

Generation of Vinyl Alcohol in Solution and its Slow Conversion into Acetaldehyde

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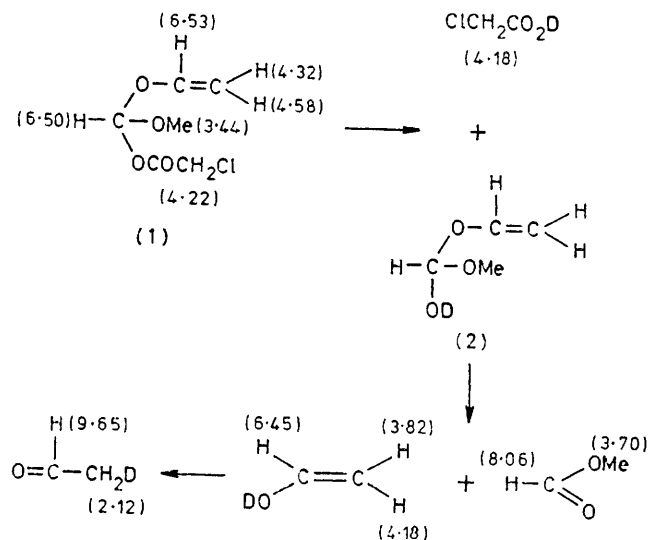
Summary Methoxyvinylloxymethyl chloroacetate and acetate have been used as precursors to generate vinyl alcohol in aqueous acetonitrile, and its formation and conversion into acetaldehyde have been followed by ^1H and ^{13}C n.m.r. spectroscopy.

THE enols of simple monoaldehydes and ketones are thermodynamically unstable species ($K_{\text{enol}} = [\text{enol}]/[\text{keto}] = 2 \times 10^{-3}$ — 5×10^{-9})¹ and, although frequently postulated as reaction intermediates, they have rarely been detected. Examples of their detection include that of vinyl alcohol in the gas phase by microwave spectroscopy on dehydration of ethylene glycol² and of vinyl alcohol³ and other enols⁴ generated photochemically in the liquid phase at low concentration by CIDNP. There is, however, no simple method for the generation of enols at high concentration in solution that would enable their ketonisation to be studied directly. Nevertheless it appeared that the rate constants for the ketonisation of enols under acid conditions

are not especially high. Thus Lienhard and Wang⁵ have estimated that the rate constant for the H_3O^+ -catalysed ketonisation of 1-hydroxycyclohexene in H_2O is $56 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C and Toullec and Dubois⁶ have estimated that for isopropenyl alcohol to be $1700 \text{ l mol}^{-1} \text{ s}^{-1}$. Both sets of authors emphasized that the rate constants for the acid-catalysed ketonisation of enols should be similar to those for the hydrolysis of the corresponding enol ethers. On this basis the rate constant for ketonisation of vinyl alcohol in H_2O should be *ca.* $21 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C .⁷ It therefore seemed that the failure to detect enols, except in the reactions mentioned above, may stem not from an excessively high reactivity, but from the method normally used for their generation, *i.e.*, enolisation of aldehydes and ketones, being very slow.

In order to generate vinyl alcohol we have used a method similar to that which we used to generate hemioorthoesters, the tetrahedral intermediates in *OO*-acyl transfer reactions.⁸ The first precursor chosen was methoxyvinylloxymethyl

chloroacetate (1).⁹ By analogy to our earlier work this should be hydrolysed to yield methyl vinyl hemioorthoformate (2) which should break down to vinyl alcohol and methyl formate (or methanol and vinyl formate). The ¹H n.m.r. spectrum of (1) (0.15 mol l⁻¹) in [²H₃]acetonitrile at -20 °C 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; J_{AB} 14.7, J_{AC} 4.9, and J_{BC} 1.7 Hz. The signals for the CH, chloroacetate, and methoxy group are as shown in the Scheme. On addition of 10% by volume of D₂O (or H₂O)



a new vinyl group is formed with concurrent disappearance of the orthoester CH signal and formation of the spectrum of methyl formate (δ 8.06 and 3.70). The new vinyl group has δ_A 6.45, δ_B 4.18, δ_C 3.82; J_{AB} 14.2, J_{AC} 6.4, 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. 16 min, changing into the spectrum of CH₂DCHO (δ 9.65 and 2.12, br m). On addition of an excess of sodium deuteroxide at -20 °C this change takes place immediately. When 10% H₂O is used instead of 10% D₂O the conversion of the initial product into acetaldehyde (now MeCHO) is faster and the n.m.r. spectrum of the latter has a sharp quartet (δ 9.65) and doublet (δ 2.12). Complementary changes in the ¹³C n.m.r. spectrum were also observed. The vinyl group of the starting material (0.3 mol l⁻¹) showed resonances at δ 146.2 and 94.4 in CD₃CN and on addition of 10% D₂O (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 [²H₁]acetaldehyde [δ 202.8 and 30.85 (t, J_{HD} 19.3 Hz)] plus some acetaldehyde (δ 31.1) which presumably arises from the presence of HDO in the D₂O and a favourable isotope effect. When H₂O was added instead of D₂O a small isotope effect (Δδ 0.2) was observed on the downfield ¹³C resonance (δ 149.2) but not on the upfield one (δ 88.0).

The same vinyl species was also generated from methoxyvinylloxymethyl acetate but the relative rates of its formation and disappearance are less favourable and it is necessary to use a more aqueous solvent. This precursor does however have the advantage that with it there is no chloroacetate signal in the ¹H n.m.r. spectrum which partially obscures one of the vinyl resonances when (1) is used as the precursor.

On the basis of these results we conclude that the new vinyl group is that of vinyl alcohol. 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 ¹H signals should occur at lower field (vinyl acetate ¹H, δ 7.26, 4.88, and 4.56; ¹³C, δ 141.8 and 96.8 p.p.m.).¹⁰ The observation of an isotope effect on the downfield ¹³C vinyl signal is also consistent with this conclusion but as the two species were not observed simultaneously in the same solution this piece of evidence is not conclusive. In addition both the ¹H and ¹³C n.m.r. spectra show the formation of the other species (methyl formate and chloroacetic acid) consistent with the formation of vinyl alcohol according to the stoichiometry shown in the Scheme. So far we have been unable to detect the hemioorthoester (2) and there appears to be no formation of vinyl formate and methanol. Presumably (2) reacts faster than the previously detected⁸ dimethyl hemioorthoformate with preferential expulsion of the vinyloxy group which probably has a lower pK_a than the methoxy group.

It is interesting that in the solutions that we have used the rate of conversion of vinyl alcohol into acetaldehyde is considerably greater than the rate of formation of acetaldehyde from ethyl vinyl ether (ca. 100 fold). This means that either, contrary to the predictions mentioned above, the acid-catalysed ketonisation reaction is faster than the hydrolysis of an analogous vinyl ether or that the vinyl alcohol is undergoing a rapid spontaneous or even base-catalysed reaction under our conditions.

The method reported in this communication for the generation of vinyl alcohol provides for the first time a way of studying a simple enol-keto system in the thermodynamically favourable direction (enol → keto) rather than in the unfavourable direction (keto → enol) and may be extendible to other enols. We are at present investigating such possibilities.

(Received, 31st May 1979; Com. 572.)

¹ R. P. Bell and P. W. Smith, *J. Chem. Soc. (B)*, 1966, 241; J. Hine and K. Arata, *Bull. Chem. Soc. Japan*, 1976, **49**, 3085, 3089; J. P. Guthrie and P. A. Cullimore, *Canad. J. Chem.*, 1979, **57**, 240; J. P. Guthrie, *ibid.*, p. 797; S. K. Pollack and W. S. Hehre, *J. Amer. Chem. Soc.*, 1977, **99**, 4845.

² S. Saito, *Chem. Phys. Letters*, 1976, **42**, 399; cf. W. J. Bouma, D. Poppinger, and L. Radom, *J. Amer. Chem. Soc.*, 1977, **99**, 6443; W. J. Bouma and L. Radom, *Austral. J. Chem.*, 1978, **31**, 1167, 1649; *J. Mol. Structure*, 1978, **43**, 267.

³ B. Blank and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 506.

⁴ B. Blank, A. Henne, G. P. Lariff, and H. Fischer, *Pure Appl. Chem.*, 1975, **41**, 475.

⁵ G. E. Lienhard and T.-C. Wang, *J. Amer. Chem. Soc.*, 1969, **91**, 1146.

⁶ J. Toullec and J. E. Dubois, *Tetrahedron*, 1973, **29**, 2851, 2859; *J. Amer. Chem. Soc.*, 1974, **96**, 3524.

⁷ Cf. A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 1973, **95**, 803.

⁸ B. Capon, J. H. Gall, and D. McL. A. Grieve, *J.C.S. Chem. Comm.*, 1976, 1034; B. Capon and D. McL. A. Grieve, *J.C.S. Perkin II*, in the press.

⁹ Cf. J. W. Scheeren, J. E. W. Van Melick, and R. J. F. Nivard, *Rec. Trav. chim.*, 1971, **90**, 1123.

¹⁰ C. J. Pouchert and J. R. Campbell, 'The Aldrich Library of NMR Spectra,' vol III, spectrum 35C; L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley-Interscience, New York, 1972, spectrum 61.