for an intermediate whose breakdown to products is acidity dependent. The dependence of the thiol ester yield on H_c at [$HClO_4$] < 3 M is approximately sigmoid with a midpoint at 1.0–1.2 M $HClO_4$. As has been suggested[5a] for **4**, it is likely that a neutral tetrahedral adduct **5** expels predominantly mercaptan and accounts for the products formed at pH > 0. At higher acidity, protonation of **5** yields a cationic intermediate which expels 35% ethanol and 65% ethyl mercaptan. The observed product mix presumably reflects the interplay between the better leaving ability of the protonated thioether group and its lower concentration, relative to the protonated alcohol function.[33] That the product transition with **2** occurs at higher acidity than that of **4** (product transition at pH 1.66) is consistent with the greater acidity of the cationic intermediate derived from **2**. The relatively low yield of thiol ester obtained from **2** in acid (no more than 35%) continues a trend noted earlier which indicates that the partitioning of cationic intermediates related to **5** increasingly favors mercaptan expulsion as electron withdrawal in the acyl group increases.[36] The gradual decrease in thiol ester yield at [$HClO_4$] > 3 M does not seem to be as ionic strength effect (Table IV), but more likely results from the changing relative basicities of ethers and sulfides in concentrated acids.[35] The much greater solvation requirements of the protonated ether favor protonation of the thioether function in strongly acidic media, and may thus affect the partitioning of the cationic intermediate.



5 6 7

Unlike the hydrolysis of methyl thiolformate[5a] and a thiolactonization reaction,[5b] the hydrolysis of ethyl dichlorothiolacetate gives no clear evidence for a change in rate-determining step in acidic solution (Table II). This means either (a) that the tetrahedral intermediate expected to be formed by addition of water to the thiol ester carbonyl group behaves differently from its O-methyl analog derived from **2**; (b) that experimental scatter conceals the at best small deviation from a simple rate law of the type $k_{obsd} = k_H[H^+] + k_{H_2O}$ which would reveal the change in rate-limiting step; or (c) that the rate measurements on the thiol ester, carried out in HCl solutions, are not directly comparable to the product study done in $HClO_4$ for the hydrolysis of **2**.

Although measurements could be made only over a limited range of acidity (0.8–3.3 M HCl), the hydrolysis of **1** was found to yield predominantly phenol as the initial product. Though no direct experimental support is available, it is probable that the hydrolysis of **1** proceeds via tetrahedral intermediates also, so that the mode of breakdown of **6** (and/or of its cationic form) consists solely of the expulsion of phenol. This is in contrast to the pathway of breakdown of the related intermediate **7** derived from coumarinic acid, which expelled phenol from a neutral intermediate and water from the cationic species, with a transition at pH 1–3, depending on the nature of the aromatic substituent.[37] On the other hand, the pH–rate profiles for the hydrolysis of phenyl formate and phenyl dichloroacetate showed no evidence for intermediates at acid pH, suggesting either that intermediates are not formed in these reactions, or, more likely, that the partitioning of the intermediates and hence the nature of the rate-limiting step do not vary significantly over the pH range examined.

The acidic hydrolysis of two unsymmetrical ketene O,O-acetals (2-ethoxydihydropyran and 2-ethoxy-4-methyldihydropyran) has been reported to yield exclusively the ring-opened products. These selective reactions have been ascribed to stereoelectronic control of the decomposition of the tetrahedral intermediates.[38]

Assuming that the hydrolysis of **3** also proceeds via a tetrahedral adduct, it appears that the departure of phenol competes successfully with that of ethyl mercaptan in the range of pH 2–5, possibly from a neutral intermediate analogous to **5**. No conclusions can be drawn concerning the pathways of breakdown of cationic or anionic species of the

intermediate, though the preliminary observations that acetate buffers enhance the expulsion of mercaptan suggest that a change in products may occur at higher pH.

Two different types of evidence indicate the participation of intermediates in the hydrolysis of ketene acetals. (a) The nonlinear effect of buffers on the rate of hydrolysis suggests that a step which is susceptible to buffer catalysis at low buffer is followed by a step which is not catalyzed by buffer and which becomes rate determining at high buffer. The intermediate formed in the first step is presumably a carbonium ion. (b) The independent influences of acidity on the rates and products of the reaction indicate that the product-determining step is different from the rate-determining step. While it is in principle conceivable that the direct conversion of the carbonium ion to products might be pH dependent, it seems chemically more reasonable to postulate that hydration of the carbonium ion to a tetrahedral intermediate is followed by the pH-dependent transformation to products (eq 1). According to this proposal, step a is rate determining when BH = H_3O^+ or H_2O, and at low buffer concentration; step b becomes rate determining at high buffer, and steps c and d are product determining. It seems unlikely that attack of solvent on the carbonium ion would lead directly to ester or thiol ester. While thiol ester formation by direct displacement on the R group of the OR substituent is possible, the kinetically favored process is nucleophilic addition to the electron-deficient central carbon atom.[39]

Experimental Section

2,2-Dichloro-1-ethoxy-1-phenoxyethylene (1) was prepared from 1,1-difluoro-1,2,2-trichloroethane (Pierce Chemical Co.) according to McBee and Bolt:[11] NMR (neat) δ 1.05 (3 H, t), 3.75 (2 H, q), 7.1 (5 H, m); uv max (CH_3CN) 271.5 nm (ϵ 640), 265 (820), 259 (710); mass spectrum molecular ion at *m/e* 232.

2,2-Dichloro-1-ethoxy-1-ethylthioethylene (2). A. 2,2-Dichloro-1,1-difluoro-1-ethylthioethane (8) was prepared by a modification of the procedure of McBee and Bolt.[11] To a suspension of 8.3 g (0.1 mol) of sodium ethylmercaptide in 75 ml of ether–25 ml of acetonitrile was added dropwise 17 g (0.1 mol) of 1,1-difluoro-1,2,2-trichloroethane, and the reaction mixture was stirred overnight. After filtration, the product was obtained as a colorless liquid by fractional distillation: yield 13 g; bp 35–37° (1.3 mm); NMR (CCl_4) δ 1.35 (3 H, t), 2.95 (2 H, q), 5.80 (1 H, t). Anal. Calcd for $C_4H_6Cl_2F_2S$ (195.07): C, 24.62; H, 3.10; Cl, 36.65; S, 16.44. Found: C, 24.82; H, 3.14; Cl, 36.24; S, 16.69.

B. Conversion of **8** to **2** was accomplished by heating a solution of 7 g (0.036 mol) of **8** and 14 g of KOH in 150 ml of ethanol for 24 hr at reflux temperature. After cooling, the reaction mixture was diluted with 200 ml of water and extracted with three 100-ml portions of chloroform. The pooled $CHCl_3$ extracts were dried over anhydrous Na_2CO_3 and distilled at reduced pressure. Redistillation of the fraction boiling at 44–45° (0.2 mm) gave 5 g (69% yield) of a colorless liquid whose ir spectrum was free of carbonyl absorption at 5–6 μ: bp 39° (0.1 mm); NMR (neat) δ 1.25 (6 H, m), 2.75 (2 H, q), 3.9 (2 H, q); uv max (CH_3CN) 257 nm (ϵ 5560); mass spectrum molecular ion at *m/e* 201. Anal. Calcd for $C_6H_{10}Cl_2OS$ (201.12): C, 35.82; H, 5.02; Cl, 35.26; S, 15.94. Found: C, 36.14; H, 5.19; Cl, 34.78; S, 15.54.

1-Ethylthio-1-phenoxyethylene (3). β-Chlorophenetole was converted[40] to phenyl vinyl ether, which was brominated to yield 1,2-dibromo-1-phenoxyethane (**9**), bp 92–98° (0.7–1.0 mm) [lit.[41] bp 129–130° (12 mm)]. To 250–300 ml of liquid NH_3 (Dry Ice) was added 300 mg of $FeCl_3$ followed by 0.5 g of sodium. When a black precipitate had formed, 6.9 g of sodium was added, followed by (after 30 min) 12 g (0.043 mol) of **9**. The solution was stirred for 2 hr and 15 g of ethyl mercaptan was added dropwise over 1 hr. After stirring for 2 hr in a Dry Ice–acetone bath, NH_3 was allowed to evaporate and the reaction flask was flushed with nitrogen overnight. The residue was dissolved in 200 ml of ice water and extracted with five 50-ml portions of ether. The pooled extracts were dried over K_2CO_3 and distilled at reduced pressure, yielding **3** as a faintly yellow liquid (1.8 g, 23%): bp 60–63° (0.3 mm) [lit.[6c] bp 89° (3 mm)]; uv (CH_3CN) λ_{max} 274 nm (ϵ 600), 268 (840), 241 (3600); NMR ($CDCl_3$) δ 1.23 (3 H, t), 2.7 (2 H, q), 4.75 (2 H, m), 7.0 (5 H, m); mass spectrum molecular ion at *m/e* 180.

Phenyl dichloroacetate[15] had mp 47–48°. The preparation of **ethyl dichlorothiolacetate** has been previously described.[36] **Phenyl formate**,[42] prepared using formic–acetic anhydride,[43] had bp 106–108° (70 mm) [lit.[44] bp 90° (30 mm)]. 3,3'-Dithiobis(6-nitrobenzoic acid) was recrystallized from ethyl acetate–ligroin.

Kinetic Methods. Acetonitrile was purified as previously described.[36] Buffers and inorganic salts were of reagent grade and were used without further purification. Glass-distilled water was employed in the preparation of all solutions. D_2O (99.7% D) was obtained from Merck Sharpe and Dohme of Canada.

Stock solutions of the ketene acetals (10^{-2}–10^{-3} *M*) were prepared in dry acetonitrile immediately after synthesis and contained ca. 10^{-3} triethylamine. The rates of hydrolysis of **1–3** at 30° in the solvents given in the footnotes to Table I were determined spectrophotometrically by the changes in absorbance at 280, 250, and 270 nm for **1**, **2**, and **3**, respectively. Concentrations of the ketene acetals were 1–2 × 10^{-4} *M*. Reactions were initiated by the addition of a small volume (<0.5 ml) of stock solution of the ketene acetal to the aqueous buffer equilibrated at 30° in the cell compartment of a Cary 15 spectrophotometer. Reactions were followed for at least 3 half-lives and generally for more than 6. The absorbance change involved in the hydrolysis of **1** and **3** was only 0.05–0.1 units, requiring the use of the expanded scale of the Cary spectrophotometer. Rate constants were calculated as previously described.[36]

The hydrolysis of phenyl dichloroacetate and phenyl formate (under the conditions stated in the Results section) were followed at 30° by the increase in absorbance at 270 nm, with ester at 5–6 × 10^{-4} *M*. The details of the hydrolysis of ethyl dichlorothiolacetate have been previously reported.[36]

Product Analysis. The yield of phenol formed on hydrolysis of **1** (10^{-4} *M*) was determined from the infinity absorbance reading of each kinetic experiment at 280 nm where neither ethyl dichloroacetate nor phenyl dichloroacetate have a measurable absorbance at the concentration employed. The release of phenol was found to be invariably first order. The absorbance expected for 100% formation of phenol is about 0.07 units.

The yield of ethyl dichlorothiolacetate produced on hydrolysis of **2** (at 3.5 × 10^{-4} *M*) was based on the measurement of the absorbance at 250 nm after 6 or more half-lives of reaction. At this wavelength, ϵ_{max} for the thiol ester is 4500 and no other product has significant absorbance.

Complete spectra taken on completion of the hydrolysis of **3** (1.5 × 10^{-4} *M*) at pH 2–3 (HCl) were identical with those of an equimolar mixture of ethyl thiolacetate and phenol. When hydrolysis was carried out at pH 4–5 (0.02 *M* acetate buffer), the decreases in the absorption maxima at 235 nm (thiol ester) and 270 nm (phenol) suggested that the yields of phenol and thiol ester were about 90%. Assay of the reaction mixtures using a modification of the Ellman procedure[22] and L-cysteine as a standard indicated a yield of 8–10% of thiol, under conditions where ethyl thiolacetate is stable to hydrolysis.

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Registry No.—**1**, 55913-32-1; **2**, 55913-33-2; **3**, 25195-35-1; **8**, 5187-60-0; **9**, 42220-93-9; 1,1-difluoro-1,2,2-trichloroethane, 354-21-2; sodium ethylmercaptide, 811-51-8; ethyl dichlorothiolacetate, 41880-03-9.

Supplementary Material Available. Table III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2940.

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Carbon-13 CIDNP during Photolysis of Di-*tert*-butyl Ketone in Carbon Tetrachloride[1]

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Carbon-13 Fourier transform (FT) NMR was used to observe CIDNP during the photolytic decomposition of di-*tert*-butyl ketone in CCl_4. Recombination of the triplet *tert*-butyl–pivaloyl radical pair (I) was unambiguously established. The polarizations from 2,2-dimethylpropanal (1) and 2,2-dimethylpropanoic acid chloride (3) also result from triplet radical pair I. Other polarized products may come from singlet or triplet radical pair precursors. The observed polarization signs agreed with those predicted for all identified products.

The use of carbon-13 FT NMR to study CIDNP holds great promise as a mechanistic and kinetic tool for the investigation of radical reactions.[2] The major advantages of studying carbon-13 CIDNP are the large chemical shift range and the ability to make all carbons appear as singlets by proton decoupling. In addition, FT NMR techniques enable the entire spectrum to be recorded in a matter of seconds.

As part of our program of defining the pathways of material degradation, we have examined by carbon-13 FT NMR the CIDNP during the photochemical decomposition of di-*tert*-butyl ketone (DTBK) in CCl_4. Analysis of the polarization signs provided insight into the various degradation steps and the multiplicities of radical pair precursors. Proton CIDNP during the photolysis of DTBK has been previously studied using continuous-wave NMR.[3]

Results

Figure 1 shows proton decoupled carbon-13 FT NMR spectra of a 25% DTBK solution in CCl_4 obtained before, during, and after irradiation. The center spectrum, obtained during the first 1000 sec of photolysis, shows emis-