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A Study of the Aluminum Hydride Reduction of Unsaturated Cyclic Epoxides

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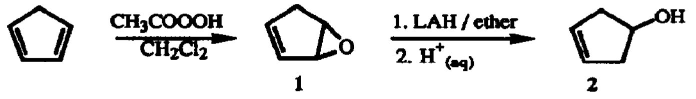
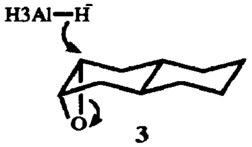
Abstract : The aluminum hydride reduction of 3,4-epoxycyclopentene to 3-cyclopentenol has been previously observed[1] and the complete regiospecificity of the reaction is confirmed here. A mechanism is proposed involving initial complexation of the aluminum hydride anion with the double bond followed by hydride transfer to the 3-Carbon. Analysis of the atomic charges determined from semiempirical electrostaic potentials support the proposed mechanism. Spectroscopic analysis of the resultant alcohol indicates the presence of an O-H⋯π intramolecular hydrogen bonded interaction.

The epoxidation of cyclopentadiene with peracetic acid yields epoxide **1**. Reduction of **1** with Lithium Aluminum Hydride in ether yields only 3-cyclopentenol, **2**, in 65% yield. Use of a threefold excess of LAH increased this yield to 85%.



NMR analysis of the product [δ 5.6, triplet (2H); δ 4.3, quintet (1H); δ 3.7, singlet (1H); δ 2.2–2.4, multiplet (4H)], and comparison with the NMR of pure 2-cyclopentenol, formed by LAH reduction of 2-cyclopentenone, [δ 5.8, triplet (2H); δ 4.8, doublet (1H); δ 4.3, singlet (1H); δ 2.0–2.4, multiplet (2H); δ 1.4–1.8, multiplet (2H)], confirms the complete regiospecificity of the reduction. Aluminum Hydride reduction of saturated cyclic epoxides such as 3 occurs via an S_N2 mechanism to yield only the axial alcohol.[2] For 3,4-epoxycyclopentene however geometry optimization using the MNDO semiempirical procedure[3] gives the puckering of the ring, as determined by the $C_1C_2C_3C_4$ dihedral angle, to be only 1° indicating an essentially planar system This indicates that S_N2 attack by AlH_4^- at carbons 3 and 4 should be comparable due to the very similar geometric environments.



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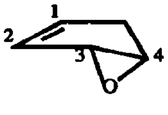

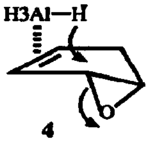

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A novel mechanism is proposed for the LAH reduction of **1** involving initial complexation of the AlH_4^- with the double bond, **4**. Sole formation of the 3-cyclopentenol is now proposed to be due to the geometric constraints imposed on H^- transfer due to the formation of complex **4**, limiting hydride attack to C_3.

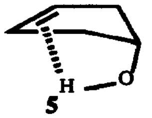
Table I summarizes the electrostatic potential (ESP) derived atomic point charges calculated using the MNDO semiempirical wavefunction for both 3,4-epoxycyclopentene and $^-AlH_4$. The MNDO method has been shown to be superior to the AM1[4] procedure for the calculation of ESP derived charges, and when scaled appropriately the MNDO ESP technique has been shown to yield charges of 6-31G* quality.[5] Both MNDO ESP and MNDO ESP Scaled charges are reported in Table I.

Table I

	q (C_1)	q (C_2)	q (C_3)	q (C_4)	q (Al)
MNDO /ESP	- 0.19	- 0.12	- 0.02	- 0.13	+ 0.67
Scaled	- 0.27	- 0.17	- 0.03	- 0.19	+ 1.04

Analysis of the charge distribution for **1** supports the proposed initial complexation of the aluminum hydride with the double bond by predicting significant charge buildup at the C_1 and C_2 carbons. Hydride transfer will now occur preferentially at C_3 due to the much shorter H_3AlH-C_3 distance. The significant negative charge calculated for C_4 will further inhibit hydride transfer at this position, reinforcing the steric constraints imposed by complexation.

FT-IR analysis of a dilute solution of 3-cyclopentenol, 0.04M in cyclohexane, shows a splitting of the O-H stretch into two absorption maxima at 3624 cm^{-1} and 3600 cm^{-1}, corresponding to the free O-H stretch and a stretch associated with an O-H·····π intramolecular hydrogen bonded interaction, **5**.



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The $\Delta\nu$ observed of 24 cm^{-1} is comparable with that observed for other unsaturated acyclic alcohols ($\Delta\nu$ = 14 - 35 cm^{-1}), where such O-H·····π interactions have been clearly identified.[6]

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