

CONFORMATIONAL ANALYSIS OF 3-BUTEN-2-OL: A MODEL ASYMMETRIC OLEFIN

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**Abstract:** The conformational energy of 3-buten-2-ol has been investigated using ab initio molecular orbital theory. Six energy minima have been located, the lowest energy two of which are the same as those assigned in a recent microwave study of the molecule. Rationale for the observed preferences are advanced.

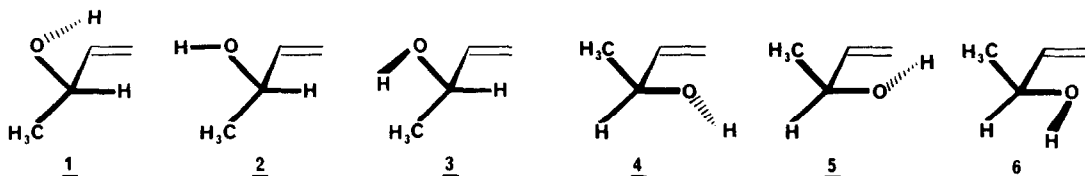
Heightened interest in acyclic stereo-control has made it apparent that knowledge of the conformational preferences of asymmetric molecules, and of the origins of these preferences, are crucial to mechanistic reasoning [1]. Not only must the identity of the ground-state conformer be assigned, but relative equilibrium populations of all low-energy conformers established. A little-abundant but highly reactive conformer may dictate overall product stereochemistry [2]. In contrast to the experimental difficulties in determining the complete energy surface of even a moderately complex molecule [3], computational methods permit identification of all stable conformers. Here we report a theoretical study of the conformational profile of 3-buten-2-ol. This serves as a model for the class of allylic alcohols and ethers which have found widespread utilization for the induction of asymmetry in electrophilic reactions of olefins [4,5].

Six minima have been located on the conformational energy profile for 3-buten-2-ol [6,7], three conformers with the CO linkage (approximately) in the plane of the CC double bond, 4-6, and three conformers with C-H and C=C coplanar, 1-3. Conspicuously missing are stable conformers in which the terminal methyl group eclipses the olefin. Calculations performed at

Table. Conformational Energies<sup>a</sup> and Equilibrium Abundances<sup>b</sup> of 3-Buten-2-ol

Structure	6-31G <sup>*</sup> //3-21G	Experiment <sup>c</sup>
<u>1</u>	0.0 (57)	0.0 (58)
<u>2</u>	1.9 (2)	-
<u>3</u>	2.7 (1)	-
<u>4</u>	0.6 (21)	0.52 (42)
<u>5</u>	0.8 (15)	-
<u>6</u>	1.6 (4)	-

a) kcal mol<sup>-1</sup>; b) In parentheses following relative energies; e<sup>-ΔE/RT</sup> normalized to 100% at 298 K; c) Reference 11.



the 6-31G<sup>\*</sup> level [10] using 3-21G geometries should provide accurate estimates of conformational energy differences; these are summarized in the Table.

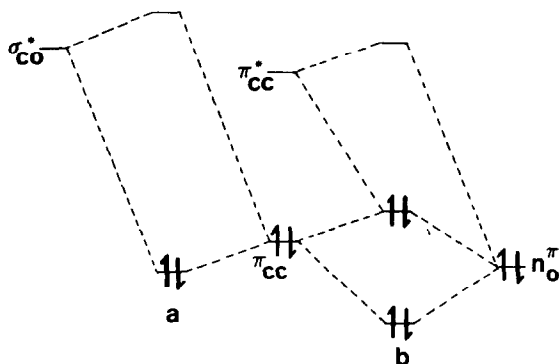
The most stable conformer of 3-buten-2-ol at the 6-31G<sup>\*</sup>//3-21G level is one in which the CH linkage eclipses the CC double bond, 1. Slightly higher in energy are two conformers, 4 and 5, with the CO bond eclipsing the olefin; these are less stable by 0.6 and 0.8 kcal mol<sup>-1</sup>, respectively. All of these conformers have the hydroxylic hydrogen juxtapose to the olefinic  $\pi$  bond; this has previously been suggested as evidence for hydrogen bonding between the hydroxylic hydrogen and the  $\pi$  bond [11]. The relative instability of conformers 2, 3, and 6 is presumably due to unfavorable overlap of the oxygen lone pair(s) with the CC double bond.

A microwave spectrum of 3-buten-2-ol has been interpreted in terms of 1 as the ground-state conformer, and 4 as 0.52 kcal mol<sup>-1</sup> higher in energy [11]. The present results are in complete accord. Several prominent

unassigned transitions in the spectrum leave open the possibility of other stable conformers.

Rationalizations of the conformational preferences of related allylic alcohols and ethers have been advanced [4,5,12,13]. The preference for 1 over 4 and 5 follows from the energetically favorable mixing of  $\sigma_{CO}^*$  and  $\pi_{CC}$  which is possible only with the CO linkage skew to the double bond. As shown in Figure 1a, this interaction should lower  $E_{\pi}$ , and thereby deactivate the olefin toward electrophilic attack. Coplanarity of the C=C and CO bonds allows effective mixing of  $\pi_{CC}$  and  $\pi_{CC}^*$  and the  $\pi$  type lone pair on oxygen, resulting in an "homoallylic anion" (Figure 1b). Concomitant with the lowering of  $E_{\pi}$ , will be the raising of  $E_{\pi}$ ; this suggests olefin activation. Thus, the higher energy conformation of 3-buten-2-ol, 4, should be more reactive toward electrophiles than the ground-state conformer, 1. These arguments suggest that electron-rich allylic alcohols (ethers) will adopt conformations with the CO bond (approximately) coplanar with the  $\pi$  orbital, thereby facilitating  $\sigma_{CO}^*-\pi_{CC}$  overlap, and that electron-poor olefins will assume conformations with the CO bond eclipsing the olefin, thereby enabling the delocalization of the oxygen lone pair into the double bond. The available experimental data seem to concur [4,12].

Figure 1.



In conclusion, more than a single conformer of 3-buten-2-ol is accessible. Given the likelihood that the ground-state form is not the most reactive species, it is clear that any analysis of product stereochemistry based solely on this conformer may not be valid. The description of the relative reactivity and stereoselectivity of the conformers of 3-buten-2-ol and related asymmetric molecules is currently under study in our laboratory.

#### References and footnotes.

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