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The Theoretical Structure of Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene and the Potential Isolation of Bicyclo[1.1.0]but-1(3)-ene

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The C_4H_4 potential surface contains a number of molecules that are unusually interesting to both experimentalists and theoreticians. Computed infrared spectra have proved to be useful in the identification of two of these, cyclobutadiene[1] and methylenecyclopropene,[2] and are likely to be so in the eventual identification of others such as tetrahedrane[3] and cyclobutyne.[4] In a recent computation[5] of the vibrational spectrum of bicyclo[1.1.0]but-1(3)-ene (**1**) it was found that two theoretical structures suggested earlier with the assumption of C_{2v} symmetry were in fact not local minima on the respective potential surfaces (STO-3G[6a] and 4-31G[6b] basis sets), since both had one imaginary frequency. However, we found that when polarization functions on carbon (6-31G*) were included SCF, MP2, TCSCF, and CISD calculations all predict **1** to be a minimum on the C_4H_4 potential surface. This molecule might therefore be observable at low temperature, even though it is computed to be of considerably higher energy than the two observed C_4H_4 isomers, cyclobutadiene and methylenecyclopropene.[5]

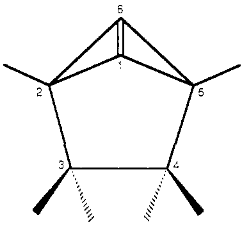
1

Table I. Theoretical Geometry of Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene (**2**)

	computation			
parameter[a]	SCF/ STO-3G	SCF/ 3-21G	SCF/ 6-31G*	MP2/ 6-31G*[c]
$C_1{-}C_2$	1.518	1.527	1.493	1.502
$C_1{-}C_6$	1.373	1.356	1.332	1.390
$C_2{-}C_3$	1.546	1.534	1.532	1.531
$C_3{-}C_4$	1.565	1.579	1.565	1.560
$C_2{-}H_2$	1.084	1.064	1.071	1.084
$C_3{-}H_3$	1.088	1.082	1.085	1.095
$<C_1C_2C_6$	53.8	52.7	53.0	55.2
$<C_2C_1C_5$	94.6	95.9	96.4	95.7
$<C_2C_1C_6$	63.1	63.6	63.5	62.4
$<C_2C_3C_4$	102.4	103.0	102.5	102.6
$<C_1C_2H_2$	120.9	121.0	120.7	120.4
$<C_2C_3H_3$	111.1	110.7	111.1	111.0
$<C_3C_2H_2$	122.7	123.8	124.0	124.5
$<C_4C_3H_3$	112.0	111.5	112.1	112.1
τ^b	110.9	111.9	112.7	113.5
energy	−227.65429	−229.14007	−230.47329	−231.28998

[a] Bond distances in angstroms, angles in deg, energies in au. C_{2v} symmetry was imposed. [b] Dihedral angle of the bicyclobutene ring. [c] Frozen core approximation.

Although bicyclo[1.1.0]but-1(3)-ene (**1**) has as yet not been observed, Szeimies and co-workers[7] have isolated compounds apparently formed by the trapping of bridged derivatives of **1**. This suggests that these derivatives can at least exist fleetingly as reactive intermediates. To check that our computational methods do predict these strained compounds to be energy minima, we have undertaken a theoretical study of one of Szeimies molecules, tricyclo[3.1.1.0^{2,6}]hex-1(6)-ene (**2**). SCF geometry optimizations with the STO-3G and 3-21G basis sets (C_{2v} symmetry was imposed) were carried out (see Table I). Analytical vibrational analyses[8] of these two optimized structures gave one imaginary B_1 frequency in both basis sets, showing that **2** is not a minimum on these potential surfaces. The σ_v plane distinguishing B_1 from B_2 symmetry passes through atoms 1 and 6 in structure **2**. A similar result was found for **1** with these two basis sets. The geometry of **2** was then optimized with the 6-31G* basis set (Table I), and a vibrational analysis again yielded an imaginary frequency (228i) of B_1 symmetry. This is in contrast to the vibrational analysis of **1** with the 6-31G* basis set where all real frequencies were found.



2

Finally the geometry of **2** was reoptimized in an MP2/6-31G* calculation with the frozen core approximation (Table I). As was found[5] for **1** a significant increase (0.058 Å) in the carbon–carbon double bond was the only major change in the geometry. A subsequent vibrational analysis (MP2/6-31G*) of the B_1 symmetry block predicts that **2** should be a minimum since all B_1 frequencies were real (477, 672, 845, 1030, 1194, and 3181 cm^{-1}).

The dihedral angle of the bicyclobutene ring in **2** is predicted to be 113.5° (MP2/6-31G*) which is significantly smaller than that predicted (138.1°) for bicyclo[1.1.0]but-1(3)-ene (**1**). The smaller dihedral angle for **2** and the increased pyramidalization of its sp^2 carbon atoms indicate that the diradical character of **2** is probably even greater than that of **1**. Schulman and Disch[9] have published an MP2/6-31G* frozen core calculation of benzvalene, an isomer of **2** with the double bond between atoms 3 and 4 rather than 1 and 2. This isomer would be expected to be less strained than **2**, and Schulman and Disch's computed energy for benzvalene is 0.047 au = 30 kcal/mol lower than our

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value for **2**. Given that our theoretical calculations predict **2** to be an energy minimum, but a less stable minimum than **1**, and that Szeimies has been able to trap **2** as well as other bridged bicyclobutenes, it appears that the unbridged bicyclobutene **1** is likely to exist and might be observable in a low-temperature matrix.

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Photoinduced Lactonization. A Useful but Mechanistically Complex Single Electron Transfer Process

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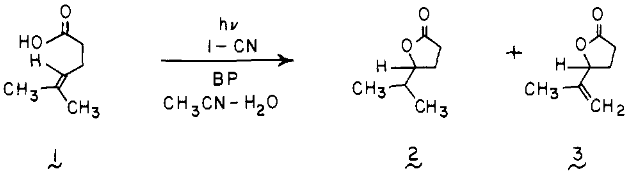
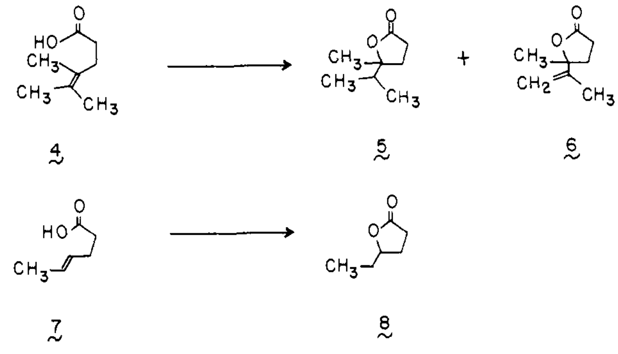
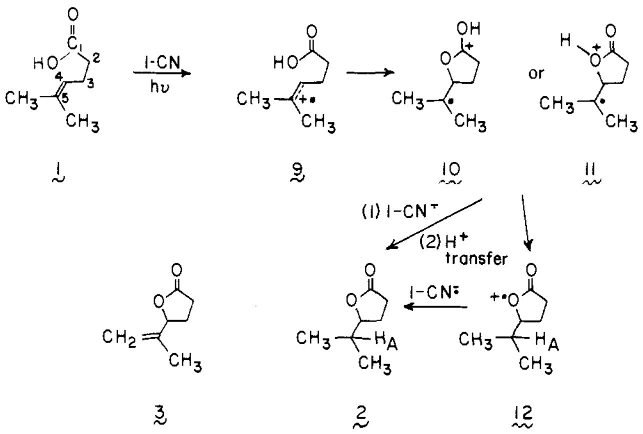
A wide variety of biologically active natural products contain the five-membered lactone moiety. Often, these lactones are the products of the anti-Markovnikov intramolecular addition of a carboxylic acid to a carbon-carbon double bond. Synthetically, this type of lactonization can be difficult to achieve. We now report that this transformation can be accomplished in acceptable yields through a mechanistically complex single electron transfer photoprocess.

In general, any organic molecule with an $E_{1/2}$ for oxidation of 2.2 V or less (vs SCE) should be susceptible to oxidation via a photosensitized single electron transfer process.[1,2] The resulting cation radical should be highly reactive and, under the proper conditions, should collapse either intermolecularly or intramolecularly with available nucleophiles.[3] This concept is nicely demonstrated by the photoinduced cyclization of γ,δ-unsaturated carboxylic acids to γ-lactones.[4] In a typical procedure, a Pyrex vessel containing a 65:35 acetonitrile/water solution (240 mL), 4.27 g of **1**,[5,6] 2.57 g (0.5 equiv) of 1-cyanonaphthalene (1-CN), and 2.55 g (0.5 equiv) of biphenyl (BP) was irradiated for 8 h in a Rayonet reactor fitted with 16 3000-Å lamps. The reaction mixture was steam distilled, and the steam distillate, after workup, yielded 43% of **2** and 5% of **3**.[7,8] When this reaction was carried out for 145 min in 55:45 acetonitrile/water, GLC analysis indicated the presence of 51% of **2** and 10% of **3**. This mixture was readily converted to **2** through catalytic reduction over 5% palladium on carbon. Utilizing the same general procedure, **4**[5] gave 69% of **5**[9a] and 10% of **6**[6,10] after 85 min, and **7**[5] gave 36% of **8**[9b] after 800 min. As these examples demonstrate, the photolactonization reaction shows a propensity for five-membered ring formation, even when this results in an anti-Markovnikov addition as in the conversion of **1** into **2**.





Mechanistically, the conversion of **1** into **2** might be viewed as occurring through the transfer of an electron from **1** ($E_{1/2}{}^{ox}$ vs SCE = 1.80 V) to excited state 1-CN ($E_{1/2}{}^{red}$ vs SCE = 1.83 V) to yield the cation radical **9**. Cyclization would be expected to yield the distonic cation radicals **10** or **11**.[11,12] The fate of **10**/**11** was surprisingly complex (vide post). It was immediately obvious that *at least* two paths from **10**/**11** to **2** must exist. The presence



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(12) Attack of the carbonyl oxygen on the initially generated cation radical would produce **10**. The relative stabilities of **10**, **11**, and **12** are unknown.