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THE STEREOCHEMISTRY OF SIMPLE ENOLS IN SOLUTION

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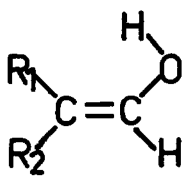
Abstract. On the basis of their ^1H n.m.r. spectra it is concluded that vinyl alcohol and trans-1-propenol exist mainly in the syn-conformation and that cis-1-propenol and 2-methyl-1-propenol exist mainly in the anti conformation.

Simple enols[1] can exist in two planar conformations syn, 1, and anti, 2. Saito interpreted the microwave spectrum of vinyl alcohol in the gas phase in



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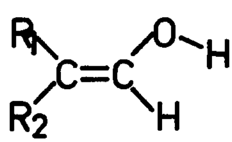

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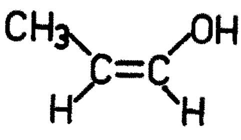
terms of the syn-conformation (1, $R_1 = R_2 = H$)[2] and this is also the conformation favoured by theoretical calculations.[3] We recently measured the ^1H n.m.r. spectrum of vinyl alcohol under slow exchange conditions in slightly aqueous acetone and determined the coupling constants J (OH-αCH) and J (OH-trans-βCH) to be 9.8 and 0.4 Hz respectively.[4] However, in the absence of suitable models, we were unable to assign definitely the conformation, but we now report the spectra of cis- and trans-1-propen-ol (3 and 4) and of 2-methyl-1-propen-ol (5)

Table I. Coupling Constants (Hz, ±0.2 Hz) in the ^{1}H n.m.r. Spectra of Simple Enols in Aqueous Acetone (0.72 - 1.48% H_2O) at -80°C.

	J(OH-α-CH)	J(OH-*trans*-βCH)
vinyl alcohol[a]	9.8	0.4
cis-1-propenol	6.0	0.8
trans-1-propenol	9.3	-
2-methyl-1-propenol	5.5	-

[a]Ref. 4



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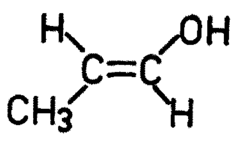

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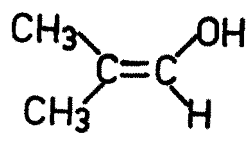

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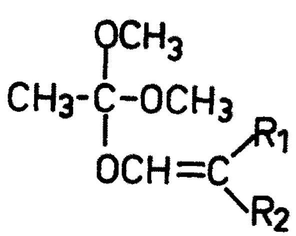
(Table I) which provide further information. The *cis*-enol (3), and (5) were generated from the corresponding orthoacetate 6 in CD_3COCD_3-H_2O (0.72 - 1.48% H_2O) which contained HCl (1.48 - 2.89 x 10^{-4} M) at -10° to +10° and the



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trans-enol 4 was generated similarly in a mixture of 70% cis-enol and 30% trans-enol from orthoacetate 6 of similar sterochemical composition. Under these conditions the labile orthoacetate protecting group can be removed much more rapidly than the enols undergo ketonization (cf. ref. 4) and the 1-propenols are sufficiently stable to have their n.m.r. spectra measured up to +30° and 2-methyl-1-propenol sufficiently stable to have its spectrum measured up to +40°C.

It was found that whereas vinyl alcohol[4] and the trans-enol 4 have a coupling constant J (OH-αCH) greater than 9 Hz at -80° the two enols 3 and 5 with a methyl group cis to the hydroxyl have values of 6.0 and 5.5 Hz for this coupling constant. We interpret these results as indicating that the vinyl alcohol and 4 exist mainly in the syn-conformation but that the stability of this conformer is reduced when there is a cis-methyl group and that 3 and 5 exist mainly in the anti-conformation, 2. This interpretation is supported by the long-range coupling J (OH-trans-βCH) which for vinyl alcohol is 0.4 Hz[4] but for 3 is 0.8 Hz. If 3 had the anti-conformation OH the trans-βCH would have a W relationship which is the most favourable for a long-range allylic coupling.[5]

The coupling constants for vinyl alcohol[4] and 4 are within experimental error independent of temperature from -80° up to -10° and +30° respectively which suggests that they exist overwhelmingly in one conformation in this temperature range. However the values of J(OH-αCH) for 3 and 5 increased from 6.0 and 5.5 Hz at -80° to 6.9 and 6.0 Hz on going to +30° and +40° respectively. Therefore with these enols there may be some of the syn-conformer present at the higher temperatures.

A similar conformational isomerism has been studied for enol ethers by n.m.r. spectroscopy[6] but here the absence of a proton directly bonded to the oxygen means that less direct methods must be used and interpretation of the spectra is more difficult.[7]

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