

bond, but now the oxygens are syn, due to electrostatic attraction for the metal cations.

All previous semiempirical and ab initio calculations have predicted a preference for linear hydride transfer.^{4,11} By contrast, all of our transition structures are bent but with rather easy bending of the C-H...C angle. Our results are consistent with the ease of hydride transfer in polycyclic 4-hydroxycyclohexanones⁸⁻¹⁰ and with experimental isotope effects in NAD-(P)⁺/NAD(P)H models.^{12,13}

Another interesting feature revealed by these calculations is the attack angle of hydride on the carbonyl (109-118°), consistent with the Dunitz-Bürgi¹⁴ predictions.¹⁵ In the transition structures for hydride transfer, the negative charge on the transferring hydride is only -0.1 to -0.2, similar to the charge found on hydrogen for concerted sigmatropic hydrogen shifts.¹⁶ That is, there is little hydride character on the migrating hydrogen and the transition state is "tight". Additional transition structures for hydride transfers by amines and NAD(P)H models will be reported shortly.

Acknowledgment. We are grateful to the National Science Foundation for research and supercomputer grants and the Harris Corporation for a computer grant. This study was initiated as the result of stimulating discussions with Professors Gordon Hamilton and Steven Benkovic at Pennsylvania State University.

Registry No. Methoxide, 3315-60-4; formaldehyde, 50-00-0.

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Electronic and Conformational Effects on π -Facial Stereoselectivity in Nucleophilic Additions to Carbonyl Compounds

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Received August 18, 1986

Since the early 1950's, when Cram proposed a rule to rationalize the stereoselectivities of nucleophilic additions to acyclic chiral carbonyl compounds¹ and Dauben proposed an unrelated rationale for these reactions of cyclohexanone derivatives,² many other rules and explanations have been proposed for these phenomena.³⁻⁸ We

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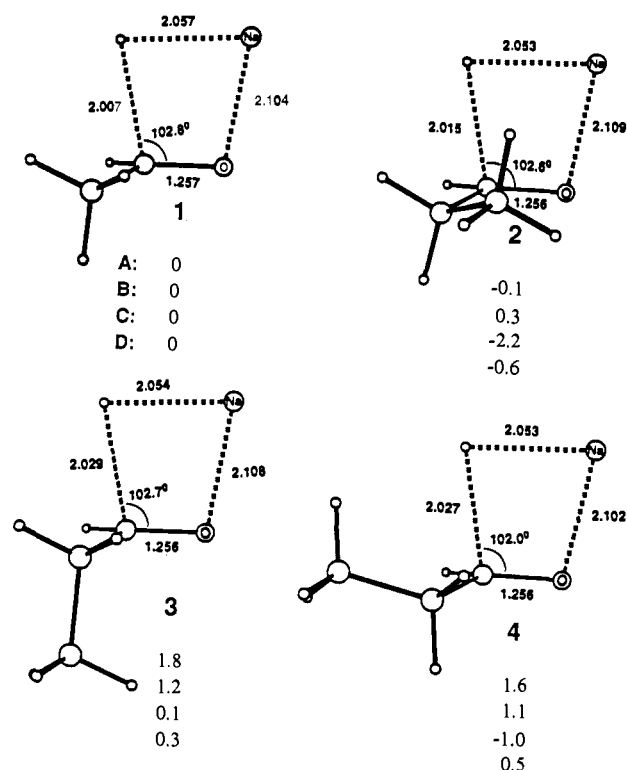


Figure 1. 3-21G transition structures and relative activation energies for reactions of NaH with acetaldehyde and propionaldehyde: A, 3-21G; B, 6-31G*/3-21G; C, 6-31G*/3-21G (Na⁺ removed); D, 6-31G*/3-21G relative energies of distortion of aldehydes into transition-state geometries.

have studied these reactions computationally⁹ and report quantitative support for the Felkin model⁴ for both acyclic and cyclic carbonyl compounds.

The transition structures for NaH addition to acetaldehyde (1) and propionaldehyde (2-4) are shown in Figure 1.¹⁰ The relative activation energies obtained by ab initio calculations with the 3-21G (A) and 6-31G* (B) basis sets show that an inside methyl has little effect on the activation energy, relative to acetaldehyde, while anti or outside methyl groups raise the activation energy. Removal of Na⁺ gives relative energies, C, indicating that anti is disfavored, while removal of NaH gives relative energies, D, indicating that the anti methyl is disfavored even in the distorted ground states.¹¹ The anti methyl group is disfavored relative to anti CH, because the former is a better donor and destabilizes the electron-rich transition structure. An outside methyl is disfavored relative to anti methyl for steric reasons. This conclusion differs from that of Anh and Eisenstein, whose calculations predicted that an anti methyl stabilizes such transition states.⁵ Cieplak proposed that an anti CH stabilizes nucleophilic transition states by electron donation and that CH is a better donor than CC,⁶ contrary to much experimental evidence which shows that CC is a better donor.¹² We conclude that an anti methyl destabilizes the electron-rich transition state because it is a better donor than a CH bond.¹³

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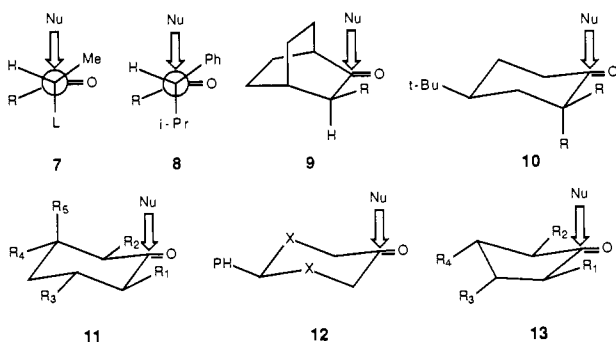
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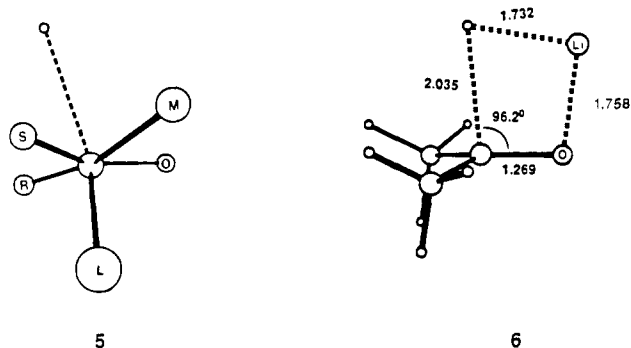
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Compound	Reagent	Stereochemistry	
		Expt.	Calc.
7a. L=C ₆ H ₁₁ , R=Me	LAH	62 : 38	69 : 31
b. R=Et	LAH	67 : 33	72 : 28
c. R=i-Pr	LAH	80 : 20	79 : 21
d. R=t-Bu	LAH	62 : 38	80 : 20
e. L=Ph, R=Me	LAH	74 : 26	60 : 40
f. R=Et	LAH	76 : 24	67 : 33
g. R=i-Pr	LAH	83 : 17	79 : 21
h. R=t-Bu	LAH	98 : 2	94 : 6
8a. R=Me	LAH	97 : 3	93 : 7
b. R=H	MeMgBr	45 : 55	36 : 64
9a. R=Me	LAH	50 : 50	35 : 65
b. R=Et	LAH	68 : 32	46 : 54
c. R=i-Pr	LAH	72 : 28	58 : 42
d. R=t-Bu	LAH	15 : 85	30 : 70
e. R=Ph	LAH	5 : 95	7 : 93
10a. R=H	LAH	88-91 : 12-9	88 : 12
b. R=Me	LAH	95 : 5	90 : 10
11a. R ₁ =Me, R ₂ =R ₃ =R ₄ =R ₅ =H	LAH	60-82 : 40-18	82 : 18
b. R ₁ =R ₂ =Me, R ₃ =R ₄ =R ₅ =H	LAH	62 : 38	73 : 27
c. R ₃ =Me, R ₁ =R ₂ =R ₄ =R ₅ =H	LAH	84-87 : 16-13	88 : 12
d. R ₃ =R ₄ =R ₅ =Me, R ₁ =R ₂ =H	LAH	20-48 : 80-52	30 : 70
12a. X=CH ₂	LAH	91 : 9	89 : 11
b. X=O	LAH	94 : 6	96 : 4
c. X=S	LAH	15 : 85	9 : 91
a. X=CH ₂	MeMgI	45 : 55	68 : 32
b. X=O	MeMgI	98 : 2	94 : 6
c. X=S	MeMgI	7 : 93	3 : 97
13a. R ₁ =Me, R ₂ =R ₃ =R ₄ =H	LAH	74-84 : 26-16	70 : 30
b. R ₃ =Me, R ₁ =R ₂ =R ₄ =H	LAH	40-27 : 60-73	46 : 54
c. R ₁ =R ₂ =Me, R ₃ =R ₄ =H	LAH	----	93 : 7
d. R ₃ =R ₄ =Me, R ₁ =R ₂ =H	LAH	90 : 10	73 : 27

Figure 2. Comparisons of experimental and calculated¹⁶ isomer ratios.

In the Felkin-Anh model, **5**, the largest alkyl group is anti to the attacking nucleophile. Calculations show that when the

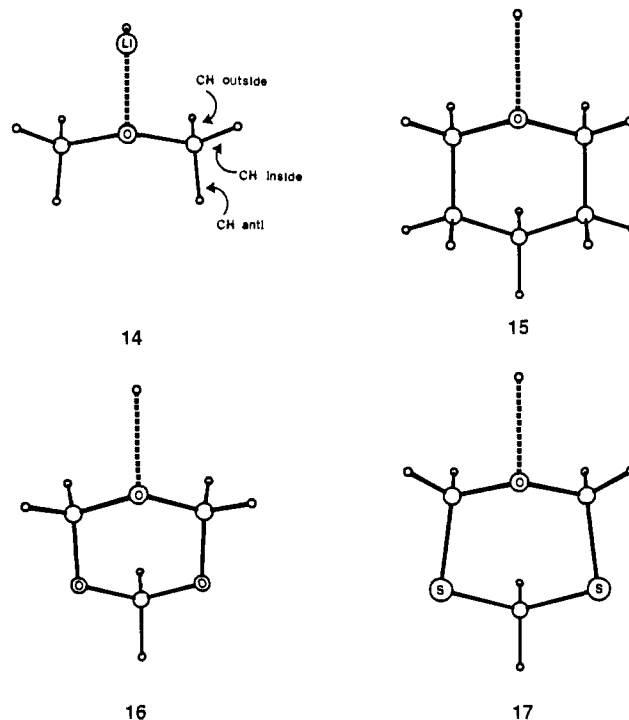


stereogenic α -carbon is secondary, the preferred transition-state geometry has one anti alkyl and one inside alkyl, because when alkyls are placed outside and inside, they cannot simultaneously achieve their preferred dihedral angles. Thus, in spite of the fact that an anti CH is preferred relative to an anti CC, the largest alkyl group prefers to be anti to the attacking nucleophile, as in **5**.

When the energetic effects embodied in **1-4** are implemented into Allinger's MM2 force field,¹⁴ this model accounts quantitatively for the stereoselectivity of LiAlH₄ reductions.¹⁵ For the

natural transition structure geometry, the ab initio transition structure of the LiH-acetone reaction, **6**, was used. The metal cation was removed in the computational model.¹⁶ The conformational preferences of the α -substituent shown in Figure 1 were incorporated into the model by redefining the torsional parameters for dihedral angles about the C _{α} -C_{CO} bond. If normal torsional effects are used, the results are qualitatively correct, but the predicted stereoselectivity is lower than found experimentally. Figure 2 shows a comparison of predicted and experimental results for LAH reductions and some methyl Grignard additions.¹⁶ There is excellent agreement for acyclic, cyclic, and bicyclic ketones. For acyclic systems, we differ from Felkin's model only in that it is M and L, not S and M, which trade places in the transition state leading to the minor product, as in the Karabatsos model.³

The stereochemistry of cyclohexanone reductions arises from torsional effects which were identified by Felkin.⁴ In the absence of steric hindrance, axial attack is preferred in order to minimize torsional repulsion. Structure **14** is an end-on view of **6**. The two outside C-H bonds are nearly parallel in **14**. The formation of



a six-membered ring by replacement of these two CH bonds with a trimethylene fragment gives a transition state corresponding to axial attack and can be achieved without introducing any significant ring strain. However, the two anti C-H bonds are not parallel. There must be rotation about the two C _{α} -C_{CO} bonds and introduction of some torsional strain in order to form **15**, the transition state for equatorial attack. A C-O bond is shorter than a C-C bond, and the torsional strain in the transition structure for equatorial attack, **16**, is even more significant relative to that for axial attack. The 1,3-dithian-5-one (**12c**) gives high equatorial attack stereoselectivity. A C-S bond is longer than a C-C bond, and torsional problems are absent in the transition structure of equatorial attack, **17**, but the transition structure for axial attack has torsional strain.¹⁷

In summary, electronic effects cause an anti CH to be preferred over an anti CC. The Felkin torsional model, combined with steric effects, accounts quantitatively for the stereoselectivities of nu-

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cleophilic additions to alkyl ketones.¹⁸

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Synthesis and Structure of a Diiron Divinylidene Complex Formed by Oxidative Carbon-Carbon Coupling

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Received June 27, 1986

Revised Manuscript Received November 15, 1986

Transition-metal vinylidene complexes and higher metal-lacumulenes¹ are carbon-rich species which model reactive intermediates formed from surface carbides in heterogeneously catalyzed CO reduction and acetylene conversion reactions.² Of particular interest are reactions in which carbon-carbon bonds are formed, modeling hydrocarbon chain growth or graphite layer formation. We report here an oxidatively induced coupling of iron vinylidene complexes.

On the basis of Gladysz's conversion of methylene to form-aldehyde on rhenium,³ we anticipated that reactions of cationic iron vinylidene complexes⁴ $[\text{Fe}(\text{C}=\text{CR}_2)(\text{PR}_3)_2(\text{Cp})]^+$ with oxygen atom donors would lead to ketene complexes $[\text{Fe}(\text{O}=\text{C}=\text{CR}_2)(\text{PR}_3)_2(\text{Cp})]^+$. However, $[\text{Fe}(\text{C}=\text{CMe}_2)(\text{dppe})(\text{Cp})]^+$ does not react with either trimethylamine *N*-oxide or iodosobenzene, and $[\text{Fe}(\text{C}=\text{CHMe})(\text{dppe})(\text{Cp})]^+$ (**1**) is simply deprotonated by Me_3NO .⁴ The reaction of $[\text{Fe}(\text{C}=\text{CHMe})(\text{dppe})(\text{Cp})][\text{BF}_4]$ (**1**, 0.39 g, 0.60 mmol) with iodosobenzene⁶ (1.2 g, 5.45 mmol) in acetonitrile (20 mL) under nitrogen at room temperature for 4 h, followed by evaporation and recrystallization of the residue from dichloromethane/ethyl ether, gave deep red-purple crystals of $[\text{Fe}_2(\mu\text{-C}_4\text{Me}_2)(\text{dppe})_2(\text{Cp})_2][\text{BF}_4]$ (**2**, 0.30 g, 77%).⁷ The most striking feature of the X-ray crystal structure⁸ of **2** (Figure 1)

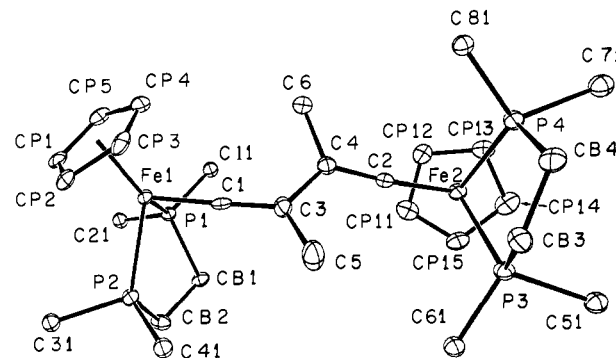


Figure 1. ORTEP²⁰ plot of the central portion of the cation in $[\text{Fe}_2(\mu\text{-C}_4\text{Me}_2)(\text{dppe})_2(\text{Cp})_2][\text{BF}_4]$; showing 50% probability ellipsoids. Phenyl groups are abbreviated for clarity. Important distances (Å) and angles: Fe1-C1 1.746 (9), Fe1-P1 2.222 (3), Fe1-P2 2.223 (3), Fe2-C2 1.766 (9), Fe2-P3 2.207 (3), Fe2-P4 2.201 (3), C1-C3 1.33 (1), C3-C4 1.50 (1), C3-C5 1.54 (1), C2-C4 1.32 (1), C4-C6 1.52 (1); C1-Fe1-P1 88.6 (3)°, C1-Fe1-P2 92.6 (3)°, C2-Fe2-P3 96.8 (3)°, C2-Fe2-P4 88.7 (3)°, Fe1-C1-C3 174.9 (7)°, C1-C3-C4 120.4 (9)°, C1-C3-C5 121.0 (9)°, C4-C3-C5 118.4 (8)°, Fe2-C2-C4 170.0 (8)°, C2-C4-C3 123.7 (8)°, C2-C4-C6 118.3 (8)°, C3-C4-C6 118.0 (8)°.

is that the $\text{C}_\beta\text{-H}$ bonds of **2** equify of **1** have been replaced by a carbon-carbon bond. A 2,3-dimethyl-1,3-butadien-1,4-diylidene ligand bridges the two iron atoms. The configuration at the C3-C4 single bond is *s*-trans (the C1-C3-C4-C2 torsional angle is -150.7°). The predicted dihedral angle between the symmetry plane of a $[\text{FeL}_2(\text{Cp})]$ group and an attached vinylidene ligand is 90° .^{1,9,10} The (CP0-Fe-C1)¹¹ to (C1-C3-C4-C5) dihedral angle in **2** is exactly 90.0° , whereas the (CP10-Fe-C2)¹¹ to (C2-C4-C3-C6) dihedral angle of 117.2° deviates considerably. This may be due to steric crowding, since there are close (3.5-3.8 Å) intramolecular contacts between methyl groups (C5 and C6) and the aromatic rings of the dppe ligands. The 27° twisting of the vinylidene ligand on Fe2 may account for the lengthening of Fe2-C2 relative to Fe1-C1, due to less effective orbital overlap.

The formation of **2** is evidently due to one-electron oxidation of vinylidene complex **1**, which can also be effected by using copper(II) acetate in methanol. $[\text{Fe}(\text{C}=\text{CHPh})(\text{dppe})(\text{Cp})][\text{PF}_6]$ is also oxidatively coupled in this way, but $[\text{Fe}(\text{C}=\text{CH}_2)(\text{dppe})(\text{Cp})][\text{PF}_6]$ gives a mixture of products. One-electron oxidation of $[\text{FeXL}_2(\text{Cp})]$ (X = halide, Me, SnMe₃, etc.; L = CO, phosphine, phosphite, isonitrile) complexes leading to low-spin iron(III) complexes has been studied by several groups.¹³⁻¹⁶ In

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(8) Crystal data for **2**: crystal dimensions 0.4 × 0.4 × 0.5 mm; Enraf-Nonius CAD4 diffractometer; Mo K α radiation; 8088 reflections collected, 4716 with $(F_o)^2 \geq 3\sigma(F_o)^2$ used; space group $P2_1/n$; $Z = 4$; $a = 11.763$ (5) Å, $b = 28.05$ (1) Å, $c = 18.739$ (6) Å, $\beta = 102.33$ (3)°, $V = 6040.9$ Å³, $\rho_{\text{calcd}} = 1.419$ g·cm⁻³, $\mu = 6.70$ cm⁻¹. The structure was solved by using MULTAN 77 and difference Fourier methods. Least-squares refinement with isotropic phenyl carbons, fixed hydrogens, and all other atoms anisotropic led to $R = 7.6\%$ and $R_w = 9.0\%$.

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