The terminal Ti-H distance is similar to bridging Ti-H distances (1.7-1.8 Å) found in titanium(III) alumino- or borohydrides.[21]

While the reaction chemistry of this and related hydrides[22] promises to be interesting, extension of this study to zirconocene and hafnocene dicarbonyls will be especially desirable since zerovalent carbonyls of these elements are either extremely rare (Zr) or nonexistent (Hf).[23,24]

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Supplementary Material Available: Details of the X-ray structural analysis, a drawing of independent molecule A of the unit cell, and tables of positional parameters and their esds, general temperature factor expressions, and bond lengths and angles for $C_5H_5Ti(CO)_2(dmpe)H$ (15 pages); tables of observed and calculated structure factors for $C_5H_5Ti(CO)_2(dmpe)H$ (12 pages). Ordering information is given on any current masthead page.

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Origin of Enhanced Axial Attack by Sterically Undemanding Nucleophiles on Cyclohexenones

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Small nucleophiles, such as lithium aluminum hydride (LAH), undergo predominantly axial nucleophilic additions to cyclohexanones[2] and this axial selectivity is substantially enhanced in 2-cyclohexenones.[3-6] We have applied our recently developed computational model[2a] to this problem and show that the torsional explanation of Felkin[2c] quantitatively accounts for these phenomena.

Different explanations have been offered previously. Toromanoff concluded that axial attack on cyclohexenones is preferred because this maintains continuous overlap of the forming bond with the π system.[3] Baldwin proposed that the approach vector of nucleophiles on enones was different from saturated ketones and caused greater steric preference for axial attack.[4]

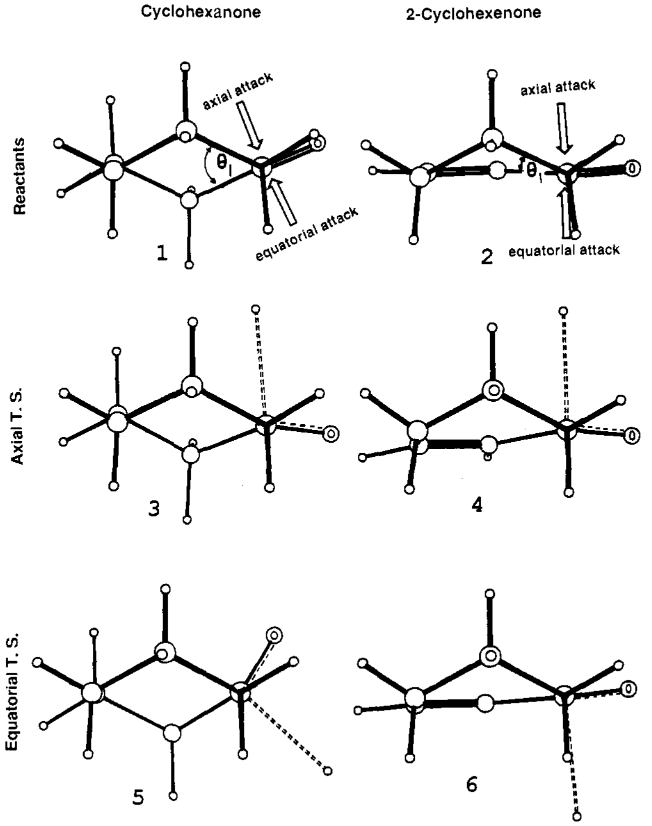

Figure 1. Newman projections along the C_2C_1 bonds for cyclohexanone, **1**, and 2-cyclohexenone, **2**, and for the transition structures for the axial and equatorial attack of hydride on cyclohexanone, **3** and **5**, and 2-cyclohexenone, **4** and **6**. The drawings are constructed with the modified MM2 model described in the text.

Alkynyllithium reagents typically give axial selectivities of about 6-8:1 with saturated ketones[6] but greater than 20:1 with enones.[5] Metalated acetonitriles show typical axial preferences with conformationally rigid cyclohexanones of 5-7:1 but greater than 20:1 with the corresponding enones.[7]

We have previously reported a modified MM2 model which reproduces ratios of attack of LAH upon the axial and equatorial positions of cyclohexanones.[2a] For cyclohexenones, the only new parameters required define the torsional energies for rotation about the C_1C_2 bond. The V_2 torsional parameters for dihedral angles $O{=}C{-}C{=}C$ and $O{=}C{-}C_{sp^2}{-}H(C)$ are set to 2.0 mdyn/deg. This causes the enone to be approximately coplanar in transition states. When these parameters are reduced to zero, thus removing

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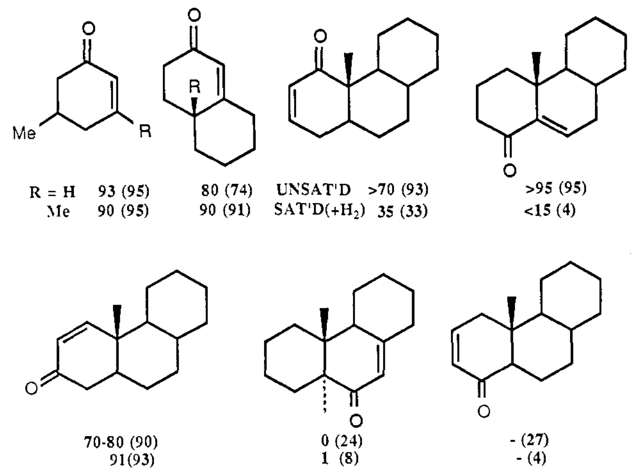


Figure 2. Experimental[4] (calculated) percentages of axial attack on cyclohexanones and cyclohexenones.

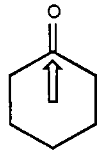
the coplanarity restraint of the enone, the predicted stereochemistry resembles that of the analogous cyclohexanones.

Figure 1 shows Newman projections sighting along the C_2C_1 bond of cyclohexanone, **1**, and 2-cyclohexenone, **2**, and of the transition states for axial and equatorial attack by hydride on these species. Even in the reactants, it is clear that the introduction of a double bond has greatly modified the dihedral angles along these bonds. In particular, the "internal dihedral", marked θ_i in the drawings, has decreased from its value of 51° in cyclohexanone to 22° in 2-cyclohexenone. This geometrical change results in a pronounced difference in torsional interactions upon axial and equatorial attack, which are designated qualitatively by arrows drawn perpendicular to the carbonyl plane in the drawings **1** and **2** in Figure 1.

The modified MM2 force field predicts that structures **3** and **5** in Figure 1 differ in energy by 1.2 kcal/mol, implying that the axial/equatorial attack ratios for hydride reduction of simple cyclohexanones should be 88:12 at 25°. Experimentally, these are 84–97:16–3.[2] Axial attack on cyclohexanone, **3**, occurs with less eclipsing of the forming H–C bond as compared to equatorial attack, **5**, as proposed by Felkin. With cyclohexenone, the difference between axial attack **4** and equatorial attack **6** is even more pronounced. Therefore, the axial/equatorial energy difference increases from 1.2 kcal/mol between **3** and **5** to 2.0 kcal/mol between **4** and **6**. At 25°, this corresponds to a 97:3 ratio.

How does this rationalization compare with the alternative proposals by Toromanoff and Baldwin? Our model indicates that overlap of the forming bond with the adjacent π bond is maintained upon axial attack as proposed by Toromanoff. However, the overlap is also maintained upon equatorial attack but is accompanied by severe torsional problems.

Baldwin proposed that the approach vector is different in ketones and α,β-unsaturated ketones.[4] The proposed approach vectors for cyclohexanone and cyclohexenone are shown in **7** and **8**. Our computations provide no support for this contention.



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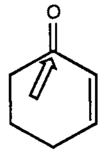

8

When a hydride is fixed 1.5 or 2 Å from the carbonyl carbon of acrolein or of acetaldehyde and full optimizations are carried out, a 0–3° tilt of hydride toward hydrogen is found. Furthermore, our force field model, which predicts no alteration of approach vector in unsaturated ketones, gives excellent semiquantitative agreement with experimental LAH stereoisomer ratios for reactions of a variety of cyclohexanones and the corresponding cyclohexenones (see Figure 2).

Although for rigid cyclohexenones, the stereoselectivity is higher than for rigid cyclohexanones, cyclohexenones with small alkyl substituents may react with low stereoselectivity. For example, our model predicts that 4-methyl-2-cyclohexenone will react with low selectivity, since the transition state with a quasi-axial 4-methyl substituent is only 0.7 kcal/mol higher in energy than that with a quasi-equatorial 4-methyl group.

To verify that the differences in selectivity really can arise from changes in staggering about the C_1C_2 bond, we calculated the rotational barrier about the single bond of acetone in the ab initio transition structure for the addition of lithium hydride to acetone.[2a] Although the H---C bond is only partially formed, the rotational barrier is 3.2 kcal/mol by these calculations. This is more than enough to indicate that the energy differences among the transition structures **3–6** can be accounted for by torsional effects. This applies to hydride, acetylide, and cyanomethyl anion additions.

In summary, we have found that the high stereoselectivity in nucleophilic additions of unhindered nucleophiles to cyclohexenones can be accounted for quantitatively in terms of a torsional model such as proposed by Felkin to rationalize cyclohexanone stereoselectivities.[2c]

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The Crystal Structures of Two Cesides Show That Cs$^-$ Is the Largest Monotomic Ion

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Although we have synthesized over 30 alkalides and eight electrides since the first sodide Na$^+$(C222)·Na$^-$ (C222 = cryptand[2.2.2]) was prepared in 1974,[1,2] only recently have suitable crystal-growing and -handling techniques been developed for single-crystal structure determinations.[3,4] The ceside, Cs$^+$(18C6)$_2$·Cs$^-$ (I) (18C6 = 18-crown-6) was characterized by optical and solid-state NMR methods.[5-8] Polycrystalline samples of a second ceside, Cs$^+$(C222)·Cs$^-$ (II), were first thought to contain no ceside anions because the expected Cs$^-$ peak was not seen in the ^{133}Cs MAS-NMR spectrum.[9] We report here the crystal structures of both cesides, which permit assignment of an effective average radius of 3.5 Å for Cs$^-$ and which may explain the presence of a Cs$^-$ NMR peak in I and its absence in II.

Polycrystalline samples were prepared as previously described.[10] Saturated solutions in dimethyl ether–trimethylamine mixtures which contained a number of seed crystals were cooled from –45

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