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Vinylic vs Allylic Deprotonation: An Ab Initio Molecular Orbital Study of 2,3-Dihydrooxepin and 1,3-Cycloheptadiene

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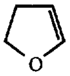
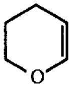
Abstract: The 2,3-dihydrooxepin ring opens upon deprotonation with strong base presumably through an allylic anion which is predicted to be 15 kcal/mol lower in energy than the vinylic anion. Allylic deprotonation occurs with allyl angle expansion whereas vinylic deprotonation results in vinyl angle compression. The vinyl anion of 2,3-dihydrooxepin is stabilized by 8 kcal/mol relative to the vinyl anion of 1,3-cycloheptadiene suggesting that the presence of the oxygen lowers the energy of the vinyl anion. Copyright © 1996 Elsevier Science Ltd

The question of vinylic vs allylic deprotonation has been investigated experimentally for vinyl ethers **1a**-**3a**, **5a**.[1,2] Compounds **1a**-**3a** exhibit vinylic deprotonation. In the case of 2,3-dihydrooxepin (**5a**), treatment with strong base[2] affords 1-lithio-1- oxaheptatriene. This process may occur through the formation of an allylic anion (**9b**). Another possibility may be that vinyl deprotonation (**5b**) precedes a rapid isomerization to the allylic anion, which subsequently ring opens.[2] It is therefore important to address the relative stability of both the vinylic and allylic anions (and their corresponding lithiated species) of 2,3-dihydrooxepin. As a comparative study, *ab initio* calculations were performed on 1,3-cycloheptadiene (**6a**), 2,3-dihydrofuran (**1a**) and cyclopentene (**4a**) in an attempt to establish whether the presence of the oxygen atom in **5a** and **1a** has any notable effect on 1) the site of deprotonation, as has been previously hypothesized to be a potential contributing factor[2] 2) relative stability.


1a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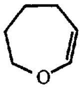
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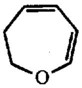
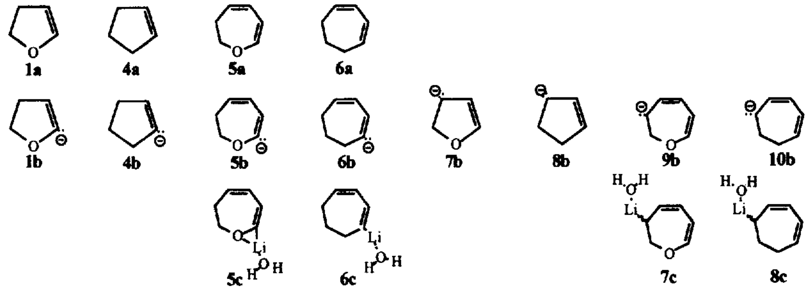

5a

Ab initio calculations were executed using Gaussian 94[3]. Geometry optimizations were performed on structures shown in Chart I at the Restricted Hartree-Fock (RHF) level of theory using the 6-31G(d,p) and 6-31++G(d,p) basis sets (Table 1). Additionally, we present single point Møller Plesset 2 (MP2) calculations of these optimized geometries. Each stationary point was verified as a minimum using

Chart I. Structures

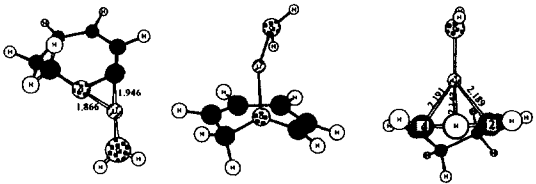


analytical second derivative vibrational frequency calculations.

Ab initio calculations predict (Table 1) that the allylic anions (**8b**, **9b** and **10b**) are more stable than the corresponding vinyl anions (**4b**, **5b** and **6b**) by about 4, 15 and 25 kcal/mol (RHF) and 11, 22 and 31 kcal/mol (MP2) respectively. These results suggest that formation of vinyl anions, in these cases, is not an energetically favorable process as compared to the formation of allylic anions. By comparison, the vinyl anion (**1b**) is stabilized over the allyl anion (**7b**) by approximately 11 kcal/mol (RHF) and 6 kcal/mol (MP2). The oxygen atom in **1a** stabilizes the vinyl anion, whereas in the absence of oxygen (**4a**), the allyl position is favored computationally. The stabilities of the lithiated structures are also presented in Table I. Ether solvation is modeled by a water molecule bound to lithium. The structure found for **5c** (Figure 1) is consistent with calculations on α and β lithiated vinyl ethers[4] where the

Table 1. Relative Energies (kcal/mol) of Carbanions and Lithiocarbanions

	Hartree-Fock 6-31++G(d,p)	MP2 Single Point 6-31++G(d,p)		Hartree-Fock 6-31G(d,p)	MP2 Single Point 6-31G(d,p)	Hartree-Fock 6-31++G(d,p)	MP2 Single Point 6-31++G(d,p)
1b	-10.8	-5.5					
7b	0.00	0.00					
4b	4.0	10.6					
8b	0.00	0.00					
5b	15.2	22.1	**5c**	11.1	20.2	10.8	20.1
9b	0.00	0.00	**7c**	0.00	0.00	0.00	0.00
6b	24.9	30.9	**6c**	17.8	28.9	17.0	27.8
10b	0.00	0.00	**8c**	0.00	0.00	0.00	0.00



5c **7c** **8c**

Figure 1. Chem 3-D Plots of Solvated Structures Optimized in Basis Set 6-31G(d,p) (bond lengths in Å)

lithium atom coordinates to both the carbon atom bearing the negative charge (anion) and the vinyl ether oxygen atom. A local minimum of **7c** (Chart I) can be found where solvated lithium coordinates to the propenyl system at carbons 3-5 that is about 7 kcal/mole **higher** in energy than that reported in Table 1, Figure 1. The lithium atom in **8c** is coordinated to positions 2-4 of the pentadienyl system. Ab initio calculations (Table 1) also predict that the allyl lithiocarbanions (**7c** and **8c**) are more stable than the corresponding vinyl lithiocarbanions (**5c** and **6c**) by about 11 and 18 kcal/mol (RHF) and 20 and 29 kcal/mol (MP2), respectively.

In Table 2, the relative proton affinities of the vinylic and allylic carbanions of **1a**, **4a**, **5a** and **6a** disclose the acidifying effect of oxygen. The presence of an oxygen atom in **5a** and **1a** stabilizes the vinyl anions when compared to **6a** and **4a**. The vinyl ether anions (**1b** and **5b**) are stabilized by approximately 11 and 8 kcal/mol (RHF and MP2) respectively more than the corresponding vinyl anions (**4b** and **6b**). The allyl anions (**8b** and **10b**) are predicted to be slightly more stable by about 4 and 2 kcal/mol (RHF) and 6 and 1 kcal/mol (MP2) respectively compared to the allyl ether anions (**7b** and **9b**).The observation that vinyl anions α to an ether oxygen exhibit higher stability than other types of

Table 2. Relative Proton and Lithium Cation Affinities of Carbanions (kcal/mol)

	Rel. H^+ Affinity			Rel. $[Li\text{-}H_2O]^+$ Affinity	
	Hartree-Fock 6-31++G(d,p)	MP2 Single Point 6-31++G(d,p)		Hartree-Fock 6-31++G(d,p)	MP2 Single Point 6-31++G(d,p)
1b	14.9	20.8			
7b	25.7	26.3			
4b	26.2	31.3			
8b	22.2	20.7			
5b	16.7	23.0	**5b**	9.0	4.7
9b	1.6	0.9	**9b**	4.6	2.6
6b	24.9	30.9	**6b**	7.9	3.2
10b	0.00	0.00	**10b**	0.00	0.00

Table 3. Vinylic and Allylic Angles (°) Optimized Using Basis Set 6-31++G(d,p)

Compound	Vinylic X-$\overset{(-)}{C}$=C Angle*	Allylic $\overset{(-)}{C}$-C=C Angle	Compound	Vinylic X-$\overset{(-)}{C}$=C Angle*	Allylic $\overset{(-)}{C}$-C=C Angle
1a	115.0	108.5	**5a**	129.0	125.9
1b	106.3	113.1	**5b**	117.8	123.7
7b	112.6	111.4	**9b**	126.3	128.7
4a	112.2	112.2	**6a**	128.7	128.7
4b	104.7	116.6	**6b**	117.4	128.3
8b	105.6	114.0	**10b**	125.8	131.2

* X= O, C

vinyl anions is consistent with previous work done by Harris et al.[4] The relative solvated lithium cation affinities (Table 2) show that for both RHF and MP2 levels of theory, the higher energy (vinyl) anions of **5a** and **6a** have the highest affinities for solvated lithium.

Optimized vinyl anions exhibit (Table 3) a vinyl angle compression of 8-11°. Calculations indicate that the vinylic angle in methoxyethene contracts about 15° upon vinyl deprotonation.[5] Optimized allyl anions exhibit an allyl angle expansion of 1.8-2.9° compared to the protonated compounds.

The degree (and nature) of aggregation of the lithiated cyclic vinyl ethers is unknown but is expected to be solvent and concentration dependent. It should be noted that the published NMR data do not require aggregate structures for these reagents.[1,2]

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