10, 61223-74-3; **11**, 61223-75-4; **12**, 57584-97-1; **13**, 17059-74-4; **14**, 61223-76-5; **15**, 490-03-9; **16**, 3008-41-1; **17**, 57287-71-5; **18**, 579-07-7; **19**, 134-81-6; **20**, 13706-89-3; **24**, 5762-56-1; **25**, 101-97-3; **26**, 14062-18-1; **27**, 123-66-0; **28**, 72011-31-5; **29**, 76344-78-0; **30**, 97391-34-9; **31**, 1603-79-8; **32**, 40140-16-7; **33**, 5753-96-8; **34**, 931-20-4; **35**, 931-20-4; **36**, 872-50-4; **37**, 5291-77-0; **38**, 97391-35-0; **39**, 97403-50-4; **40**, 59157-01-6; **41**, 97391-36-1; **42**, 30932-86-6; **43**, 30932-82-2; **44**, 42599-26-8; **45**, 58486-00-3; **46**, 34094-42-3; **47**, 34094-39-8; $Me_2N^+{=}CHOMe\ MeOSO_3^-$, 21511-55-7; Me_2NH, 124-40-3; $Me_2NCH{=}NMe_2^+\ MeOSO_3^-$, 2013-91-4; Me_2NCHO, 68-12-2; Me_2NCOCl, 79-44-7; $Me_2NCH{=}NMe_2^+\ Cl^-$, 1071-38-1; Me_2NLi, 3585-33-9.

Simple Enols. 4. Generation of Some New Simple Enols in Solution and the Kinetics and Mechanism of Their Ketonization

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The simple enols [O-^{2}H]-2-hydroxypropene, [O-^{2}H]-3-chloro-2-hydroxypropene, 2,2-dichlorovinyl alcohol, and hydroxypropadiene have been generated from reactive precursors in solution and characterized by NMR spectroscopy. The kinetics of ketonization of 3-chloro-2-hydroxypropene, hydroxypropadiene, and of the previously described (Z)-prop-1-en-1-ol and 2-methylprop-1-en-1-ol were studied by UV spectrophotometry at 15 °C. It was found that k_0 varied with pH according to the equation $k_0 = k_{H_2O} + (k_{H^+}10^{-pH}) + (k_{HO^-}K_w)/10^{-pH}$ and values of k_{H_2O}, k_{H^+}, and k_{HO^-} were evaluated for these four enols. Solvent isotope effects, k_{H^+}/k_{D^+}, were determined and the acid-catalyzed ketonization of 3-chloro-2-hydroxypropene and 2-methylprop-1-en-1-ol were studied in water–Me_2SO mixtures. The kinetics of the acid-catalyzed hydrolyses of the methyl enol ethers that correspond to these enols were also investigated. It is concluded that the kinetic results were best explained by concerted mechanisms for the hydronium ion catalyzed and spontaneous ketonization and by a stepwise mechanism for the hydroxide ion catalyzed ketonization.

We have recently shown how vinyl alcohol may be generated in solution from reactive precursors and characterized by NMR spectroscopy, and the kinetics of its conversion into acetaldehyde have been studied by UV spectrophotometry.[2,3] An investigation of the NMR spectra of (E)- and (Z)-prop-1-en-1-ol and of 2-methylprop-1-en-1-ol led to the conclusion that vinyl alcohol and (E)-prop-1-en-1-ol exist predominently in the S–cis conformation and that (Z)-prop-1-en-1-ol and 2-methylprop-1-en-1-ol exist predominantly in the S–trans conformation.[4] We now report how a variety of other enols may be generated in similar ways and describe an investigation of the kinetics of ketonization of some of them.

Generation and Characterization of Enols

The NMR spectral data of the enols and their precursors and the conditions under which the enols were generated are given in Table I.

[O-^{2}H]-2-Hydroxypropene (1). This is the enol of acetone. It has previously been generated photochemically and characterized by IR spectroscopy,[5] CIDNP,[6,7] NMR spectroscopy,[8] and UV spectroscopy.[9] It has also been generated thermally by flash thermolysis of its Diels–Alder adduct with anthracene.[10] In the slightly acidic solutions that we used for its generation 2-hydroxypropene undergoes ketonization more rapidly than vinyl alcohol and we were unable to convert the precursor **2** completely into **1** before it was partially converted into [^{2}H]acetone. This appears to be similar to what was found with the other methods of generation. Under our conditions the chemical shifts of the two vinyl protons were identical with δ 3.96. Henne and Fischer who used acetonitrile as solvent reported two signals with δ 3.97 and 3.71. Our value for the chemical shift of the methyl group (δ 1.74) is almost identical with that of the value of Henne and Fischer (δ 1.75).

[O-^{2}H]-3-Chloro-2-hydroxypropene (3). The introduction of a chlorine into 2-hydroxypropene decreases the rate of ketonization in acidic solution and [O-^{2}H]-3-chloro-2-hydroxy-propene (**3**) could be generated from both precursors **4** and **5** without any conversion into [^{2}H]-chloroacetone.

2,2-Dichlorovinyl Alcohol (6). Both the OH and OD forms of this enol which is tautomeric with 2,2-dichloroacetaldehyde were generated. It is much more stable in acidic solutions than vinyl alcohol and was obtained from ketal **7** and orthoformate **8** precursors in slightly aqueous acetone which contained a small amount of acid (Table I). It was not possible to detect the signal of the OH proton of this enol in a similar way to which that of vinyl alcohol was detected.[2] On cooling a solution in 99.5% CD_3COCD_3–0.5% H_2O which contained 5×10^{-4} M HCl to −100 °C, no signal for the OH proton could be detected, but there was some broadening of the signal of the α-CH proton at δ 6.98. This suggests that exchange of the OH proton of this enol is much faster than that of vinyl alcohol, which would be expected on the basis of the electron-withdrawing effects of the chlorines.

Hydroxypropadiene (9). This is the enol of acrylaldehyde. It was first generated from the orthoacetate precursor **10** under the conditions given in Table I. The α-CH was a triplet (δ 6.69) and the γ-CH a doublet (δ 5.19)

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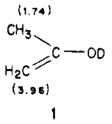
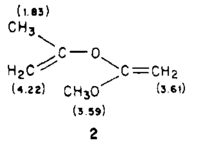
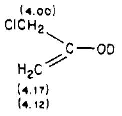
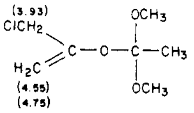
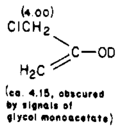
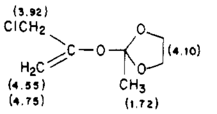
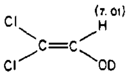
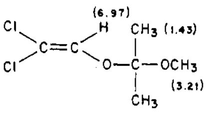
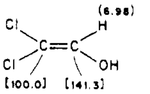
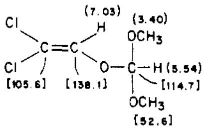
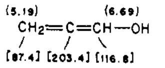
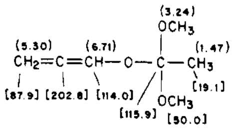
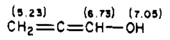
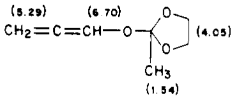
Table I. Generation of Enols[a]

enol	precursor	conditions
 1	 2	CD_3COCD_3 (80%) D_2O (20%) CD_3CO_2D (9 × 10^{-2} M) −30 °C
 3	 4	CD_3COCD_3 (90%) D_2O (10%) DCl (1.34 × 10^{-3} M) −5 °C
	 5	D_3CCOCD_3 (90%) D_2O (10%) DCl (1.34 × 10^{-2} M) −5 °C
 6	 7	CD_3COCD_3 (97.5%) D_2O (2.5%) DCl (2.10 × 10^{-4} M) 0 °C
	 8	CD_3COCD_3 (98%) H_2O (2%) HCl (1.7 × 10^{-4} M) −10 to 0 °C
 9	 10	CD_3COCD_3 (96.2%) H_2O (3.8%) HCl (3.8 × 10^{-4} M) −30 to −15 °C
	 11	CD_3COCD_3 (99%) H_2O (1%) HCl (1.2 × 10^{-4} M) −40 to −20 °C

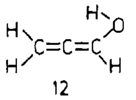
[a] δ (^{1}H) values are given in parentheses and δ (^{13}C) values in brackets.

Table II. Rate Constants for the Ketonization of Enols in Water at 15.0 °C (I = 1.00 M)[a]

	k_{H^+}/M^{-1} s^{-1}	k_{HO^-}/M^{-1} s^{-1}	k_{H_2O}/s^{-1}
vinyl alcohol[b]	20.2 (0.22)	1.50 × 10^7 (2.3 × 10^5)	1.38 × 10^{-2} (1.4 × 10^{-3})
(Z)-prop-1-en-1-ol	2.80 (0.08)	5.03 × 10^4 (2.6 × 10^3)	5.4 × 10^{-3} (4.8 × 10^{-3})[c]
2-methylprop-1-en-1-ol	0.370 (0.005)[d]	1.38 × 10^3 (31)	9.19 × 10^{-4} (3.5 × 10^{-4})[c]
3-chloro-2-hydroxypropene	6.18 (0.15)	4.74 × 10^7 (1.1 × 10^6)	6.01 × 10^{-2} (3.8 × 10^{-3})
hydroxypropadiene	5.67 (0.05)	1.11 × 10^9 (1.7 × 10^7)	7.61 × 10^{-3} (4.8 × 10^{-4})

[a] Esds given in parentheses. [b] From ref 3. [c] Rate constant not well defined. [d] A value of 0.59 M^{-1} s^{-1} at 25 °C is given by: Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122.

with apparent coupling constant 5.8 Hz. When the more reactive 2-methyldioxolane precursor **11** was used the hydroxypropadiene could be generated in solutions that contained less water and acid, and the signal of the HO proton could also be detected. At −40 °C this was a doublet at δ 7.05 (splitting 9.5 Hz), and the signal of the α-CH proton (δ 6.73) was now a double triplet. Decoupling experiments showed that these protons were coupled to one another, and addition of D_2O caused the doublet to disappear and the double triplet to collapse to a single one. On cooling to −100 °C the doublet moved downfield, and on warming to −20 °C it moved upfield, which is also consistent with it being that of a hydroxyl proton. At −20 °C the chemical shifts of the OH and α-CH protons are very close to one another so that they form the AB part of an ABX_2 system. The 9.5-Hz coupling between the OH and α-CH protons suggests that the S-cis conformation **12** is the predominant one as was proposed for vinyl alcohol.[4]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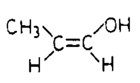
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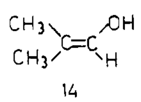

14

The ^{13}C NMR spectrum of hydroxypropadiene was also measured, and signals were assigned as shown in Table I.

When solutions of hydroxypropadiene were left at room temperature the spectra were transformed into those of acrylaldehyde (δ(^{1}H) 9.56, 6.64–6.26; δ (^{13}C) 195.8, 139.1, 139.3).

Kinetics of Ketonization

The pH-rate profiles for the ketonization of enols **3**, **9**, **13**, and **14** are similar to those for the ketonization of vinyl

Table III. Solvent Deuterium Isotope Effect for the Hydronium Ion Catalyzed Ketonization of Enols at 15.0 °C (I = 1.00 M)[a]

	k_{D^+}/M^{-1} s^{-1}	k_{H^+}/k_{D^+}
vinyl alcohol[b]	4.25 (0.050)	4.75 (0.076)
(Z)-prop-1-en-1-ol	0.780 (0.043)	3.59 (0.23)
2-methylprop-1-en-1-ol	0.143 (0.0036)	2.59 (0.07)[c]
3-chloro-2-hydroxypropene	1.08 (0.034)	5.72 (0.23)
hydroxypropadiene	1.53 (0.024)	3.71 (0.07)

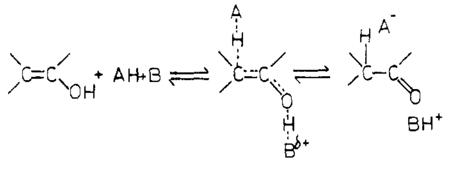
[a] Esds given in parentheses. [b] From ref 3. [c] A value of 2.83 ± 0.08 at 25 °C was reported by: Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122.

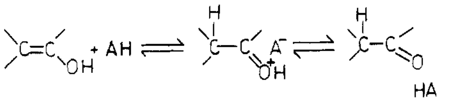
alcohol[3] (see Table S1–S8, supplementary material) and follow eq 1. The values of the rate constants k_{H_2O}, k_{H^+},

$$k_o(H_2O) = k_{H_2O} + (k_{H^+}10^{-pH}) + k_{HO^-}K_w(H_2O)/10^{-pH} \quad (1)$$

and k_{HO^-} are given in Table II. The solvent deuterium isotope effects were measured for the hydronium ion catalyzed reaction and are given in Table III. For comparison the hydrolyses of the corresponding enol ethers were also studied and values of k_{H^+} and k_{D^+} are listed in Table IV.

Hydronium Ion Catalyzed Reaction. In a previous paper it was concluded that kinetic results on the ketonization of vinyl alcohol were best explained by a concerted mechanism (eq 2) rather than by a stepwise mechanism (eq 3). In particular the following observations were thought to be significant: (i) k_{H^+} for the ketonization of vinyl alcohol is 27.8 times greater than k_{H^+} for the hydrolysis of methyl vinyl ether at 25 °C; (ii) k_{H^+}/k_{D^+} for the ketonization of vinyl alcohol is 4.75 at 15 °C compared to 2.98 for the hydrolysis of ethyl vinyl ether and an estimated value of ca. 3.5 for the hydrolysis of an enol ether with similar reactivity to that of vinyl alcohol; (iii) the effect of Me_2SO on the rate of ketonization of vinyl alcohol is different from that on the hydrolysis of ethyl vinyl ether, which results in k_{H^+}(vinyl alcohol) being 325 times greater than k_{H^+}(ethyl vinyl ether) in 92.5 mol % Me_2SO; (iv) Me_2SO causes an increase in the solvent isotope effect, k_{H^+}/k_{D^+}, for the ketonization of vinyl alcohol but a decrease in that for the hydrolysis of ethyl vinyl ether. Thus k_{H^+}/k_{D^+} for the ketonization changes from 4.75 in water to 5.33 in water–Me_2SO mixtures (C_{Me_2SO} = 82.9 mol %) while that for the hydrolysis changes from 2.98 to 2.05.


(2)


(3)

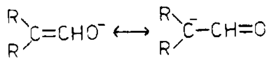
We have now studied the ketonization of four more enols, **3**, **9**, **13**, and **14** with qualitatively similar results (Tables V–VII). Thus k_{H^+} for their ketonization are about 20–70 times greater than k_{H^+} for the hydrolysis of the corresponding methyl ethers in water at 15 °C, and the isotope effect, k_{H^+}/k_{D^+}, is 1.34 to 1.83 times greater for the ketonization of the enol than for hydrolysis of the corresponding enol ether. In water–Me_2SO mixtures the ratio of k_{H^+} for ketonization of the enol to k_{H^+} for hydrolysis of the methyl enol ethers is greater than that in water. Thus for 2-methylprop-1-en-1-ol it is 262 (C_{Me_2SO} = 47.3 mol %) (Table VII) and for 3-chloro-2-hydroxy/propene it is ca. 290 in 85–96 mol % Me_2SO (Table VI). The isotope effect, k_{H^+}/k_{D^+} for the ketonization of 2-methylprop-1-en-1-ol increases from 2.59 in water to 3.30 in 47.2 mol % Me_2SO but that for the hydrolysis of the corresponding methyl ether decreases from 2.03 to 1.18. Similar figures for 3-chloro-2-hydroxypropene are as follows: enol, 5.72 (water), 6.18 (water–Me_2SO, Me_2SO mol % 85.4); methyl ether, 3.13 (water), 2.25 (water–Me_2SO, Me_2SO mol % 86.0). Thus as with the ketonization of vinyl alcohol the difference in kinetic behavior between the ketonization reaction and the hydrolysis of the corresponding enol ether seems to be best explained by a concerted mechanism.

Hydroxide Ion Catalyzed Reaction. The main conclusion that can be drawn is that substituents at the α-carbon of vinyl alcohol have only a small effect on k_{HO^-} but that substituents at the β-carbon have a quite large effect. Thus, from the results reported by Kresge and his coworkers[9] k_{HO^-} for the ketonization of the enol of acetone is 3.43 × 10^7 M^{-1} s^{-1} at 25 °C, which is very similar to that for vinyl alcohol (1.50 × 10^7 M^{-1} s^{-1} at 15 °C) and slightly less than that for 3-chloro-2-hydroxypropene (4.74 × 10^7 M^{-1} s^{-1} at 15 °C). On the other hand the introduction of one β-cis-methyl substituent into vinyl alcohol causes a 300-fold decrease in k_{HO^-} and the introduction of two β-methyl substituents a greater than 10^4-fold decrease. These effects are much larger than on k_{H^+}. In contrast k_{HO^-} for ketonization of the allenic enol hydroxypropadiene is 74 times greater than for that of vinyl alchol. The mechanism of the base-catalyzed ketonization is thought to involve general-acid-catalyzed C-protonation of the enolate anion (eq 4 and 5). The enolate anion has two resonance

$$R_2C{=}CHOH + A^- \rightleftarrows R_2C{=}CHO^- + AH \quad (4)$$

$$R_2C{=}CO^- + AH \rightarrow R_2CHCH{=}O + A^- \quad (5)$$

forms (**15** and **16**), and when R is changed from H to Me the ion should be destabilized. Therefore if the transition state for protonation resembles the carbanion, as would be expected on the basis of Hammond's postulate,[12] a rate


15 16

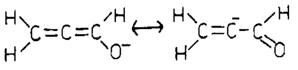

17 18

Table IV. Rate Constants for the Hydrolysis of Enol Ethers at 15 °C[a]

	$10^2\,k_{H^+}$/M^{-1} s^{-1}	$10^2\,k_{D^+}$/M^{-1} s^{-1}	k_{H^+}/k_{D^+}
vinyl ethyl ether[b]	119 (1.1)	40.0 (0.58)	2.98 (0.051)
(Z)-prop-1-enyl methyl ether	24.5[c]		2.45[c]
2-Methylprop-1-enyl methyl ether	1.56 (0.07)	0.768 (0.029)	2.03 (0.12)
3-Chloroprop-1-en-2-yl methyl ether	8.85 (0.30)	2.83 (0.05)	3.13 (0.12)
Allenyl methyl ether	21.0 (0.18)	7.61 (0.044)	2.76 (0.03)

[a] Esds given in parentheses. [b] Reference 3. [c] At 25 °C: Salomaa, P.; Nissi, P. *Acta Chem. Scand.* **1967**, *21*, 1386.

Table V. A Comparison of the Kinetics of Ketonization of Some Simple Enols and the Hydrolysis of the Corresponding Methyl Enol Ethers at 15 °C

	k_{H^+}(enol)/ k_{H^+}(enol ether)	[k_{H^+}/k_{D^+}(enol)]/ [k_{H^+}/k_{D^+} (enol ether)]
vinyl alcohol	17.0[a]	1.59[a]
(*Z*)-prop-1-en-1-ol	28.6[b]	1.46
2-methylprop-1-en-1-ol	23.7	1.28
3-chloro-2-hydroxypropene	69.8	1.83
hydroxypropadiene	27.0	1.34

[a] Value for ethyl vinyl ether, ref 3. [b] Based on a value of k_{H^+} (enol ether) = 9.8×10^{-2} M^{-1} s^{-1} extrapolated from the values at higher temperatures: Salomaa, P.; Nissi, P. *Acta Chem. Scand.* **1967**, *21*, 1386.

Table VI. Rate Constants for the Ketonization of 3-Chloro-2-hydroxypropene and Hydrolysis of 3-Chloroprop-1-en-2-yl Methyl Ether in Mixtures of Dimethyl Sulfoxide and Water

ketonization k_{H^+}[a] (Me_2SO/mol %)	hydrolysis $10^2 k_{H^+}$[a] (Me_2SO/mol %)
6.79 (0)	6.95 (0)
	4.61 (3.9)
	3.06 (9.7)
	2.08 (14.0)
2.06 (20.0)	1.08 (19.5)
1.67 (26.8)	0.493 (26.5)
	0.211 (35.15)
0.734 (47.2)	0.149 (48.0)
0.649 (62.5)	0.215 (63.4)
0.860 (69.6)	0.322 (72.5)
1.65 (85.2)	0.564 (86.3)
2.58 (92.25)	
0.270 (85.4)[b,c]	0.249 (86.0)[b,d]

[a] Based on C_{H^+}; units M^{-1} s^{-1} [b] In D_2O, k_{D^+} [c] k_{H^+} extrapolated to same conditions 1.67; k_{H^+}/k_{D^+} = 6.18 [d] $10^2 k_{H^+}$ extrapolated to same conditions 0.560; k_{H^+}/k_{D^+} = 2.25

Table VII. Rate Constants[a] for the Ketonization of 2-Methylprop-1-en-1-ol and for the Hydrolysis of Methyl 2-Methylprop-1-enyl Ether in Water–Me_2SO Mixtures (Me_2SO, 47.3 mol %) at 15 °C

ketonization	hydrolysis
k_{H^+}[a] = 0.134	k_{H^+}[a] = 5.12×10^{-4}
k_{D^+}[a] = 0.0395	k_{D^+}[a] = 4.35×10^{-4}
k_{H^+}/k_{D^+} = 3.39	k_{H^+}/k_{D^+} = 1.18

[a] Units M^{-1} s^{-1}; based on C_{H^+}

decrease would be observed. On the other hand the enolate anion derived from hydroxypropadiene (17 ↔ 18) has one resonance which is from a vinylic carbanion, and since vinylic carbanions[11] are more stable than alkyl carbanions the base-catalyzed ketonization of hydroxypropadiene should be faster than that of vinyl alcohol, as observed.

Water-Catalyzed or Spontaneous Reaction. Two mechanisms for the water-catalyzed or spontaneous ketonization of vinyl alcohol were considered,[3] a stepwise mechanism (eq 6) similar to that proposed for the base-

$$CH_2{=}CHOH + H_2O \rightleftarrows CH_2{=}CHO^- + H_3O^+ \rightarrow CH_3CHO + H_2O \qquad (6)$$

catalyzed ketonization and a concerted mechanism. The limited results obtained in this investigation suggest that the concerted mechanism probably explains the experimental observations better than the stepwise mechanism. On the basis of the stepwise mechanism it would be expected that on changing the structure of the enol k_{H_2O} should change in a similar way to k_{HO^-}, but this is not so. Thus k_{HO^-} for the ketonization of 1-hydroxypropadiene is 74 times greater than that for vinyl alcohol, but k_{H_2O} is 1.8 times smaller. It therefore seems that the concerted mechanism explaains these results best.

Experimental Section

Boiling points are uncorrected. NMR spectra were measured on Perkin-Elmer R-32 (90 MHz ^1H) and Bruker WP80 SY (80 MHz, ^1H; 20 MHz, ^{13}C) spectrometers. Chemical shifts are reported in parts per million downfield from Me_4Si. All the precursors for the enols are unstable liquids and satisfactory analyses could not be obtained.

Chloroacetaldehyde 1-Chloroprop-2-yl Methyl Acetal. Equimolar amounts of chloroacetaldehyde dimethyl acetal and 1-chloro-2-propanol were heated with a small amount of methanesulfonic acid in a Dean and Stark apparatus until 1 equiv of methanol had distilled. The product (1:1 mixture of diastereoisomers) was purified by distillation: bp 50–55 °C (0.03 mmHg); ^1H NMR ($CDCl_3$) δ 4.86 and 4.82 (2 t, 1 H, $CCHO_2$), 4.36–3.80 (m, 1 H, $OCHC_2$), 3.70 and 3.66 (2 d, 2 H, J = 6 Hz, $ClCH_2$), 3.63 and 3.59 (2 d, 2 H, J = 6 Hz, $ClCH_2$), 3.55 and 3.52 (2 s, 3 H, CH_3O), 1.47 and 1.43 (2 d, J = 6 Hz, 3 H).

Ketene Methyl Prop-1-en-2-yl Acetal (2). The mixture of diastereoisomers of chloroacetaldehyde 1-chloroprop-2-yl methyl acetal was dehydrochlorinated by heating with NaH/*t*-BuOH (40% excess) in diethylene glycol dimethyl ether (5 mL/1 g of *t*-BuOH) at 110 °C for 110 h (cf. ref 13). The product was purified by distillation: bp 50–55 °C (20 mmHg); ^1H NMR ($CDCl_3$) δ 4.36 (d, 1 H, J = 1.8 Hz, $OC({=}CH_2)CH_3$), 4.25 (d, 1 H, J = 3.3 Hz, $(RO)_2C{=}CH_2$), 3.60 (s, 3 H, OCH_3), 3.52 (d, 1 H, J = 3.3 Hz, $(RO)_2C{=}CH_2$), 1.86 (s, 3 H, $OC({=}CH_2)CH_3$).

1,3-Dichloropropan-2-yl Dimethyl Orthoacetate (21). An equimolar amount of 1,3-dichloropropan-2-ol (Aldrich) was added to a solution of ketene dimethyl acetal in *tert*-butyl alcohol.[4] The reaction mixture was set aside for 2 h, the *tert*-butyl alcohol distilled off at atmospheric pressure, and the product purified by distillation: bp 54 °C (0.05 mmHg); ^1H NMR ($CDCl_3$) δ 4.24 (quin, 1 H, J = 6.0 Hz, $CH(CH_2Cl)_2$), 3.74 (d, 4 H, J = 6.0 Hz, $CH(CH_2Cl)_2$), 3.30 (s, 6 H, OCH_3), 1.49 (s, 3 H, CH_3).

3-Chloroprop-1-en-2-yl Dimethyl Orthoacetate (4). This was prepared by dehydrochlorination of **21** with NaH/*t*-BuOH in 1,2-dimethoxyethane (cf. ref 13) and purified by distillation: bp 36 °C (0.25 mmHg); ^1H NMR ($CDCl_3$) δ 4.75 (d, 1 H, J = 1.5 Hz, $C{=}CH_2$), 4.56 (d, 1 H, J = 1.5 Hz, $C{=}CH_2$), 3.93 (s, 2 H, CH_2Cl), 3.33 (3, 6 H, OCH_3), 1.60 (s, 3 H, CH_3).

2-(1,3-Dichloro-2-propoxy)-2-methyl-1,3-dioxolane (22). 1,3-Dichloro-propan-2-ol (Aldrich) was added carefully to 2-methylene-1,3-dioxolane.[14] An exothermic reaction took place, and the product was purified by distillation: bp 70 °C (0.25 mmHg); ^1H NMR ($CDCl_3$) δ 4.06 (m, 5 H, $CH(CH_2Cl)_2$ and OCH_2CH_2O), 3.68 (d, 4 H, J = 6.0 Hz, $CH(CH_2Cl)_2$), 1.57 (s, 3 H, CH_3).

2-[(3-Chloroprop-1-en-2-yl)oxy]-2-methyl-1,3-dioxolane (5). This was prepared by dehydrochlorination of **22** with NaH/*t*-BuOH in 1,3-dimethoxyethane (cf. ref 13) and purified by distillation: bp 60 °C (0.25 mmHg); ^1H NMR ($CDCl_3$) δ 4.77 (1 H, d, J = 1.5 Hz, $C{=}CH_2$), 4.56 (1 H, d, J = 15 Hz, $C{=}CH_2$), 4.08 (4 H, m, OCH_2CH_2O), 3.91 (2 H, s, CH_2Cl), 1.72 (3 H, s, CH_3).

Acetone Methyl 2,2-Dichlorovinyl Acetal. 2,2,2-Trichloroethanol (35.9 g, 0.24 mol) was added slowly to 2-methoxypropene (20 g, 0.28 mol) in methylene chloride at 5–10 °C. The solvent was removed on a rotary evaporator, and the crude acetone methyl trichloroethyl acetal was dehydrochlorinated with NaH/*t*-BuOH in 1,2-dimethoxyethane: ^1H NMR ($CDCl_3$) δ 6.76 (s, 1 H, $OCH{=}CCl_2$), 3.22 (s, 3 H, OCH_3), 1.42 (s, 6 H, CH_3).

Dimethyl 2,2,2-Trichloroethyl Orthoformate (23). This was prepared by acid-catalyzed exchange of trimethyl orthoformate and 2,2,2-trichloroethanol at 90–100 °C and purified by distillation: bp 90–93 °C (20 mmHg); ^1H NMR ($CDCl_3$) δ 5.28 (s, 1 H, CH), 4.16 (s, 2 H, OCH_2CCl_3), 3.40 (s, 6 H, OCH_3).

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Dimethyl 2,2-Dichlorovinyl Orthoformate. This was prepared by dehydrochlorination of **23** (19 g) with NaH (3 g)/*t*-BuOH (3 mL) in 1,2-dimethoxyethane (15 mL).[12] The product, which is very unstable, was purified by distillation: bp 38–41 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.82 (s, 1 H, $OCH{=}CCl_2$), 5.31 (s, 1 H, CH).

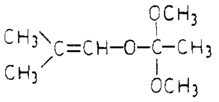
Dimethyl Prop-2-yn-1-yl Orthoacetate. Propargyl alcohol was added dropwise to an ice-cooled solution of ketene dimethyl acetal in methylene chloride, which contained a few drops of methanesulfonic acid. After reaction the acid was neutralized with sodium methoxide, and the product was purified by distillation: bp 70–72 °C (20 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.19 (d, 2 H, $CH_2C{\equiv}CH$), 3.30 (s, 6 H, OCH_3), 2.51 (t, 1 H, $CH_2C{\equiv}C\mathit{H}$), 1.46 (s, 3 H, $CH_2C{\equiv}C\mathit{H}$). The ketene dimethyl acetal was prepared by dehydrochlorination of chloroacetaldehyde dimethyl acetal with NaH/*t*-BuOH in diethyleneglycol diethyl ether. By the use of excess NaH all the *t*-BuOH is converted to its sodium salt so that the ketene dimethyl acetal can be distilled directly from the reaction mixture uncontaminated.

Allenyl Dimethyl Orthoacetate (10). Dimethyl prop-2-yn-1-yl orthoacetate (10 g) was heated with potassium *tert*-butoxide (1 g) at 70–75 °C for 20 min. The product was purified by distillation and stored in sealed ampules at −20 °C: bp 22–25 °C (0.2 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.65 (t, 1 H $OC\mathit{H}{=}C{=}CH_2$), 5.32 (d, 2 H, $OCH{=}C{=}C\mathit{H}_2$), 3.32 (s, 6 H, OCH_3), 1.53 (s, 3 H, CH_3).

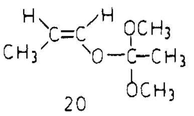
2-Methyl-2-(propargyloxy)dioxolane (24). Propargyl alcohol (6.52 g, 0.12 mol) was added dropwise to 2-methylene-1,3-dioxolane[14] (10 g, 0.11 mol) at 5 °C. The product was purified by distillation: bp 48–50 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.20 (d, 2 H, J = 2 Hz, $C\mathit{H}_2C{\equiv}CH$), 4.11 (m, 4 H, OCH_2CH_2O), 2.37 (t, 1 H, J = 2 Hz, $CH_2CC\mathit{H}$), 1.53 (s, 3 H, CH_3).

2-(Allenyloxy)-2-methyl-1,3-dioxolane (11). This was prepared by heating **24** (10 g) with NaH (1.25 g)/*t*-BuOH (1.5 g) in 1,2-dimethoxyethane (10 mL) at 75–80 °C for 1.30 h. The cooled reaction mixture was extracted with cooled diethyl ether, and the solvents were evaporated under vacuum. The product was used without further purification as attempts at distillation led to decomposition: ^{1}H NMR ($CDCl_3$) δ 6.42 t, 1 H, $OC\mathit{H}{=}C{=}CH_2$), 5.19 (d, 2 H, $OCH{=}C{=}C\mathit{H}_2$), 3.97 (m, 4 H, OCH_2CH_2O), 1.53 (s, 3 H, OCH_3).

Dimethyl 2-Methylprop-1-en-1-yl Orthoacetate (19) and Dimethyl 2-Prop-1-en-1-yl Orthoacetate (20). These were prepared as described previously.[4]



19



20

3-Chloroprop-1-en-2-yl Methyl Ether. 1,3-Dichloropropan-2-ol was methylated with diazomethane in the presence of $AlCl_3$. The 1,3-dichloropropanyl methyl ether was purified by distillation [bp 50 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.65 (5 H, br signal), 3.47 (3 H, s)] and dehydrochlorinated with NaH/*t*-BuOH to yield and enol ether: bp 30 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.29 (d, 1 H, J = 2.7 Hz, $C{=}CH_2$), 4.13 (d, 1 H, J = 2.7 Hz, $C{=}CH_2$), 3.95 (s, 2 H, CH_2Cl), 3.58 (s, 3 H, OCH_3).

Methyl 2-Methylprop-1-enyl Ether. 2-Methylprop-2-en-1-ol (Aldrich) was methylated with dimethyl sulfate and aqueous sodium hydroxide,[15] and the product was isomerized with potassium *tert*-butoxide in dimethyl sulfoxide:[16] bp 69 °C; ^{1}H NMR ($CDCl_3$) δ 5.73 (m, $OC\mathit{H}{=}C(CH_3)_2$), 3.49 (s, 3 H, OCH_3), 1.54 and 1.60 (d, with fine splitting, 3 H each, J_1 = 1.5 Hz, J_2 = 0.5 Hz, $OCH{=}C(C\mathit{H}_3)_2$).

Table VIII. Conditions Used for Kinetic Measurements

enol	precursor	pH range	λ/nm
3-Chloroprop-1-en-1-ol	4	1.33–4.03	210
	enol	4.56–6.07	210
2-methylprop-1-en-1-ol	18	0.97–4.52	210
	enol	5.34–9.62	210
(*Z*)-prop-1-en-1-ol	19	1.00–3.82	210
	enol	4.11–8.87	210
1-hydroxypropadiene	10, 11	1.79–4.06	220[a]
1-(deuteriooxy)propadiene	enol	4.63–5.15[b]	220[a]

[a] Formation of acrylaldehyde followed. [b] pD

Kinetic Measurements. These were carried out as described previously.[3] For the more acidic solutions 20 μL of a stock solution of the precursor (10^{-2}–10^{-3}M) in dioxane was added to 2 mL of the reaction solution in the thermostated cell carrage of a Cary 16 or a Pye-Unicam SP 8-200 spectrophotometer, which operated online with respectively an Apple II and a Commodore Pet Microcomputer. Eighty absorbance values were collected at suitable time intervals, and first-order rate constants were calculated by a generalized least-squares method.[17,18] At higher pHs the rate of ketonization of the enols was comparable to or faster than their rates of formation from the precursors, and so stock solutions of the preformed enols similar to those used on the NMR spectroscopic investigations were used. Generally the disappearance of the enol was followed at 210 nm, but with hydroxypropadiene formation of the product of ketonization, acrylaldehyde was followed at 220 nm. The conditions are described in more detail in Table VIII. The reactions in water–Me_2SO mixtures were followed at wavelengths that corresponded to formation of the keto forms: chloroacetone (269.5 nm); isobutyraldehyde (293 nm).

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Registry No. **1**, 97190-81-3; **2**, 69814-54-6; **3**, 97190-82-4; **4**, 97190-83-5; **5**, 97190-84-6; **6**, 97190-85-7; **7**, 97190-86-8; **8**, 97190-87-9; **9**, 81788-96-7; **10**, 97190-88-0; **11**, 97190-89-1; **21**, 97210-69-0; **22**, 97190-92-6; **23**, 26825-96-7; **24**, 97190-94-8; dimethyl 2-propynyl orthoacetate, 97190-93-7; 3-chloroprop-1-en-2-yl methyl ether, 32730-64-6; 1,3-dicloropropan-2-yl methyl ether, 2419-76-3; 2-methyl-1-propen-3-ol, 513-42-8; 3-chloro-2-hydroxypropene, 97190-95-9; chloroacetaldehyde 1-chloroprop-2-yl methyl acetal (isomer 1), 97190-90-4; chloroacetaldehyde 1-chloroprop-2-yl methyl acetal (isomer 2), 97190-91-5; chloracetaldehyde dimethyl acetal, 97-97-2; 1-chloro-2-propanol, 127-00-4; 1,3-dichloro-2-propanol, 96-23-1; ketene dimethyl acetal, 922-69-0; 2-methylene-1,3-dioxolane, 4362-23-6; 2,2,2-trichloroethanol, 115-20-8; 2-methoxy-1-propene, 116-11-0; trimethyl orthoformate, 149-73-5; propargyl alcohol, 107-19-7; methyl 2-methyl-1-propenyl ether, 17574-84-4.

Supplementary Material Available: Tablers of first-order rate constants for the ketonization of 2-methylprop-1-en-1-ol, (*Z*)-prop-1-en-1-ol, 3-chloro-2-hydroxypropene, and hydroxypropadiene in water and D_2O (13 pages). Ordering information is given on any current masthead page.

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