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(16) From its spectral characteristics (^{1}H NMR, ^{13}C NMR), the corresponding complex bears the same *i*-PrNHOH-derived ligand as complex I (vide infra) and its isolation is under way.

(17) This last entity is completely formed after addition of 4 × 10^{-3} M Py. The addition of larger amounts of Py (4 M) leads to the formation of FeTPP $(Py)_2$.

(18) FeTPP $(Py)_2$ prepared according to J. O. Alben et al., *Biochemistry*, **7**, 624 (1968), gives three signals in ^{1}H NMR (C_5D_5N), δ 8.73 (8 H), 7.98 (8, H), 7.46 ppm (12 H), and seven signals in ^{13}C NMR (C_5D_5N, $CDCl_3$), δ 145.1, 141, 133, 132.2, 125.1, 124.6, 118.5 ppm.

(19) The NMR spectra were recorded on a Bruker WH 90 working in FT mode, in $CDCl_3$ at 23 °C (δ from TMS).

(20) At 20 °C, bound and free Py are in rapid exchange relative to the NMR time scale. At −60 °C, this exchange is slow and the signals of bound Py can then be identified and are those indicated in the text.

(21) Its higher peak (*m/e* 668) corresponds to FeTPP.

(22) The fast transformation of nitrosoalkanes, bearing a hydrogen α to NO, to the corresponding oximes in solution is well known[1] and is particularly favored in the presence of bases.

(23) It is noteworthy that the conversion of the hydroxylamine to the nitrosoalkane is a two-electron oxidation, the iron(III) porphyrin being the first one-electron oxidant. The second oxidant could be oxygen, but, as the reaction can be run under argon, it could also be the hydroxylamine itself. Accordingly, the dismutation of hydroxylamines has been reported to occur in the presence of $[Fe(CN)_5H_2O]^{3-}$ leading to the corresponding nitrosoalkane–iron(II) complexes.[13] (We thank a referee for suggesting this comment.)

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Vinyl Alcohol. A Stable Molecule

Sir:

Vinyl alcohol, the simplest member of the enol class of molecules has proved an elusive target for experimental observation. Attempts to prepare vinyl alcohol have generally produced its keto isomer acetaldehyde,[1] a result which could be taken to indicate a low energy pathway connecting the enol and keto structures. Recently, however, Saito[2] was able to prepare and identify vinyl alcohol in the gas phase. On the basis of the observation in interstellar space of structurally related molecules including CH_3OH,[3] CH_3CH_2OH,[4] CH_3CHO,[5] and $CH_2{=}CHCN$,[6] Saito suggested that vinyl alcohol $CH_2{=}CHOH$ may also be an interstellar molecule. In this connection, we note that, because of the large intermolecular distances and hence infrequent collisions between molecules, the interstellar medium offers favorable conditions for the existence of molecules which are stable with respect to *intra*molecular rearrangement but which are very difficult to observe under normal laboratory conditions owing to *inter*molecular or ionic rearrangements. A relevant example is hydrogen isocyanide which was observed[7] several years ago in interstellar space but has only very recently been observed in the laboratory.[8] Theoretical calculations[9] have shown that there is indeed a large barrier to the intramolecular rearrangement of HNC to HCN. In order to assess the stability of vinyl alcohol as an isolated molecule and, in particular, to examine the likelihood of vinyl alcohol existing in the interstellar medium, it is therefore important to establish the magnitude of the barrier for rearrangement to acetaldehyde. In this paper, we apply ab initio molecular orbital theory to this problem.

Table I. Optimized Geometric Parameters[a] for Vinyl Alcohol (I), Acetaldehyde (II), and the Transition States (IIIA, IIIB) Separating I and II

	I	IIIA	IIIB	II
Symmetry constraint	C_s	C_1	C_1	C_s
No. of independent parameters	11	15	15	10
Bond distances, Å				
C_1–C	1.312	1.448	1.413	1.537
C–O	1.390	1.293	1.378	1.217
C–H	1.089	1.097	1.098	1.104
O–H_3	0.990	(1.163)	(1.662)	
C_1–H_1	1.080	1.087	1.080	1.085
C_1–H_2	1.077	1.082	1.080	1.087
C_1–H_3		1.475	1.743	1.087
C–H_3			(1.164)	
Bond angles, degrees				
$\angle C_1CO$	126.9	102.6	124.6	124.3
$\angle C_1CH$	122.2	136.5	115.3	114.3
$\angle CC_1H_1$	122.0	108.1	119.8	110.5
$\angle CC_1H_2$	121.2	118.8	121.5	108.8
$\angle CC_1H_3$		67.1	41.7	108.8
$\angle COH_3$	105.2			
Dihedral angles, degrees				
$\angle HCC_1O$	180.0[b]	183.1	188.5	180.0[b]
$\angle H_1C_1CO$	0.0[b]	−81.8	−10.4	0.0[b]
$\angle H_2C_1CO$	180.0[b]	151.7	−183.8	120.6
$\angle H_3C_1CO$	0.0[b]	3.3	−75.3	−120.6

[a] Derived (nonindependent) values shown in parentheses. [b] Values determined by symmetry.

Standard LCAO SCF MO theory was used with a modified

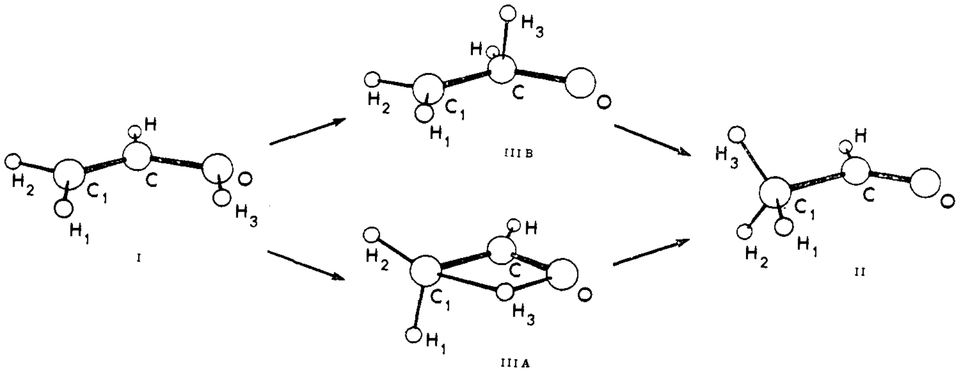

Figure 1. 1,3-Sigmatropic shift in vinyl alcohol/acetaldehyde.

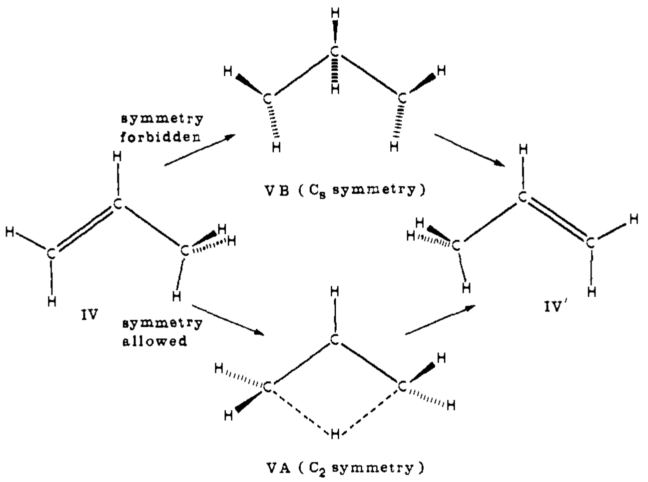

Figure 2. 1,3-Sigmatropic shift in propene.

Table II. Calculated Total Energies (E, Hartrees) and Relative Energies (ΔE, kcal mol^{-1})

Species	STO-3G		4-31G	
	E	ΔE	E	ΔE
I	−150.91668	18.4	−152.66632	11.7
IIIA	−150.77020	110.3	−152.53144	96.4
IIIB	−150.68740	162.3	−152.49927	116.5
II	−150.94599	0	−152.68499	0

version of the Gaussian 70 series of programs[10] and the STO-3G[11] and 4-31G[12] basis sets. Optimized STO-3G geometries for vinyl alcohol (I)[13] and acetaldehyde (II) and for the transition states (IIIA, IIIB, Figure 1), separating them, were obtained using direct search procedures described elsewhere[15,16] and are summarized in Table I. Calculated energies are shown in Table II.

We begin by noting that, for the isoelectronic hydrocarbon propene, the analogous, and in this case degenerate, 1,3-sigmatropic shift IV → IV′ is symmetry allowed if antarafacial (VA) and symmetry forbidden if suprafacial (VB, Figure 2).[17] Although it is somewhat less satisfactory to apply the orbital symmetry considerations to our less symmetrical vinyl alcohol → acetaldehyde rearrangement, we note that our transition-state structures IIIA and IIIB resemble the symmetry-allowed (VA) and symmetry-forbidden (VB) structures, respectively. An important structural feature in IIIA is the manner in which the bridging hydrogen causes a narrowing of the CCO angle to 102.6° compared with values of 126.9° in I, 124.3° in II, and 124.6° in IIIB. We may think of IIIA as the transition state on a pathway involving a direct 1,3-hydrogen shift. In the transition state IIIB, the short distance (1.164 Å) between the migrating hydrogen and the central carbon is worth noting. The reaction path in this case may be considered to proceed via successive 1,2 shifts.

Both basis sets predict (Table II) that the "symmetry-allowed" structure IIIA is the favored transition state. Our better (4-31G) calculations predict an activation energy for the vinyl alcohol → acetaldehyde transformation of 85 kcal mol^{-1} and an energy difference between vinyl alcohol and acetaldehyde of 11.7 kcal mol^{-1}. The latter result is in reasonable agreement with an indirect experimental estimate[18] of 13.2 kcal mol^{-1}. Although our results, particularly for the "symmetry-forbidden" transition state IIIB may be modified in a more sophisticated treatment, i.e., one which uses a larger basis set and which incorporates electron correlation, our calculated activation energies are sufficiently large that we predict with some confidence that vinyl alcohol is stable with respect to intramolecular rearrangement. The apparent ease with which vinyl alcohol is converted to acetaldehyde in the laboratory must be due to complicating *inter*molecular or ionic reactions.

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Synthesis and Enzymatic Formation of a *C*-Glucuronide of Δ^6-Tetrahydrocannabinol

Sir:

The primary metabolic pathways of Δ^1- and Δ^6-tetrahydrocannabinol (Δ^1-THC and Δ^6-THC (**1a**)) have been thoroughly investigated.[1] However, little is known about the nature of the water-soluble conjugates, which are frequently the predominant components of the THC excretion products.[2] Indirect evidence has suggested the presence of glucuronides.[3,4] Indeed, recently Harvey et al. reported the formation of *O*-glucuronides of cannabidiol (a cannabinoid related to THC) and some of its metabolites in mouse liver after administration of cannabidiol.[5]

We considered the possibility that, if THC conjugates were indeed glucuronides, they could be (in part at least) of the very rare *C*-glucuronide type.[6] This conjecture was based on published observations that in several chemical reactions,[7] including glucosidation,[8] the C-4′ aromatic position in some cannabinoids was substituted preferentially to the free phenolic group. In order to facilitate the identification of possible *C*-glucuronides produced in metabolic processes, we initially synthesized the appropriate *O*- and *C*-glucuronides. We chose to work in the Δ^6-THC series, rather than in the pharmacologically more important Δ^1-THC series, in order that the attempted syntheses of glucuronides (which involve acidic