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KINETIC ISOTOPE EFFECT PROBE FOR THE π-FACIAL STEREOSELECTIVITY IN NUCLEOPHILIC ADDITIONS TO CYCLOHEXANONE: A THEORETICAL STUDY

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The origin of the π-facial selectivity in nucleophilic additions to cyclohexanone was analysed by means of *ab initio* MO calculations (MP2/6–31G*//HF/6–31G*). The calculations showed that BH_3 attacks at the axial side whereas MeLi attacks at the equatorial side. Calculated kinetic and equilibrium deuterium isotope effects and the structures of the transition states (TSs) demonstrated that four factors, stabilization of the axial TS by antiperiplanar allylic bonds, destabilization of the equatorial TS by torsional strain, destabilization of the axial TS by steric hindrance between a nucleophile and the 3,5-axial hydrogens and destabilization due to the conformational deformation of the ring in both the equatorial and axial TSs, operate in the same direction and can bring about the apparent selectivity changeover. The magnitudes of *anti*-D KIEs for the MeLi and the EtLi additions to acetone were consistent with the Anh–Eisenstein model rather than the Cieplak model.

INTRODUCTION

The π-facial selectivity of nucleophilic additions to cyclohexanone is known to vary with nucleophiles; one class of nucleophiles afford equatorial alcohol selectively whereas the others give axial alcohol. Several concepts have been presented to rationalize such π-facial selectivity. These include product development control,[1] torsional strain at the equatorial transition state (TS),[2] carbonyl π and π^* orbital distortion[3–5] and stabilization by the antiperiplanar allylic bonds at the axial TS.[6,7] Recent theoretical[8–11] and experimental[12–14] studies have been devoted to interpreting the π-facial selectivity in terms of various TS models, which include the Felkin–Anh[2,7,15,16] and Cieplak[6] hypotheses, and the investigations are still continuing.

In this study, we carried out molecular orbital (MO) calculations of the reactions of cyclohexanone with a pair of nucleophiles, and determined kinetic and equilibrium isotope effects (KIE and EIE) for these reactions; these IEs can be used as a measure of possible TS structural variations of the reactions. Specifically, two nucleophiles are chosen such that one reacts selectively at the axial position and the other at the equatorial position. The investigation was focused on the origin of the overall stereochemical changeover: why does one nucleophile gives more equatorial alcohol (axial attack) and the other more axial alcohol (equatorial attack)?

COMPUTATIONS AND RESULTS

Both equatorial and axial TSs and product alcohols were fully optimized for the reactions of BH_3 and MeLi with cyclohexanone. The reactions of BH_3, MeLi, EtLi, B_2H_6 and MeLi dimer with acetone were also considered for comparison purposes. The following abbreviations are used: MeLi.ax.ts, MeLi.eq.ts, BH_3.ax.ts, and BH_3.eq.ts for the TSs of MeLi addition at the axial side, MeLi addition at the equatorial side, BH_3 addition at the axial side and BH_3 addition at the equatorial side, respectively, to cyclohexanone, and Ac.MeLi.ts, Ac.BH_3.ts and Ac.EtLi.ts for the TSs of MeLi, BH_3 and EtLi addition to acetone. All calculations were carried out with the Gaussian 92 program,[17] and geometries were optimized, unless noted otherwise, at the HF/6–31G* level[18] by using gradient procedures. Calculated geometries are shown in Figures 1 and 2 and important geometrical parameters of the TSs and the products are summarized in Table 1.

Vibrational analyses were performed in order to characterize stationary points as minima or saddle points, and the geometries were further used to calculate energies at the second-order Møller–Plesset perturbation (MP2) level.[19] Zero-point correction was made after scaling by 0·9 for overestimation of the HF frequencies. In Table 2 are listed the relative (axial vs equatorial) barrier heights and energies for the reactions

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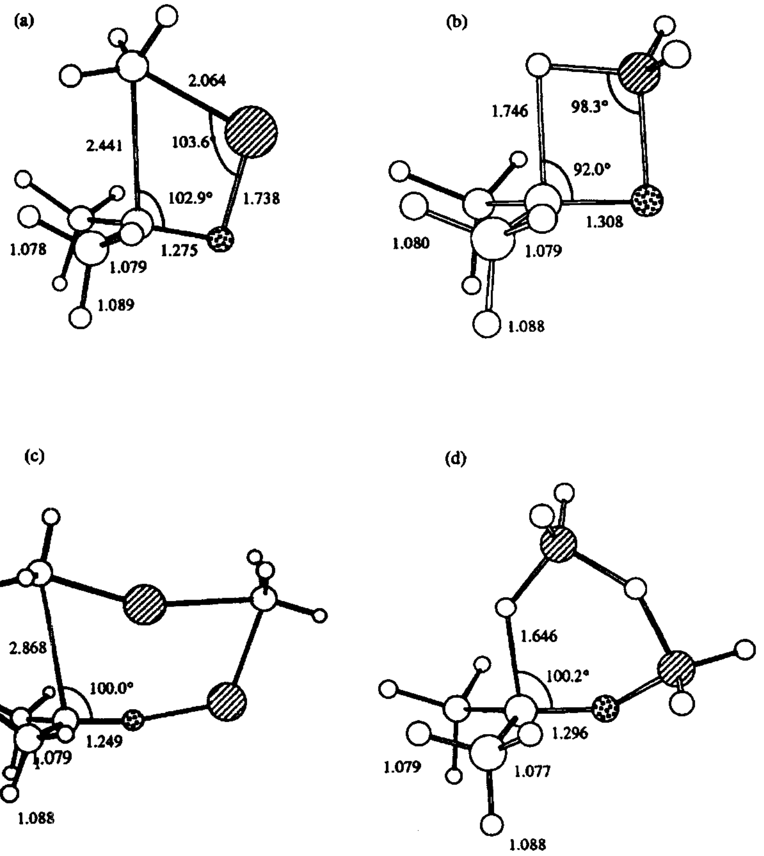


Figure 1. Geometries of transition states of the reactions of acetone with (a) MeLi (reaction-coordinate frequency, $335i\ \mathrm{cm}^{-1}$; $\mathrm{NuC}_\alpha\mathrm{C}_\beta\mathrm{H}_{\mathrm{anti}}$ dihedral angle = 170·9°), (b) BH_3 ($704i\ \mathrm{cm}^{-1}$; 178·0°), (c) MeLi dimer ($146i\ \mathrm{cm}^{-1}$; 161·2° and (d) $\mathrm{B}_2\mathrm{H}_6$ ($716i\ \mathrm{cm}^{-1}$; 179·0°), calculated at the HF/3–21G level. All angles are in degrees and bond distances in Å

of cyclohexanone with the two nucleophiles. Kinetic and equilibrium IEs were computed from the scaled HF vibrational frequencies by using Bigeleisen's equation [equation (1)], where u stands for $h\nu/kT$ and $\nu_L{}^*$ is the reaction coordinate frequency.[20] The calculated IEs are summarized in Table 3.

$$\frac{k_1}{k_2}=\left(\frac{\nu^*_{L1}}{\nu^*_{L2}}\right)\prod_i^{3n^*-7}\left(\frac{u_{1i}{}^*}{u_{2i}{}^*}\times\frac{e^{-u_{1i}{}^*/2}}{e^{-u_{2i}{}^*/2}}\times\frac{1-e^{-u_{2i}{}^*/2}}{1-e^{-u_{1i}{}^*/2}}\right)$$

$$\times\prod_i^{3n-6}\left(\frac{u_{2i}}{u_{1i}}\times\frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}}\times\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}\right)\qquad(1)$$

DISCUSSION

The first step is to find a pair of nucleophiles which exhibit different π-facial selectivities. It was found that BH_3 and MeLi fit this requirement. Table 2 shows that BH_3.ax.ts is 1·2 kcal mol^{-1} (1 kcal = 4·184 kJ) lower in energy than BH_3.eq.ts, while MeLi.ax.ts is higher than MeLi.eq.ts by 1·7 kcal mol^{-1}; hence the two nucleophiles have different selectivities. It is interesting that, for the BH_3 addition, the axial alcohol (equatorial attack) is more stable than the equatorial alcohol by 2·4 kcal mol^{-1}. This indicates that there is some additional stabilization at the axial TS relative to the equatorial TS. In contrast, for the MeLi addition, the axial alcohol (equatorial attack) is more stable only by 1·4 kcal mol^{-1} than the equatorial alcohol. Hence the equatorial preference is larger in the TS than in the product, which indicates that there are some factors that destabilize the axial TS relative to the equatorial TS for the MeLi addition reaction.

It is noteworthy that the calculated trend agrees with the experimental selectivities. Thus, the reactions of MeLi with 4-*tert*-butylcyclohexanone and 3,3,5-trimethylcyclohexanone are known to proceed selectively via the equatorial attack to give axial : equatorial alcohol

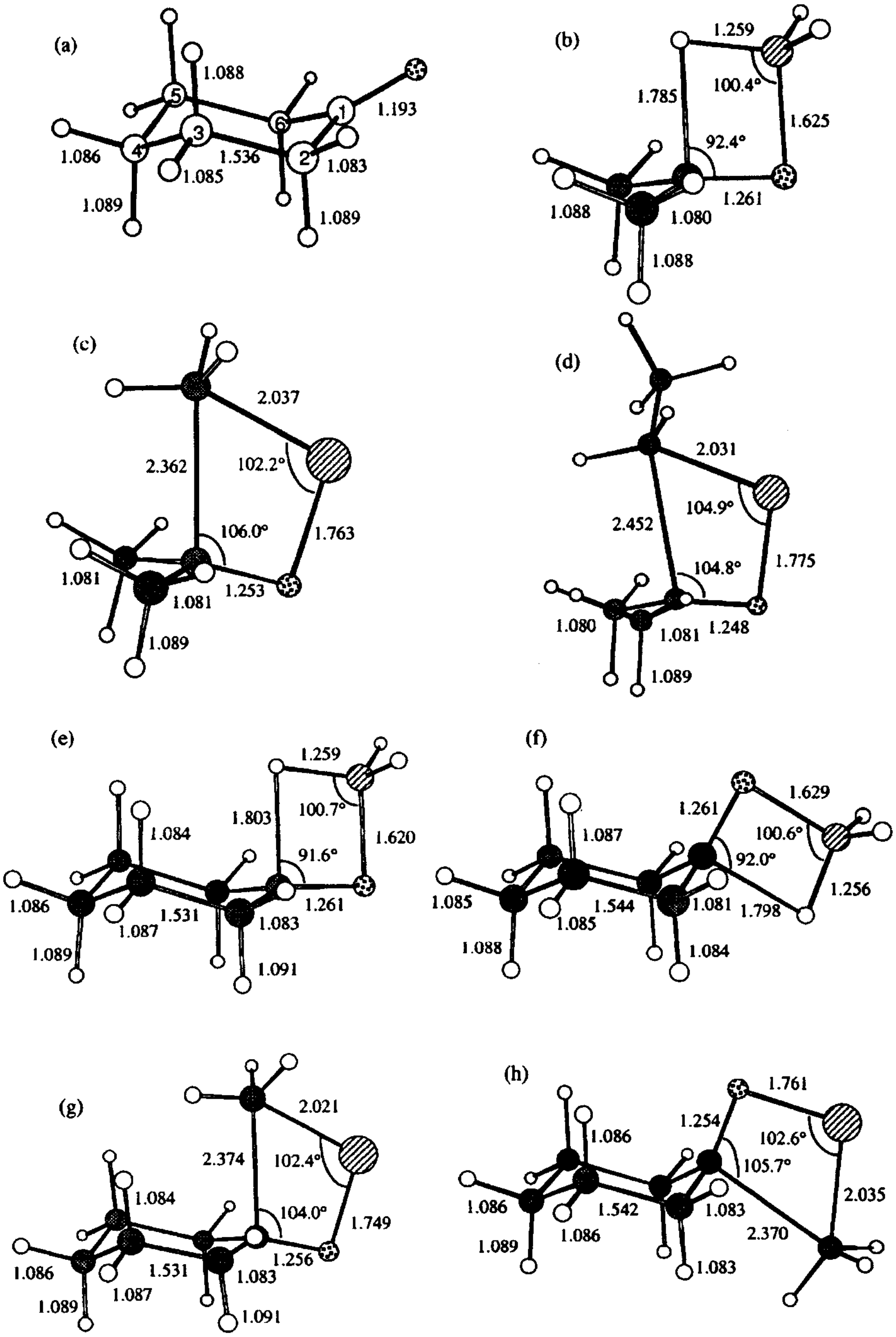


Figure 2. Geometries of cyclohexanone and the transition states: (a) cyclohexanone, (b) Ac.BH$_3$.ts (reaction-coordinate frequency, 561i cm^{-1}), (c) Ac.MeLi.ts (353i cm^{-1}), (d) Ac.EtLi.ts (262i cm^{-1}), (e) BH$_3$.ax.ts (524i cm^{-1}), (f) BH$_3$.eq.ts (531i cm^{-1}), (g) MeLi.ax.ts (356i cm^{-1}) and (h) MeLi.eq.ts (336i cm^{-1}), calculated at the HF/6–31G* level. For abbreviations, see text. All angles are in degrees and bond distances in Å

Table 1. Selected geometric parameters of the transition states, products and cyclohexanone[a]

Species[b]	Dihedral angle $NuCCH_{ax}$	Dihedral angle $OCCH_{eq}$	Angle NuCO	Dihedral angle $C_6C_1C_2C_3$ (δ)	Angle ϕ[c]
Cyclohexanone		7·6		49·0	44
BH_3.ax.ts	176·2	33·9	91·6	39·4	35
BH_3.ax.add	176·4	55·0	104·3	56·0	52
BH_3.eq.ts	47·4	25·3	92·0	61·2	56
BH_3.eq.add	54·2	56·7	108·5	53·5	49
MeLi.ax.ts	171·4	52·2	104·0	32·6	30
MeLi.ax.add	169·0	64·9	108·4	51·3	44
MeLi.eq.ts	43·4	35·0	105·7	61·6	57
MeLi.eq.add	53·3	57·0	109·5	55·7	49
	Dihedral angle $NuCCH_{anti}$	Dihedral angle $NuCCH_{inside}$	Dihedral angle $OCCH_{inside}$	Angle NuCO	
Ac.BH_3.ts	178·2	64·2	32·9	92·4	
Ac.BH_3.add	178·5	60·9	53·0	104·2	
Ac.MeLi.ts	173·0	69·6	41·6	106·0	
Ac.MeLi.add	179·7	60·9	41·6	106·0	
Ac.MeLi.add	179·7	60·9	59·3	109·6	
Ac.EtLi.ts	171·3	71·2	38·2	104·8	
Ac.EtLi.add	175·2	57·0	61·6	107·9	

[a] Angles in degree.

[b] For abbreviations, see text; subscript add refers to addition products.

[c] An angle between two planes, $C_2C_3C_5C_6$ vs $C_6C_1C_2$ for cyclohexanone.

Table 2. Relative reaction energies and barrier heights for BH_3 and MeLi additions to cyclohexanone

Reagent	$\delta\Delta E$[a]	$\delta\Delta E_a$[b]
BH_3	2·4	−1·2
MeLi	1·4	1·7

[a] $\delta\Delta E = \Delta E(\text{axial}) - \Delta E(\text{equatorial})$, kcal mol^{-1}.

[b] $\delta\Delta E_a = \Delta E_a(\text{axial}) - \Delta E_a(\text{equatorial})$, kcal mol^{-1}.

ratios of 65:35 and 100:0, respectively, in diethyl ether.[21] On the other hand, an analogous reaction of BH_3 with 2-methylcyclohexanone in THF gives the equatorial alcohol (via the axial attack) as the major product (26:74).[22] The fact that the model reactions considered here with monomeric nucleophiles exhibited the same selectivities with experiments in which the nucleophiles are believed to react as dimers or tetramers is interesting and may be rationalized by the observation that the TSs have similar characteristics for the monomer pair and the dimer reaction pair as shown in Figure 1. In particular, the C–O bond is longer and the $NuC_\alpha C_\beta H_{anti}$ dihedral angle is longer for BH_3 than MeLi; the same is true for the B_2H_6 and MeLi dimer pair.

Here we consider four factors that may control the π-facial selectivity, (1) stabilization of the axial TS by antiperiplanar allylic bonds, (2) destabilization of the equatorial TS by torsional strain, (3) destabilization of the axial TS by steric hindrance between a nucleophile and the 3,5-axial hydrogens and (4) destabilization due to the conformational deformation of the ring at both the equatorial and axial TSs, and consider which factors are responsible for the experimental selectivity.

A secondary deuterium isotope effect is a sensitive tool for examining the conformational and bonding changes at the labelled hydrogen. It would be normal (larger than unity) if the C–H(D) bond is weakened on going from the initial state to the TS. Whereas it would be inverse (smaller than unity) if the bond is strengthened at the TS,[23] hence the presence of the antiperiplanar effect can be monitored by the deuterium KIE of the β-H_{ax} (cyclohexanone) or β-H_{anti} (acetone). It is also known that steric compression at the C–H(D) bond at the TS makes a D KIE inverse.[23] Therefore, D KIEs can be a good probe for the presence of steric effects.

Stabilization by antiperiplanar allylic bonds

In the Cieplak model,[6] electron donation from the antiperiplanar σ orbitals to the σ_*^* orbital, the low-lying vacant orbital of the forming bond, is assumed to stabilize the axial TS, while the Anh–Eisenstein model[7] considers the interaction between the σ^* orbital of the allylic bonds and the σ_* orbital of the forming bond through the $\pi_{C=O}^*$ orbital. In either case, conformation

Table 3. Deuterium and carbon-13 kinetic and equilibrium isotope effects for carbonyl additions[a]

Species[b]	α-D_{ax}	α-D_{eq}	β-D_{ax}	β-D_{eq}	$^{13}C=O$
BH_3.ax.ts	1·020	0·966	0·971	0·990	1·036
	(1·004)	(1·002)	(1·000)	(1·000)	(1·012)
BH_3.ax.add	0·875	1·010	1·021	1·012	1·016
BH_3.eq.ts	0·870	0·952	0·977	0·999	1·039
	(1·002)	(1·000)	(1·002)	(1·000)	(1·011)
BH_3.eq.add	0·898	1·018	0·962	1·005	1·014
MeLi.ax.ts	0·973	1·025	0·938	1·004	1·039
	(1·008)	(1·003)	(1·003)	(1·003)	(1·014)
MeLi.ax.add	0·916	1·072	1·019	1·050	1·016
MeLi.eq.ts	0·842	1·010	0·972	1·019	1·036
	(1·003)	(1·000)	(1·000)	(1·000)	(1·009)
MeLi.eq.add	0·911	1·062	1·014	1·041	1·011
	α-D_{anti}	α-D_{inside}	α-$D_{outside}$	$^{13}C=O$	
Ac.BH_3.ts	1·028	0·963	0·871	1·031	
	(1·005)	(1·000)	(1·002)	(1·013)	
Ac.BH_3.add	0·882	1·012	0·914	1·015	
Ac.MeLi.ts	1·010	1·018	0·847	1·033	
	(1·009)	(1·003)	(1·003)	(1·014)	
Ac.MeLi.add	0·937	1·066	0·933	1·004	
Ac.EtLi.ts	1·022	1·014	0·843	1·032	
	(1·008)	(1·000)	(1·000)		
Ac.EtLi.add	0·929	1·079	0·911	1·006	

[a] D KIEs are per D_2. Numbers in parentheses are the contributions from the reaction coordinate frequencies.
[b] For abbreviations, see text; subscript add refers to addition products.

closer to the antiperiplanar alignment of an incoming nucleophile and the C_α–H_{ax} bond of cyclohexanone is expected to have a larger stabilizing effect at the axial TS.

The KIEs for additions to acetone are informative (Table 3). For the BH_3 addition, the *anti*-D KIE is normal (1·028) but KIEs of the inside D (0·963) and the outside D (0·871) are inverse. Although the D_{anti} KIE of 1·028 appears to be small, the antiperiplanar effect is in fact sizable when compared with the magnitude of the EIE of 0·882. If there is no special effect in the TS, the magnitude of the secondary KIE should be somewhere between 1·0 and an EIE; thus, the comparison of D_{anti} KIE with D_{anti} EIE suggests that there is an additional factor that leads the KIE to be positive. Assuming that the TS lays half way between the initial state and the product state, the additional factor that makes KIE larger may be estimated as 1·095 [$= 1{\cdot}028/(0{\cdot}882)^{1/2}$]. This effect apparently arises from the C–H_{anti} bond weakening. The C–H_{anti} bond is longer for Ac.BH_3.ts (1·089) than those for acetone (1·086) and Ac.BH_3.add (1·085), reflecting the bond weakening. The IE of 1·095 is not small as a secondary DIE, if one compares it with the β-D effect in *tert*-BuCl solvolysis, where the D_9 KIE was reported to be 2·33, corresponding to 1·10 per D_1.[24] The inverse KIEs for the inside and outside hydrogens imply that there is steric compression at these positions in the TS.

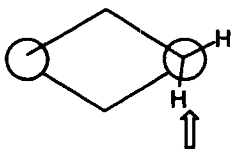
The magnitude of the D_{anti} KIE is smaller for the MeLi addition to acetone compared with the BH_3 case, which indicates that the antiperiplanar effect is smaller for MeLi. It is interesting that the D_{anti} KIE is larger for the EtLi addition than the MeLi addition. This is in accord with the Anh–Eisenstein model, that considers the electron donation from the incipient σ_* orbital to the σ^* orbital of the allylic bonds, but is inconsistent with the Cieplak model.

The α-D_{ax} KIE for the BH_3 addition to cyclohexanone (BH_3.ax.ts) is 1·020, slightly smaller than the D_{anti} KIE for the BH_3 addition to acetone. This may be due to slightly less favourable $NuCCH_{ax}$ alignment for cyclohexanone ($NuCCH_{ax}$ dihedral angle = 176·2°) than for acetone ($NuCCH_{anti}$ dihedral angle = 178·2°). On the other hand, the $NuCCH_{ax}$ dihedral angle of MeLi.ax.ts was calculated to be smaller (171·4°) and that α-D_{ax} KIE was inverse (0·973). The results indicate that the antiperiplanar effect is much smaller for the MeLi addition to cyclohexanone.

The other D KIEs for the addition reactions of cyclohexanone are similar to the corresponding KIEs for the reactions of acetone at each position. The α-D_{eq} KIE for the axial and equatorial attacks at 0·966 and 0·952 for the BH_3 addition and 1·025 and 1·010 for the MeLi addition, which are comparable to the inside D KIEs for the additions to acetone of corresponding nucleophiles. The α-D_{ax} KIEs for the BH_3 and MeLi equatorial attack to cyclohexanone at 0·870 and 0·842, respectively, which are similar in magnitude to the outside D KIEs for the reactions with acetone.

Torsional strain

The equatorial TS is considered to suffer torsional strain between incoming nucleophile and axial hydrogens (**1**),[2] and this can be monitored by the $NuC_\alpha C_\beta H_{ax}$ dihedral angle. These angles were calculated to be relatively large for both MeLi.ts.eq (43·4°) and BH_3.ts.eq (47·4°), hence this effect may not be very important. On the other hand, as is seen in Table 2, the $OCCH_{eq}$ dihedral angle at the equatorial TS is small, 25·3° at BH_3.ts.eq and 35·0° at MeLi.ts.eq. This dihedral angle is larger for the axial attack than for the equatorial attack, consistent with earlier calculations.[8,9] It is noteworthy that the dihedral angle for the additions to acetone lies between those in the axial and the equatorial TSs of the additions to cyclohexanone; this indicates larger torsional strain at the equatorial TS and smaller torsional strain at the axial TS than at the TS of the reference reaction, addition to acetone. Since the size of the $OCCH_{eq}$ dihedral angle is smaller for BH_3 than for MeLi in all cases, the destabilizing effect of the torsional strain at the equatorial TS should be smaller for the MeLi addition than for the BH_3 addition.



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Diaxial steric effect

The axial TSs become less stable when steric repulsion between an incoming nucleophile and the 3,5-diaxial hydrogens becomes larger. The D_{ax} KIEs at the β-position of cyclohexanone would be a good probe to detect the presence of steric compression. Table 3 shows that the magnitudes of the β-D IEs vary with the nucleophile and the mode of addition. For the axial attack, the product EIEs are small and normal for both BH_3 (1·021) and MeLi (1·019). By contrast, the β-D_{ax} KIE for the BH_3 attack (BH_3.ax.ts) is slightly inverse (0·971), reflecting the presence of steric compression for the β-hydrogens at the TS. Further, a much greater inverse β-D_{ax} KIE (0·938) was observed for MeLi.ax.ts; thus the steric compression is much larger at MeLi.ax.ts. The steric repulsion should make the axial TS less favourable than the equatorial TS for the MeLi addition. Two reasons may be suggested for the larger steric hindrance for the MeLi addition: (1) a Me group is bulkier than hydrogen and (2) the trajectory of the nucleophilic attack lies closer to the 3,5-diaxial hydrogens for the MeLi attack (∠NuCO = 104·0° for MeLi and 91·6° for BH_3).

Deformation of the ring

Deformation of the six-membered ring on nucleophilic additions to cyclohexanone would make the TS less stable, and may be measured by the change of dihedral angle (δ) $C_6C_1C_2C_3$ (Chart 1). The sizes of δ of cyclohexanone, the four TSs and of the four products are given in Table 1. It can be seen that the δ value increases in the products for both equatorial and axial additions and in the equatorial TSs, but decreases in the axial TSs. The excess deformation at the TSs ($\Delta\delta_{TS}$) is given by the equation

$$\Delta\delta_{TS} = \frac{1}{2}(\delta_{RT} + \delta_{ADD}) - \delta_{TS} \qquad (2)$$

$\Delta\delta_{TS}$ is zero when the δ_{TS} value lies half way between δ_{RT} and δ_{ADD}. The $\Delta\delta_{TS}$ value was calculated to be 14·5° and 12·3° for MeLi.ax.ts and BH_3.ax.ts, respectively, whereas it was 10·3° and 10·8° for MeLi.eq.ts and BH_3.eq.ts, respectively. Hence, the TSs of the axial attack, especially of MeLi, suffer larger deformation.

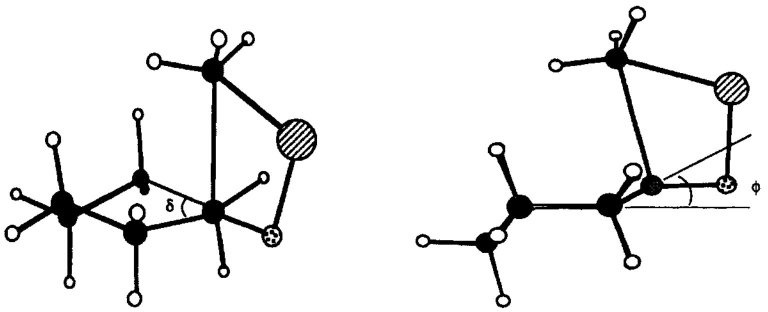

Figure 3.

Another way of looking at the extent of deformation at the TSs is to see the angle (ϕ) between the two planes defined by $C_2C_3C_5C_6$ and $C_6C_1C_2$ (Figure 3, Table 2). Here again, the angle becomes small for the axial attack, especially by MeLi.

These ring deformations are clearly related to the steric hindrance between the incoming nucleophiles and the 3,5-diaxial hydrogens at the axial TSs. Since Me is much larger than H, there should be greater steric repulsion at MeLi.ax.ts than BH_3.ax.ts, and hence the angle δ at MeLi.ax.ts becomes smaller to avoid the steric repulsion. This should make MeLi.ax.ts energetically less favourable. Furthermore, β-D_{ax} KIEs have indicated that there still remains large steric congestion at MeLi.ax.ts. Overall, the effects of diaxial steric repulsion and ring deformation are closely related to each other and both tend to make the axial TS less favourable for the MeLi addition.

CONCLUSION

We have analysed four factors (hyperconjugation of allylic bonds, torsional strain, diaxial steric repulsion and ring deformation) by means of *ab initio* MO calculations in order to see whether they can explain the different π-facial stereoselectivities in nucleophilic additions of BH_3 and MeLi to cyclohexanone. The calculated overall selectivities, the preferential axial addition by BH_3 and the equatorial addition by MeLi were analysed and were found to be rationalized in terms of these factors. The hyperconjugative stabilization as monitored by α-D_{ax} KIE shows that the stabilization for MeLi.ax.ts is smaller than that for BH_3.ax.ts. The effect of torsional strain monitored by the $OCCH_{eq}$ dihedral angle at the TSs indicates that the strain is smaller for MeLi.eq.ts than for BH_3.eq.ts. Both the 3,5-diaxial steric repulsion and the ring deformation tend to destabilize MeLi.ax.ts more than BH_3.ax.ts. The four factors operate in the same direction and give rise to the overall selectivity. Finally, the magnitudes of *anti*-D KIEs for the MeLi and the EtLi additions to acetone were found to be consistent with the Anh–Eisenstein model rather than the Cieplak model.

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