Simple Enols. 1.[1] The Generation of Vinyl Alcohol in Solution and Its Detection and Characterization by NMR Spectroscopy[2]

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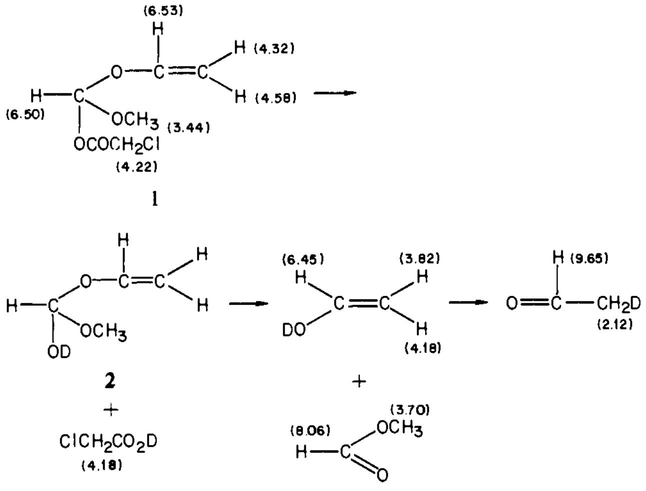
Abstract: Vinyl alcohol has been generated by hydrolysis of methoxy(vinyloxy)methyl chloroacetate and acetate (**1** and **3**), bis(vinyloxy)methyl dichloroacetate and trichloroacetate (**7** and **6**), dimethyl vinyl orthoformate (**4**), dimethyl vinyl orthoacetate (**5**), and ketene methyl vinyl acetal (**8**) in aqueous [$^2H_3$]acetonitrile or aqueous [$^2H_7$]dimethylformamide. It was characterized by ^{1}H and ^{13}C NMR spectroscopy and by its conversion into acetaldehyde. On replacement of OH by OD the ^{13}C NMR spectrum shows isotope shifts of −0.12 and −0.09 ppm for the α- and β-carbons under conditions where no such shifts were detectable for the corresponding carbons of ethyl vinyl ether. Vinyl alcohol with an HO group was generated under conditions of slow hydroxyl–proton exchange with **8** as the precursor in CD_3COCD_3 (99 v %)/H_2O (1 v %) at −10 °C and the following coupling constants were evaluated: $^3J_{trans} = +14.0$, $^3J_{cis} = +6.3$, $^2J_{gem} = -0.8$, $^3J(HOC_\alpha H) = +9.8$, $^4J(HOC_\beta H_{anti}) = +0.4$, $|^4J(HOC_\beta H_{syn})| < 0.2$ Hz. Under the conditions used vinyl alcohol was converted into acetaldehyde ca. 100 times faster than ethyl vinyl ether but could nevertheless be kept in solution for several hours below ca. −10 ° C. The postulated intermediate, methyl vinyl hemiorthoformate could not be detected in the hydrolysis of **1**, **3**, and **4** nor could methyl vinyl hemiorthoacetate be detected in the hydrolysis of **5** and **8**. However divinyl hemiorthoformate was easily detected in the hydrolysis of **6** and **7**. It was concluded that this resulted from the weaker "push" of the vinyloxy group which remained attached to the pro–acyl carbon atom compared to a methoxyl group.

Introduction

Vinyl alcohol, the simplest enol and a thermodynamically very unstable species,[3-5] has been detected on several occasions. Thus CIDNP[6,7,8] and NMR[9] spectroscopy were used to detect it (usually admixed with acetaldehyde and other species) in various photochemical reactions, microwave spectroscopy[10] was used in the gas–phase dehydration of ethylene glycol, and NMR and IR spectroscopy[11] was used in the flash thermolysis of its [2 + 4] cyclo-addition adduct with anthracene. Estimates of the rate constants for the ketonization of other enols have been reported. Thus, Lienhard and Wang[12] estimated that the rate constant for the H_3O^+-catalyzed ketonization of 1-hydroxycyclohexene in H_2O is 56 $M^{-1}\ s^{-1}$ at 25 °C, and Toullec and Dubois[13] estimated that for isopropenyl alcohol to be 1700 $M^{-1}\ s^{-1}$. Both sets of authors emphasized that the rate constants for the acid-catalyzed ketonization of enols should be similar to those for the hydrolysis of the corresponding enol ethers. On this basis the rate constant for the H_3O^+-catalyzed ketonization of vinyl alcohol should be similar to that for the hydrolysis of methyl vinyl ether,[5] i.e., 0.76 $M^{-1}\ s^{-1}$ at 25 °C.[14] Therefore it was thought that vinyl alcohol should be detectable in any reaction in which it is formed at a rate substantially greater than its rate of ketonization estimated on the basis of this rate constant and that simpler reactions than those reported above could be used for its generation. This paper reports an investigation by NMR spectroscopy of several such reactions.

Scheme I[a]



[a] The figures in parentheses are the δ values.

Results and Discussion

The first precursor chosen was methoxy(vinyloxy)methyl chloroacetate (**1**). This is analogous in structure to the precursors we have used to generate hemiorthoesters, the tetrahedral intermediates in *OO*-acyl-transfer reactions.[15] By analogy to our earlier work this should be hydrolyzed to yield methyl vinyl hemiorthoformate (**2**) which should break down to vinyl alcohol and methyl formate (or methanol and vinyl formate). The ^{1}H NMR spectrum of (**1**) (ca. 0.15 M) in [$^2H_3$]acetonitrile at −20 °C (Figure 1a) shows an approximately first-order ABC system for the vinyl group with δ_A 6.53, δ_B 4.58, and δ_C 4.32 and J_{AB} = 14.7 Hz, J_{AC} = 4.9 Hz, and J_{BC} = 1.7 Hz. The signals for the CH, chloroacetate, and methoxy groups are as shown in Scheme I. On

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(1) For an excellent review on "Simple Enols" see Hart, H. *Chem. Rev.* **1979**, *79*, 515–528.

(2) A preliminary report of some of this work has appeared: Capon, B.; Rycroft, D. S.; Watson, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 724–725.

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(12) Lienhard, G. E.; Wang, T.-C. *J. Am. Chem. Soc.* **1969**, *91*, 1146–1153.

(13) Toullec, J.; Dubois, J. E. *Tetrahedron* **1973**, *29*, 2851–2858, 2859–2866. *J. Am. Chem. Soc.* **1974**, *96*, 3524–2532.

(14) Kresge, A. J.; Sagatys, D. S.; Chen, H. L. *J. Am. Chem. Soc.* **1977**, *99*, 7228–7233.

(15) Capon, B.; Gall, J. H.; Grieve, D. McL. A. *J. Chem. Soc., Chem. Commun.* 1976, 1034–1035. Capon, B.; Grieve, D. McL. A. *J. Chem. Soc., Perkin Trans. 2* **1980**, 300–305.

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Table I. The ^{1}H NMR Spectrum of Vinyl Alcohol (OD) Generated from Different Precursors

precursor	solvent	temp, °C	δ (*J*, Hz)[a]
methoxy(vinyloxy)methyl chloroacetate (1)	CD_3CN/D_2O (9:1, v/v)	−20	6.45, 4.18, 3.82 (14.2, 6.4, 1)
methoxy(vinyloxy)methyl acetate (3)	CD_3CN/D_2O (1:1, v/v)	−20	6.43, 4.22, 3.94 (13.8, 6.3, 1.1)
dimethyl vinyl orthoformate (4)	CD_3CN/D_2O (9:1, v/v), 10^{-3} M DCl	0	6.45, 4.17, 3.84 (14.0, 6.4, 0.9)
dimethyl vinyl orthoacetate (5)	CD_3CN/D_2O (19:1, v/v), 5×10^{-4} M DCl	−10	6.44, 4.17, 3.83 (14.1, 6.6, 1.0)
bis(vinyloxy)methyl trichloroacetate (6)	DMF-d_7/D_2O (19:1, v/v)	−20	6.55, 4.16, 3.83 (14, 6, <1)
bis(vinyloxy)methyl dichloroacetate (7)	DMF-d_7/D_2O (92:8, v/v)	−20	6.52, 4.16, 3.80 (14.6, 6.7, 0.55)
ketene methyl vinyl acetal (8)[b]	CD_3CN/D_2O (9:1, v/v), 10^{-3} M DCl	−10	6.44, 4.17, 3.84 (14.0, 6.7, 1.1)

[a] Obtained by first-order analysis. [b] Small amounts of vinyl acetate and methanol are also formed with this precursor.

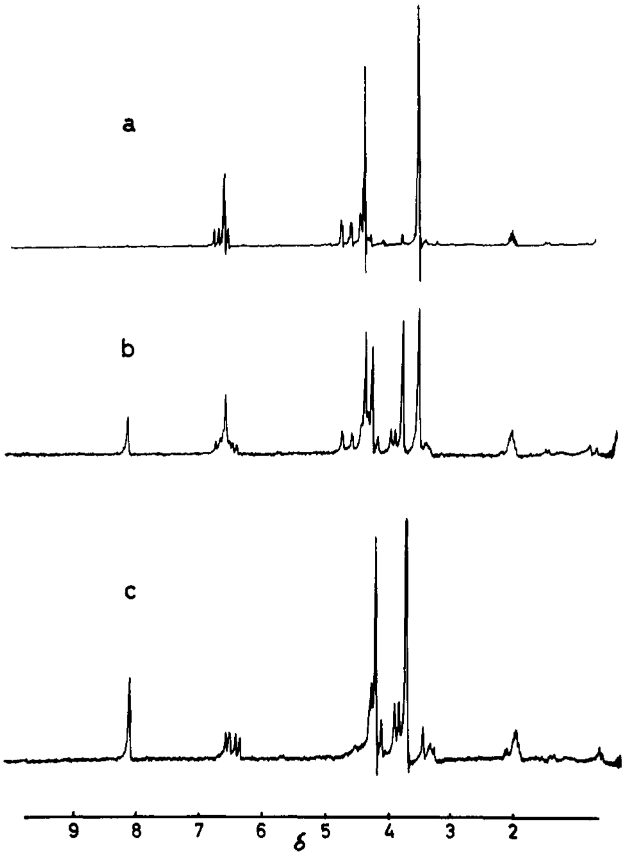


Figure 1. (a) ^{1}H NMR spectrum of methoxy(vinyloxy)methyl chloroacetate (**1**) in CD_3CN at −20 °C. (b) The spectrum immediately after addition of 10% by volume of D_2O at −20 °C. (c) The spectrum 44 min after b. The multiplet at δ 1.98 is the signal of CHD_2CN present in the solvent.

addition of 10% by volume of D_2O a new vinyl group is formed with concurrent disappearance of the orthoester CH signal and concurrent formation of the spectra of methyl formate (δ 8.06, 3.70) and chloroacetic acid (δ 4.18) (Figure 1b,c). The new vinyl group has δ_A 6.45, δ_B 4.18, and δ_C 3.82 and J_{AB} = 14.2 Hz, J_{AC} = 6.4 Hz, and J_{BC} = 1 Hz, and this spectrum is stable at −20 °C for several hours, but at +20 °C it has a half-life of ca. 10 min, changing into the spectrum of CH_2DCHO (δ 9.65, 2.12, broadened multiplets) (Figure 2a,b). On addition of excess sodium deuteroxide at −20 °C this change takes place immediately. When 10% H_2O is used instead of 10% D_2O, the conversion of the initial product into acetaldehyde (now CH_3CHO) is faster and the ^{1}H NMR spectrum of the latter has a sharp quartet (δ 9.65) and a doublet (δ 2.12). Complementary changes in the ^{13}C NMR spectrum were also observed. The vinyl group of the starting material (0.3 M) showed resonances at δ 146.2 and 94.4 in CD_3CN, and on addition of 10% D_2O (v/v) at −20 °C two new vinyl resonances were formed at δ 149.0 and 88.0. These persisted at −20 °C but at +20 °C disappeared fairly rapidly with concurrent formation of [^{2}H$_1$]acetaldehyde [δ 202.8, 30.85 (t, J_{CD} = 19.3 Hz)] plus some acetaldehyde (δ 31.1), which presumably arises from the presence of HDO in the D_2O and a favorable isotope effect.

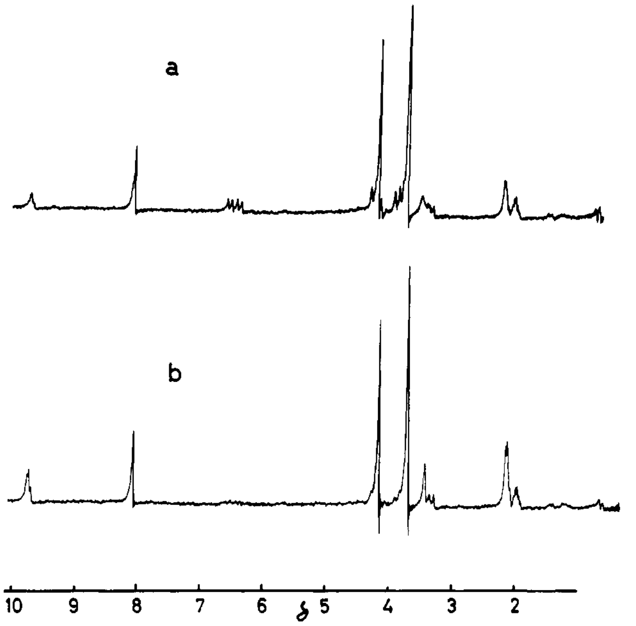
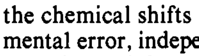


Figure 2. (a) ^{1}H NMR spectrum of vinyl alcohol (+chloroacetic acid + methyl acetate) generated as in Figure 1 after 8 min at +20 °C showing partial conversion into [^{2}H$_1$]acetaldehyde. (b) The spectrum of the same solution after 39 min at +20 °C showing complete conversion. The multiplet at δ 1.98 is the signal of CHD_2CN present in the solvent.

The same vinyl species was also generated from the six other precursors **3**–**8**, listed in Table I. When the solvent was the same,



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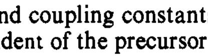

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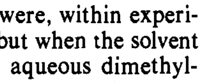

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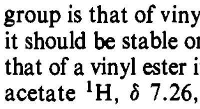

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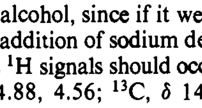

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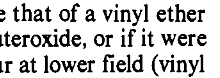

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the chemical shifts and coupling constants were, within experimental error, independent of the precursor, but when the solvent was changed from aqueous acetonitrile to aqueous dimethylformamide, there were small changes in these quantities.

On the basis of these results we conclude that the new vinyl group is that of vinyl alcohol, since if it were that of a vinyl ether it should be stable on addition of sodium deuteroxide, or if it were that of a vinyl ester its ^{1}H signals should occur at lower field (vinyl acetate ^{1}H, δ 7.26, 4.88, 4.56; ^{13}C, δ 141.8, 96.8).[16,17] This

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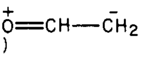
[16] Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Company, Inc.: Milwaukee, Wisconsin, 1976; Vol. III Spectrum 35c.

[17] Johnson, L. F.; Janowski, W. C. "Carbon-13 NMR Spectra"; Wiley-Interscience: New York, 1972; Spectrum 61.

Figure 3. The ^1H NMR spectrum of vinyl alcohol under conditions where exchange of the hydroxyl proton is slow; it was generated from **8** in CD_3COCD_3 (99 v %)/H_2O (1 v %) which contained 10^{-4} M HCl at −10 °C.

conclusion was confirmed in two ways: (i) by a deuterium-induced differential isotope shift (DIS)[18] on the ^{13}C NMR spectrum; (ii) by generation of OH vinyl alcohol under conditions of slow hydroxyl exchange, so that the H–O–C_α–H coupling could be observed.

It has been shown[18] by Pfeffer et al. using a dual coaxial tube arrangement that the ^{13}C NMR signals of carbons which bear hydroxyl groups in carbohydrates show an upfield shift of ca. 0.14 ppm when the OH is replaced by OD (β-shift) by changing the solvent from H_2O to D_2O; the signals of carbons attached to *O*-alkyl groups show a shift of less than 0.07 ppm. It was therefore thought that the ^{13}C NMR spectrum of the new vinyl group reported above should show a similar shift if it were that of vinyl alcohol but a smaller shift if it were that of a vinyl ether. A control experiment was carried out with ethyl vinyl ether, and no detectable shifts were observed (<0.02 ppm). However the α- and β-carbon atoms of the new vinyl group both showed shifts, 0.12 and 0.09 ppm, respectively.[19] The observation of shift of the signal of the α-carbon (β-shift) confirms that the new vinyl group is that of vinyl alcohol. The occurrence of a shift of the signal of the β-carbon (γ-shift) is also consistent with this structure, and the larger than usual γ-shift may be rationalized in terms of a variation in the contribution of resonance structure **9** when H is replaced



$$\underset{(D)}{H}\overset{+}{O}{=}CH{-}\overset{-}{C}H_2$$

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by D as a result of the difference in strengths of OH and OD bonds to the solvent.

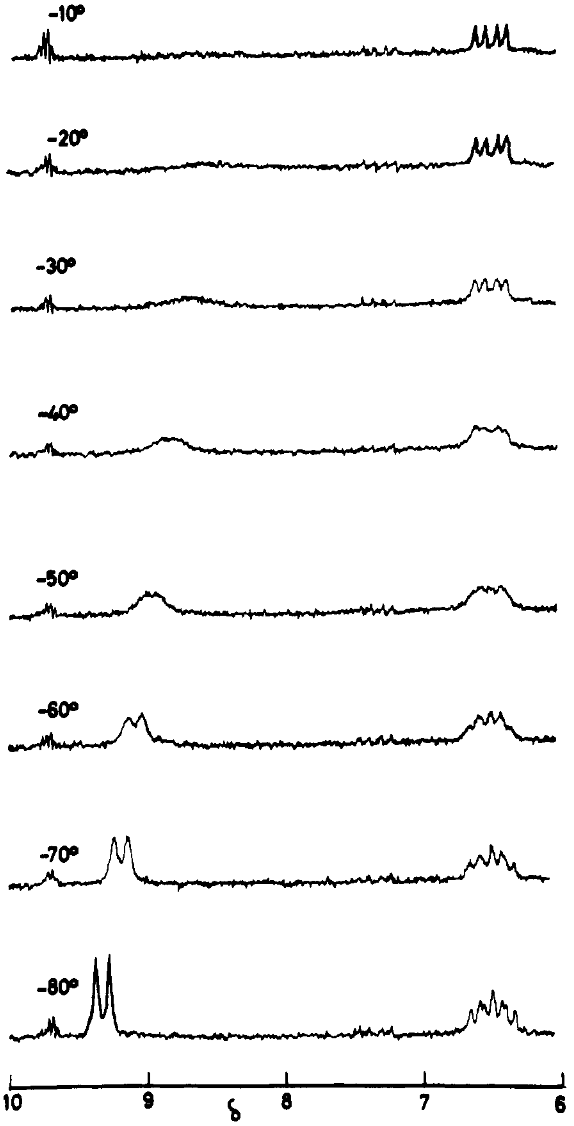
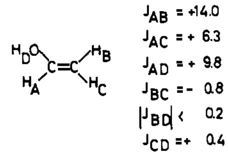


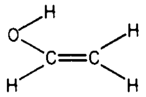
Figure 4. Temperature variation of HO and $C_\alpha H$ signals of the ^1H NMR spectrum of vinyl alcohol in CD_3COCD_3 (94.5 v %)/H_2O (5.5 v %). Note the presence of small amounts of acetaldehyde (δ 9.71) and vinyl acetate (δ 7.27).



$J_{AB} = +14.0$
$J_{AC} = +\ 6.3$
$J_{AD} = +\ 9.8$
$J_{BC} = -\ 0.8$
$|J_{BD}| < 0.2$
$J_{CD} = +\ 0.4$

Figure 5. Coupling constants (Hz) obtained by first-order analysis of the ^1H NMR spectrum of vinyl alcohol in 99% CD_3COCD_3/1% H_2O (v/v) at −10 °C.

Vinyl alcohol with an OH group was generated under conditions of slow exchange from the precursor ketene methyl vinyl acetal (**8**) in [$^2H_6$]acetone (99 v %)/H_2O (1 v %) which contained 10^{-4} M HCl. Under these conditions at −10 °C the spectrum shown in Figure 3 was obtained. Now, instead of one quartet for the single proton attached to the α-carbon, two were obtained (separation 9.8 Hz) and a doublet with a splitting of 9.8 (±0.2) Hz appeared at δ 7.95. On being cooled to −80 °C, this was unchanged within the experimental error. Decoupling experiments showed that the proton corresponding to this doublet was coupled to the α-proton. Irradiation of the OH signal of the solvent caused a decrease in intensity of this doublet to less than 50% of its original value through transfer of spin saturation.[20] Addition of 5% D_2O caused the doublet to disappear and the double quartet to collapse to a single quartet. When a similar preparation was carried out with more water (5.5%), rapid exchange was observed at −10 °C, but when it was cooled to −80 °C, a transformation to slow exchange took place (Figure 4). On the basis of these experiments it was concluded that the doublet was the signal of the OH group of vinyl alcohol, and hence the "new vinyl group" was confirmed as being that of this species. Selective decoupling and spin-tickling experiments yielded the relative signs of the coupling constants indicated in Figure 5.[21] The small positive coupling constant between H_D and H_C is consistent with vinyl alcohol having a planar structure and the coupling occurring predominantly through the σ-system.[22] Two planar conformations (**10** and **11**) are possible.



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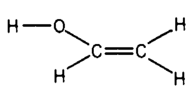

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Saito interpreted the microwave spectrum of vinyl alcohol in the gas phase at 900 °C in terms of the syn conformation (**10**).[10] A similar conformation is shown by some intramolecularly hydrogen-bonded enols, and ^3J(HCOH) is 11–12 Hz.[23] Therefore our

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[18] Pfeffer, P. E.; Valentine, K. M.; Parrish, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 1265–1274.

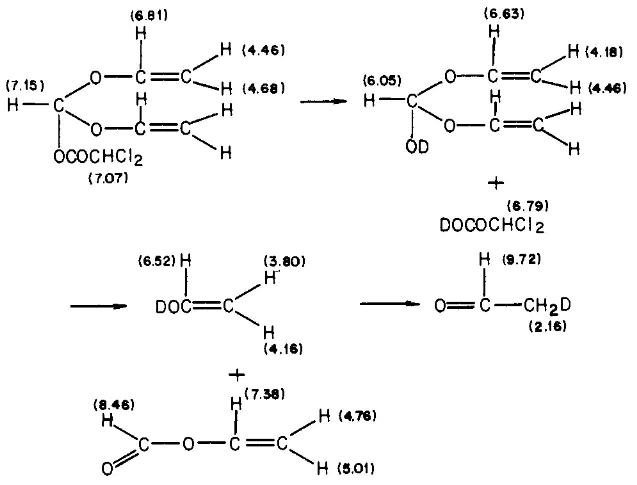
[19] $\delta(^{13}C_{H_2O}) - \delta(^{13}C_{D_2O})$ at −45 °C, 1 M in 95% CD_3CN-5% H_2O (or D_2O) with HCl (or DCl) concentration 0.4 mM.

[20] Feeney, J.; Heinrich, A. *Chem. Commun.* **1966**, 295–296.

[21] Cf. Lauterbur, P. C.; Kurland, R. J. *J. Am. Chem. Soc.* **1962**, *84*, 3405–3406.

[22] Barfield, M.; Spear, R. F.; Sternhell, S. *Chem. Rev.* **1976**, *76*, 593–624.

Scheme II[a]



[a] The figures in parentheses are δ values.

value of 9.8 Hz for vinyl alcohol may mean that the anti conformation (**11**) is present, at least partially, in solution.[24]

When **1** was used as a precursor for vinyl alcohol, the hemiorthoester intermediate **2** was not detected. The hemiorthoester was not detected also in the hydrolyses of **3** to **5** and in the hydration of **8**. Presumably **2** reacts faster than the previously detected[15] dimethyl hemiorthoformate with preferential expulsion of the vinyloxy group which probably has a lower pK_a than that of the methoxyl group. However when the divinyl compounds **6** and **7** were used as precursors, the divinyl hemiorthoformate **12** was easily detected (see Figure 6 and Scheme II). This is presumably more stable than methyl vinyl hemiorthoformate as the vinyloxy group which remains attached to the pro-acyl carbon has a weaker "push" than a methoxyl group.

We have compared the rate of hydrolysis of ethyl vinyl ether with that of ketonization of vinyl alcohol by adding the former to solutions of the latter generated from precursor **1**. In this way it was made certain that the two species were investigated under the same conditions. Although these experiments do not allow us to calculate rate constants for catalysis by individual species, it was clear that under these conditions ethyl vinyl ether is much more stable then vinyl alcohol, as their rate of disappearance differed by a factor of approximately 100. Ironically then, the initial assumption on which this investigation was based appears to be incorrect, but nevertheless vinyl alcohol is sufficiently stable to be generated in solution and for solutions to be kept for long periods below −10 °C.

Experimental Section

Materials. The precursors for vinyl alcohol derived from orthoformic and orthoacetic acids were prepared according to the methods described by Scheeren, van Melick, and Nivard,[25] purified by distillation, and identified by their ^{1}H NMR spectra. In the dehydrochlorination step it was found essential to use an excess of good quality sodium hydride. Methoxy(vinyloxy)methyl chloroacetate (**1**): bp 67 °C (0.3 mm); NMR ($CDCl_3$) δ 6.56 (s, 1), 6.53 (q, 1, J_{trans} = 14 Hz, J_{cis} = 6 Hz), 4.50 (q, 1, J_{trans} = 14 *Hz*, J_{gem} = 2 Hz), 4.20 (q, 1, J_{cis} = 6 Hz, J_{gem} = 2 Hz), 4.12 (s, 2), 3.24 ppm (s, 3). Methoxy(vinyloxy)methyl acetate (**3**): bp 42 °C (15 mm); NMR ($CDCl_3$) δ 6.47 (q, 1, J_{trans} = 14 Hz, J_{cis} = 6.5 Hz), 6.45 (s, 1), 4.61 (q, 1, J_{trans} = 14 Hz, J_{gem} = 2 Hz), 4.30 (q, 1, J_{cis} = 6.5 Hz, J_{gem} = 2 Hz), 3.46 (s, 3), 2.10 ppm (s, 3). Bis(vinyloxy)methyl trichloroacetate (**6**): bp 62–64 °C (1 mm); NMR ($CDCl_3$) δ 6.72 (s, 1), 6.51 (q, 2, J_{trans} = 14 Hz, J_{cis} = 7 Hz), 4.73 (q, 2, J_{trans} = 14 Hz, J_{gem} = 2 Hz), 4.44 (q, 2, J_{cis} = 7 Hz, J_{gem} = 2 Hz). Bis(vinyloxy)methyl dichloroacetate (**7**): bp 48–50 °C (0.2 mm); NMR ($CDCl_3$) δ 6.74 (s, 1), 6.51 (q, 2, J_{trans} = 13.9 Hz, J_{cis} = 6.2 Hz), 5.97 (s, 1), 4.71 (q, 2, J_{trans} = 13.9 Hz, J_{gem} = 2.1 Hz), 4.43 (q, 2, J_{cis} = 6.2 Hz, J_{gem} = 2.1 Hz). Dimethyl vinyl orthoformate (**4**): bp 110–114 °C; NMR ($CDCl_3$) δ 6.44 (q, 1, J_{trans} = 14 Hz, J_{cis} = 7 Hz), 5.25 (s, 1), 4.54 (q, 1, J_{trans} = 14 Hz J_{gem} = 2 Hz), 4.20 (q, 1, J_{cis} = 7 Hz, J_{gem} = 2 hz), 3.34 (s, 6). Dimethyl vinyl orthoacetate (**5**): bp 24–26 °C (10 mm); NMR ($CDCl_3$) δ 6.48 (q, 1, J_{trans} = 13.7 Hz, J_{cis} = 6.3 Hz), 4.55 (q, 1, J_{trans} = 13.7 Hz, J_{gem} = 1.0 Hz), 4.17 (q, 1, J_{cis} = 6.3 Hz, J_{gem} = 1.0 Hz), 3.30 (s, 6), 1.48 (s,3).

Ketene methyl vinyl acetal (**8**) was prepared from chloroacetaldehyde 2-chloroethyl methyl acetal by a similar method, using diethylene glycol diethyl ether instead of 1,2-dimethoxyethane as solvent: bp 78–80 °C; NMR ($CDCl_3$) δ 6.49 (q, 1, J_{trans} = 13.5 Hz, J_{cis} = 5.7 Hz), 4.72 (q, 1,

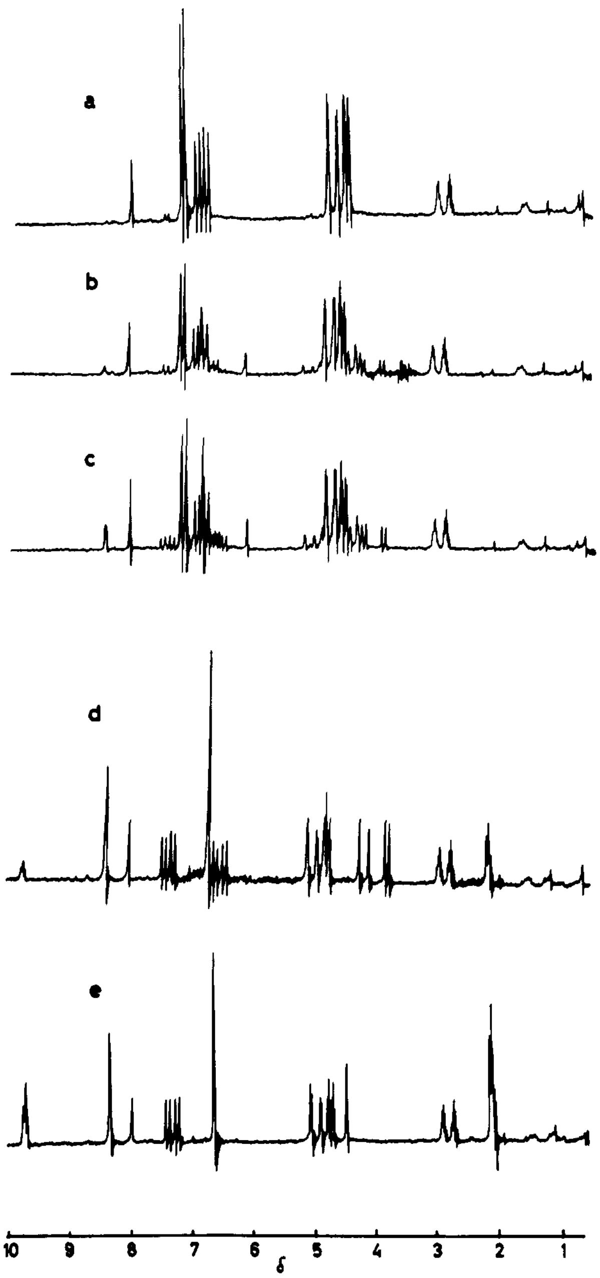


Figure 6. (a) ^{1}H NMR spectrum of bis(vinyloxy)methyl dichloroacetate (**7**) in DMF-d_7 at −35 °C. The signals at δ 2.75, 2.96, and 8.05 are of the solvent. (b) The spectrum after the addition of 8% (v/v) D_2O at −30 °C. The signal of the proton attached to the pro-acyl carbon of divinyl hemiorthoformate (**12**) is at δ 6.05. (c) The spectrum after 5 min at −20 °C. The spectra of four vinylic species are discernible in this spectrum: **7**, **12**, vinyl alcohol, and vinyl formate. (d) The spectrum after 60 min, at +5 °C. **7** and **12** have now disappeared, but vinyl alcohol is present at a concentration of about 40% of the starting concentration of **7**. There is a substantial amount of [$^2H_1$]acetaldehyde also present. (e) The spectrum after 90 min, at +25 °C. Only the final products are present: vinyl formate, dichloroacetic acid, and [$^2H_1$]acetaldehyde.

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J_{trans} = 13.5 Hz, J_{gem} = 1.7 Hz) , 4.35 (q, 1, J_{cis} = 5.7 Hz, J_{gem} = 1.7 Hz), 3.62 (s, 3), 3.37 (d, 1, J_{gem} = 4 Hz), 3.27 (d, 1, J_{gem} = 4 Hz).

Instrumentation. ^{1}H NMR spectra were recorded at 90 MHz in the continuous-wave mode on a Perkin-Elmer R32 spectrometer. Natural abundance ^{13}C NMR spectra were recorded with proton noise decoupling at 25.2 MHz in the pulsed Fourier transform mode on a Varian XL-100 spectrometer. Chemical shifts are reported as δ values relative to internal Me_4Si. Deuterium isotope shifts in the ^{13}C spectra were measured, following the method of Pfeffer et al.,[18] using a 5-mm NMR tube supported coaxially inside a 10-mm NMR tube. With this arrangement the volume of the outer annulus was ca. 3 times the volume of the same depth of the inner tube, but the resulting disparity in the intensity of the signals from the inner and outer solutions was not found to be a problem (results obtained with methyl α-D-glucopyranoside were essentially identical with those reported previously[18]). The two solutions had the same composition except that D_2O/DCl was added to the outer one and H_2O/HCl to the inner. The deuterium isotope effects were measured from spectra where the digital resolution was 0.6 Hz/data point and the line widths ca. 1.5 Hz.

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Tetrahedral Intermediates. 2.[1] The Detection of Hemiorthoesters in the Hydration of Ketene Acetals and the Mechanism of Their Breakdown

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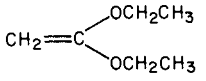
Abstract: The hemiorthoesters 2-deuterioxy-2-[$^2H_1$]methyl-4,4,5,5-tetramethyl-1,3-dioxolane (**7b**) and 2-deuterioxy-2-[$^2H_1$]methyl-1,3-dioxolane (**11**) have been detected by ^{1}H and ^{13}C NMR spectroscopy on hydration of the ketene acetals 2-methylene-4,4,5,5-tetramethyl-1,3-dioxolane (**5**) and 2-methylene-1,3-dioxolane (**9**) in mixtures of CD_3CN or CD_3COCD_3 with D_2O. **7b** was stable for several hours at −30 °C in CD_3COCD_3(90%)–D_2O (10%) (v/v) which was 1.4×10^{-2} M in CD_3CO_2D but **11** decomposed with $t_{1/2}$ = ca. 45 min at −40 °C in CD_3COCD_3 (95%)–D_2O (5%) (v/v) which was 6.8×10^{-3} M in CD_3CO_2D. The kinetics of the hydration of **5** and the decomposition of 2-hydroxy-2,4,4,5,5-pentamethyl-1,3-dioxolane (**7a**) to pinacol monoacetate (**8a**) were followed by UV spectroscopy at 205 nm and 25 °C. Above pH 6.6 only the hydration step could be detected, but below pH 6.0 this was very fast and only formation of pinacol monoacetate from **7** was observed. At intermediate pHs both steps were discernible. The breakdown of **7a** followed the equation $k_0 = 3.01 \times 10^{-2} + 77.8a_{H^+} + 1.6 \times 10^7 a_{HO^-}$ s^{-1} at 25 °C. The water reaction was considered to involve a rate-determining ionization followed by breakdown of the monoanion catalyzed by the hydronium ion within the initially formed encounter complex. The hydroxide ion catalyzed reaction was thought to involve an uncatalyzed rate-limiting breakdown of the monoanion and the hydronium-ion catalyzed reaction an acid-catalyzed breakdown of the un-ionized form, similar to the hydrolysis of orthoesters.

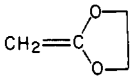
Introduction

The kinetics of the hydration of ketene acetals has been studied by several groups,[2-5] but the initially formed hemiorthoesters had never been detected. Nevertheless when strongly electron-withdrawing groups are absent from the β-carbon atom, the reported rate constants for hydration are sufficiently high to suggest that in favorable cases the intermediates might be detectable. Thus Kankaanpera and Tuominen[2] estimated that the second-order constants (k_{H+}) for the hydronium ion catalyzed hydration of ketene diethyl acetal (**1**) and 2-methylene-1,3-dioxolane (**2**) to be of the order of 10^6–10^7 M^{-1} s^{-1} at 25 °C. In contrast, we have estimated[1] on the basis of Guthrie's calculations,[6] that k_{H+} for the breakdown of methyl dihemiorthoformate (**3**) is only 10^3–10^4 M^{-1} s^{-1} at 25 °C, and McClelland and Kresge and their co-workers have determined k_{H+} for the breakdown of 2-hydroxy-2-phenyl-1,3-dioxolane (**4**) to be 300 M^{-1} s^{-1} at 25 °C.[7] These values suggest that under conditions where the rate depends mainly on k_H^+ it should be possible to detect the initially formed hemiorthoesters in the hydration of suitable ketene acetals.

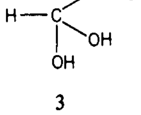


$CH_2{=}C(OCH_2CH_3)_2$

1

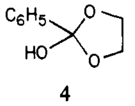


2



$H{-}C(OCH_3)(OH)(OH)$

3



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NMR Results

The first compound that we investigated was 2-methylene-4,4,5,5-tetramethyl-1,3-dioxolane (**5**). This would be expected to yield pinacol monoacetate (**8**) via two intermediates, the dioxolenium ion **6** and the hemiorthoester **7**. The proton NMR spectrum of (**5**) (Figure 1a) in CD_3CN at −30 °C showed two singlets at δ 1.25 (12 protons) and 3.04 (2 protons). When 10%

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