The Stereochemistry of the Addition of Trimethylaluminum to Decalones and Methyl-substituted Cyclohexanones

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The addition to the methyl-substituted 4-*t*-butylcyclohexanone was studied, providing that the β-axial methyl and α-axial methyl groups hindered the axial and equatorial attacks respectively. The results obtained with fused-ring system ketones (four decalones) were explained by considering the similar stereochemical influence of 2- and 3-methylene substituents as corresponding methyl substituents. A rapid conformation equilibrium was also considered for *cis*-decalones. In addition, the axial attack, especially at a molar ratio of two or more, was found to be hindered by the α-equatorial methyl group. This hindrance was explained by assuming the half-chair form of the cyclohexanone ring in the transition state.

The stereochemical factors of nucleophilic addition to cyclohexanone derivatives were reported for the first time by Dauben *et al.*[1] for the reduction by hydride, and two concepts, *i.e.*, "Steric Approach Control" and "Product Development Control", were proposed to explain the observed results.

Richer[2] excluded the concept of "Product Development Control" from his results on the addition reaction of small or rod-like reagents (*e.g.*, H^-, CN^-, $HC{\equiv}C^-$) to 4-*t*-butylcyclohexanone, and proposed that the steric course was determined by the relative seriousness of interactions between the entering group and 3,5-axial hydrogens. This concept was clarified by Marshall and Carroll,[3] considering the geometry of transition states.

On the other hand, Chérest and Felkin[4] considered "Steric strain" in the transition state of axial attack and "Torsional strain" in the transition state of equatorial attack, and proposed that the steric course of the reaction was controlled by the relative amounts of these strains.

Recently, the stereochemistry of the addition reaction of trialkylaluminum to substituted cyclohexanones was investigated by Ashby[5a] and our group. In these reactions, the steric course of the addition reaction was greatly dependent on the molar ratio of ketone to alkylaluminum. That is, in the reactions with the hydrocarbon solvent, it was found that the stereoselectivity changed with the reactant molar ratio. For example, in the cases of 4-*t*-butylcyclohexanone and trimethylaluminum in the benzene solvent, it was found that the amount of axial alcohol was about 75% of alcoholic products when the reactant molar ratio (Al/K) was one or less, and that the amount of equatorial alcohol was about 90% when the molar ratio was two or more.

Fig. 1.

The reaction of benzophenone with trimethylaluminum in benzene was investigated kinetically by Ashby *et al.*[6] They concluded that the reaction mechanism depended on the reactant molar ratio. When the molar ratio (Al/K) was unity, a slow unimolecular reaction proceeded through an intramolecular rearrangement of the ketone-Al complex, and when the molar ratio was two or more, a rapid bimolecular reaction took place between a second trimethylaluminum and a ketone-Al complex. 4-Centered and 6-centered transition states were proposed respectively. The relationship between the change in stereoselectivity in the cyclohexanone derivatives and the difference in mechanisms indicated by Ashby *et al.* is very interesting; it may be assumed that the equatorial attack corresponds to the unimolecular reaction, and the axial attack, to the bimolecular reaction.

In this paper, the reactions of fused-ring-system ketones (four decalones) with trimethylaluminum in a hydrocarbon solvent were investigated in order to clarify the stereochemistry of the addition reaction of trialkylaluminum to cyclohexanone derivatives. The reactions of several 2-alkylcyclohexanones with trimethylaluminum were also investigated in order to learn more details of the stereochemistry of this reaction.

Experimental

Materials. trans-*2-Decalone*:[7] $\Delta^{1(9)}$-Octalone-2 was synthesized by the method described in the literature. The reduction of $\Delta^{1(9)}$-octalone-2 (10 g) by liq. NH_3 and Li (2.5 g) gave *trans*-2-decalone. Quantitative analysis was carried out by GC. (Hitachi F6D model. Golay R45 column). Purity, 97%.

cis-*2-Decalone*: $\Delta^{1(9)}$-Octalone-2 (24.5 g) was hydrogenated in slightly acidic (HCl) aqueous ethanol on 2.5 g of a palladium-carbon (5%) catalyst.[8] The hydrogenation product was vacuum-distilled to give 19.7 g of a mixture of 90% *cis*-2-decalone and 10% *trans*-2-decalone (22 mmHg 126~127 °C). The mixture was purified by the recrystallization from *n*-pentane at about −100 °C. Purity, 99.2%.

cis-*1-Decalone*:[9] α-Naphthol, purified by vacuum distillation, was hydrogenated in acetic acid on platinum dioxide. *Cis-cis*-1-decalol (white solid, mp 89—90 °C. lit 88—89 °C) was obtained by the recrystallization of the hydrogenation product from *n*-hexane. A solution of 18.5 g of *cis-cis*-1-decalol in acetic acid (75 ml) was oxidized by a solution of 9 g of chromic acid in water. The subsequent vacuum distillation of the oxidation product afforded 88% *cis*-1-decalone. Purity, 88%. The only impurity was *trans*-1-decalone.

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trans-*1-Decalone*: The mother solution of the above-mentioned recrystallization (containing decalin, decalones, and decalols) was oxidized in acetone by a solution of chromic acid and sulfuric acid. The oxidation product, which contained decalin, *trans*-1-decalone, and *cis*-1-decalone (*trans* : *cis*~1 : 1), was chromatographed on activated alumina to afford sufficiently pure *trans*-1-decalone (*cis*-1-decalone isomerizes to *trans*-1-decalone on activated alumina). Purity, 92%.

cis-*2,6-Dimethylcyclohexanone*: A solution of 29 g of 2,6-xylenol (purified by recrystallization from *n*-hexane) in 75 ml of acetic acid was hydrogenated on 0.67 g of platinum dioxide. The hydrogenation product was oxidized in acetone by the use of chromic acid and sulfuric acid. Vacuum distillation afforded 87% *cis*-2,6-dimethylcyclohexanone (69.5—70 °C/23 mmHg). The only impurity was the *trans* isomer. The structure of the product was checked by 220 MHz NMR. Purity, 87%.

cis-*2-Methyl-4-t-butylcyclohexanone*: Essentially pure *cis*-2-methyl-*4-t*-butylcyclohexanone was obtained from 2-methyl-4-*t*-butylphenol by the procedure described above. Purity, 96%.

trans-2-*Methyl-4-t-butylcyclohexanone*: *Trans*-2-methyl-4-*t*-butylcyclohexanone was obtained by the isomerization of *cis*-2-methyl-4-*t*-butylcyclohexanone following the procedure described by Huff *et al.*[10] The product thus obtained contained about 70% *trans* isomer and 30% *cis* isomer.

4-t-Butylcyclohexanone: 4-*t*-butylcyclohexanone was synthesized by the oxidation of 4-*t*-butylcyclohexanol with chromic acid and sulfuric acid. Purity, nearly 100%.

2-Methylcyclohexanone, 2,2,6-trimethylcyclohexanone, 3,3,5-trimethylcyclohexanone: Commercially-available reagents were used without further purification.

The toluene was purified by distillation after reflux on lithium aluminum hydride under an argon atmosphere for one day.

The trimethylaluminum was obtained from the Ethyl Corporation and was used without further purification. The concentration of the trimethylaluminum solution (in toluene) was determined by the volume of methane evolved on treating an aliquot of the solution with water.

All the ketones were used as 1 mol/l solutions prepared by weighing out the calculated amount of ketone in a volumetric flask and by subsequently diluting with toluene.

Procedure: A three-necked flask equipped with a magnetic stirrer, a gas inlet, a self-sealing rubber cap, and a gas outlet connected to a bubbler was flushed with argon. Toluene (about 9 ml) and 1 ml of a ketone solution was flushed with argon. Toluene (about 9 ml) and 1 ml of a ketone solution were introduced into the flask at the reaction temperature, and then a calculated amount of trimethylaluminum solution was stirred in. After a four-hour reaction, the solution was hydrolyzed with a small piece of ice and then 1 ml of an ammonium chloride solution (1M). The solution was washed with water to remove the aluminum hydroxide and then dried over calcium sulfate. A Hitachi model F6D gas liquid chromatograph with a Golay R45 column was employed for the qualitative and quantitative analyses. 220 MHz NMR was also employed to determine the configurations of the products.

Results and Discussion

Reactions of Three Cyclohexanones with Trimethylaluminum. The results are summarized in Table 1. In the case of 4-*t*-butylcyclohexanone, which has no substituent on the 3,5- or 2,6-position, the stereoselectivity is reversed, depending on the reactant molar ratio of ketone to trimethylaluminum (Al/K), indicating that the equatorial attack is the main course when the molar ratio is one or less, while the axial attack is the main course when the molar ratio is two or more. On the other hand, the results obtained from the reaction of trimethylaluminum with *trans*-2-methyl-4-*t*-butylcyclohexanone show a different steric course from that of 4-*t*-butylcyclohexanone. In this ketone, the 2-methyl group occupies the axial position, so the attack of trimethylaluminum from the equatorial side is blocked, resulting in the higher yield of equatorial alcohol. As has been shown in a previous paper, in the reaction of 3,5,5-trimethylcyclohexanone, the 3-axial methyl group hinders the trimethylaluminum attacking from the axial side. Therefore, these two cyclohexanones show steric courses different from that of 4-*t*-butylcyclohexanone.

The Reactions of Decalones. The results are summarized in Table 2.

trans-2-Decalone: The steric requirement of the carbonyl group in this ketone is the same as that of 4-*t*-butylcyclohexanone, so the results are almost the same as those of 4-*t*-butylcyclohexanone.

trans-1-Decalone: Although a reversal of the stereoselectivity depending on the ketone to aluminum molar ratio is observed, axial alcohol is formed in an amount of more than 40% even when the ratio (Al/K) is two, indicating that the axial attack is depressed to some extent. This might be explained by the presence of three axial

Table 1. Reaction of ketones with trimethylaluminum

Run	Ketone	$AlMe_3$/K	[K]	Conv. (%)	Product	
					-OHax. (%)	-OHeq. (%)
1	4-*t*-Butyl-CH	0.5[a]	0.28	—	80	20
2		1.0	0.093	45.2	81.0	19.0
3		2.0	0.095	95.0	14.2	85.8
4		3.0[a]	0.48	—	12	88
5	3,3,5-Trimethyl-CH	1.0	0.095	40.0	100	0
6		2.0	0.090	98.0	73.6	26.4
7	*trans*-2-Methyl-4-*t*-butyl-CH[b]	1.0	0.094	18.3	19.3	80.7
8		2.0	0.088	83.1	12.7	87.3

a) By E. C. Ashby *et al.*, b) *trans*:*cis*~70 : 30 mixture, temp. 0 °C, time 4 hr, K; ketone, CH; cyclohexanone.

TABLE 2. REACTION OF FOUR DECALONES WITH TRIMETHYLALUMINUM AND METHYLMAGNESIUM IODIDE

Run	Ketone	$AlMe_3$/K	[K]	Temp. (°C)	Conv.(%)	Product (%)	
						-OHax.	-OHeq.
9	*trans*-1	1.0	0.1	30	61.2	93.1	6.9
10		2.0	0.1	0	99.8	41.1	58.9
11		5.0	0.083	0	100	42.3	57.7
12	*trans*-2	1.0	0.075	30	75.1	73.3	26.7
13		5.0	0.063	0	100	18.0	82.0
						cis-cis	*cis-trans*
14	*cis*-1	1.0	0.1	30	74.4	9.3	90.7
15		5.0	0.083	0	100	4.0	96.0
16	*cis*-2	0.8	0.124	30	71.2	59.2	40.8
17		1.0	0.10	30	64.8	59.3	40.7
18		5.0	0.083	0	100	8.3	91.7
		MeMgI/K				-OHax.	-OHeq.
19	*trans*-1	2.0	0.1	0	100	94.9	5.1
20	*trans*-2	2.0	0.074	0	100	81.4	18.6
						cis-cis	*cis-trans*
21	*cis*-1	2.0	0.10	0	100	20.0	80.0
22	*cis*-2	2.0	0.10	0	100	56.3	43.7

Time 4 hr

Fig. 2. *trans*-2-decalone

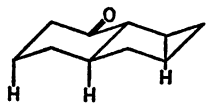

Fig. 3. *trans*-1-decalone

hydrogens (3, 8, and 10 positions) corresponding to the 3,5-axial hydrogens in cyclohexanone, which are believed to hinder the axial attack at a molar ratio of two or more. However, this ketone can be considered to be 2,3-di-equatorial-substituted cyclohexanone. It is known that the 3-equatorial substituent does not play any role in determining the stereoselectivity, so we should consider some effect of the 2-equatorial substituent. The effect of the 2-equatorial methyl substituent will be discussed below.

cis-Decalones:

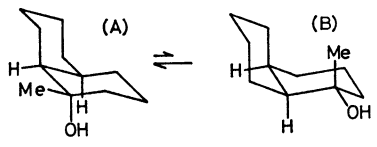

Fig. 4. Two conformations of *cis-cis*-alcohol produced by the reaction of *cis*-1-decalone and trimethylaluminum.

In the *cis*-decalone system, there exist two conformations, (A) and (B), which are believed to reach a very fast equilibrium, as is depicted in Figs. 5 and 6. The notations of the produced alcohols are as follows: in *cis-cis*-alcohol the hydroxyl group and bridge hydrogens are on the same side with the carbonyl-containing ring. On the other hand, in the *cis-trans*-alcohol they are on the opposite side. Therefore, in the case of *cis*-1-decalone, for example, as is depicted in Fig. 4, *cis-cis*-alcohol has an axial hydroxyl group in (A) and an equatorial hydroxyl group in (B) respectively.

cis-1-decalone: As is shown in Table 2, *cis-trans*-

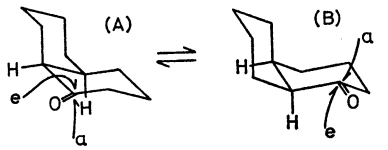

Fig. 5. *cis*-1-decalone, a; axial attack, e; equatorial attack.

alcohol is the predominant product at any molar ratio, and the steric course of the reaction apparently does not depend on the molar ratio. However, these results can be explained by the rapid conformation equilibrium between (A) and (B), considering the same steric course as in the case of 4-*t*-butylcyclohexanone.

At molar ratios of one or less, judging from the results of the reaction of trimethylaluminum with 4-*t*-butylcyclohexanone, the equatorial attack is predominant. The equatorial attack of trimethylaluminum on the (B) conformer gives *cis-trans*-alcohol. However, the equatorial attack on the (A) conformer is sterically hindered by the axial substituent (ring component). Thus, at molar ratios of one or less, the predominant reaction can be considered to be the equatorial attack of trimethylaluminum on the (B) conformer giving mainly *cis-trans*-alcohol.

At molar ratios of two or more, the prevailing attack on the cyclohexanone ring is an axial one. Accordingly, the (A) conformer gives *cis-trans*-alcohol by

the axial attack of trimethylaluminum; on the other hand, the axial attack on the (B) conformer is difficult by the presence of the 3-axial ring component.

The results can also be explained as follows: At any reactant molar ratio, trimethylaluminum attacks *cis*-1-decalone from the less hindered side (*i.e.*, the axial side in the (A) conformer and the equatorial side in the (B) conformer), so the product distribution is not affected by the reactant molar ratio. However, the axial attack at the molar ratio of unity is shown to be slow or difficult by the results obtained with *trans*-2-methyl-4-*t*-butylcyclohexanone. As is shown in Table 1, the reactivity of this ketone at the molar ratio of unity is very low (18.3%), even though the axial attack is the predominant steric course because of the fixed 2-axial methyl substituent. In addition, the equatorial attack at a molar ratio of two or more is the minor reaction path in most cases; it can become the major one only if the cyclohexanone ring contains a substituent which hinders the axial attack greatly, such as 3-axial methyl group in 3,3,5-trimethylcyclohexanone. Therefore, the latter explanation is not adequate.

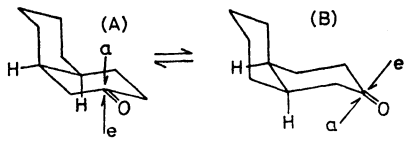

Fig. 6. *cis*-2-decalone, a; axial attack, e; equatorial attack.

cis-2-Decalone: When the molar ratio of ketone to aluminum is one or less, *cis-cis*-alcohol and *cis-trans*-alcohol are formed in nearly equal amounts; however, with an increase in the molar ratio, the *cis-trans*-alcohol increases to a large extent.

At a molar ratio of one or less, the equatorial attacks on the (A) and (B) conformers are equally favored, so *cis-trans*-alcohol and *cis-cis*-alcohol are produced from (A) and (B) respectively by the equatorial attack. Therefore, the two epimers are produced in almost equal amounts.

At a molar ratio of two or more, an axial attack on the (A) conformer is hindered by the presence of a 3-axial ring component. On the (B) conformer, however, an axial attack normally takes place and produces *cis-trans*-alcohol.

The results with four decalone isomers can be explained using the same concepts which were used in discussing the ketones listed in Table 1, considering the rapid conformation equilibrium of each isomer. Therefore, it may be concluded that, in these fused-ring-system ketones, the reactions proceed by means of the same steric course as in the monocyclic ketones.

From the results obtained by the reaction with *trans*-1-decalone, however, further study about cyclohexanones having 2-equatorial substituent is considered to be important.

Reactions of Cyclohexanones with an α-Equatorial Methyl Substituent. The results are summarized in Table 3. When the molar ratio (Al/K) is one, axial alcohols are produced in quantities of more than 96% in all the ketones investigated except 2,2,6-trimethylcyclohexanone, indicating that the stereoselectivity is greatly enhanced compared with the case of 4-*t*-butylcyclohexanone. The results for 2,2,6-trimethylcyclohexanone are anomolous. This ketone has a 2-axial methyl substituent, so the equatorial attack should be hindered. However, axial alcohol is still the main product, even though its percentage is about 10% smaller than those with other ketones.

At the reactant molar ratio of two, the extent of axial attack decreases in the order of 4-*t*-butylcyclohexanone, 2-methylcyclohexanone, and *cis*-2,6-dimethylcyclohexanone, as is shown in Table 3. It is known, therefore, that the axial attack decreases with the successive replacement of 2,6-equatorial hydrogens by methyl groups. In addition, a similar decrease in the axial attack is seen with a decrease in the flexibility of the ring system in the order of 2-methylcyclohexanone, *cis*-2-methyl-4-*t*-butylcyclohexanone, and *trans*-1-decalone. The results for *cis*-2,6-dimethylcyclohexanone and 2,2,6-trimethylcyclohexanone show that the 2-axial-methyl group plays a minor role in stereoselectivity at molar ratios of two or more. This may also be seen in the results for 4-*t*-butylcyclohexanone and *trans*-2-methyl-4-*t*-butylcyclohexanone (cf. Run 3 and Run 8 in Table 1).

Until now, the effect of the 2,6-equatorial substituent

TABLE 3. REACTION OF KETONES HAVING α-EQUATORIAL METHYL GROUP WITH TRIMETHYLALUMINUM

Run	Ketone	$AlMe_3$/K	[K]	Conv. (%)	Product	
					-OHax. (%)	-OHeq. (%)
23	2-Methyl-CH	1.0	0.094	52.8	96.0	4.0
24		2.0	0.090	100	27.8	72.2
25	*cis*-2-Methyl-4-*t*-butyl-CH	1.0	0.094	50.7	96.1	3.9
26		2.0	0.090	100	33.4	66.6
27	*trans*-1-decalone	1.0	0.10	40.2	97.8	2.2
28		2.0	0.10	100	41.1	58.9
29	*cis*-2,6-Dimethyl-CH	1.0	0.093	66.0	98.0	2.0
30		2.0	0.086	99.0	43.2	56.8
31	2,2,6-Trimethyl-CH	1.0	0.095	22.7	88.0	12.0
32		2.0	0.090	74.8	46·2	53.8

Temp. 0°C Time 4 hr, in toluene

on the stereoselectivity of the nucleophilic addition of an organometallic compound has not received any attention. However, as has been shown in the results obtained here, the 2,6-equatorial methyl groups causes a steric hindrance of the axial attack of trialkylaluminum at molar ratios of two or more.

Recently, Ashby *et al.*[5b] proposed the "Compression effect" to explain the reversal of stereoselectivity depending on the reactant molar ratio. Although the effect will be valid for the reversal of selectivity, it may be insufficient to explain the results for 2-alkylsubstituted cyclohexanones. If the "Compression effect" is enhanced through the replacement of 2,6-equatorial hydrogens by methyl groups, the axial attack should be more favored. On the contrary, the axial attack was decreased greatly by the 2,6-equatorial methyl substituent. Therefore, in working out a mechanism to explain the stereochemical effect of the 2,6-equatorial methyl group on the axial attack, one must consider the flexibility of the cyclohexanone ring.

At molar ratios of two or more, the trialkylaluminum complexed with ketone further complexed with a second trialkylaluminum moiety. The exact structure of this ketone : Al=1 : 2 complex cannot be depicted. However, as is to be expected from the amine trialkylaluminum complex, the distance between oxygen and trialkylaluminum is about 2 Å.[11] As has already been clarified, the distance between carbon and aluminum is about 2 Å. Such a structure as is shown in Fig. 7 may be considered. In this complex, the alkyl group of the first aluminum complexed to ketone has a very low activity toward carbonyl addition. Therefore the alkyl group of the second aluminum may attack the carbonyl group. In the transition state, the carbonyl plane will be distorted from the chair form to the half-chair form; consequently, the 2,6-equatorial substituent will come up to the carbonyl plane. This causes a large steric hindrance of the axial attack of

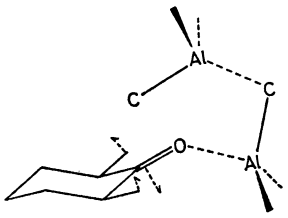

Fig. 7. ketone : $AlMe_3$=1 : 2 complex.

Table 4. Summary of the effect of hydrogen and methyl group at each position of cyclohexanone ring

$AlMe_3$/K molar ratio	1 or less		2 or greater	
Mode of attack	eq. attack	ax. attack	eq. attack	ax. attack
2,6 H(e)	—	—	—	—
2,6 H(a)	+	—	+	—
3,5 H(a)	—	+	—	+
2,6 Me(e)	—	+	—	++
2,6 Me(a)	++	—	++	—
3,5 Me(a)	—	++	—	++

+: having hindrance on the attack, —: little or no effect on the attack,

trialkylaluminum at molar ratios of two or more. In connection with this, the fact that *trans*-1-decalone gave a smaller amount of the axial attack product than did 2-methyl- or *cis*-2-methyl-4-*t*-butylcyclohexanone can be explained by the fact that the flexibility of carbonyl plane is depressed by the fused-ring system. This mechanism, which assumes the importance of the flexibility of the carbonyl group, explains the low reactivity of trimethylaluminum toward adamantanone. The reaction of trimethylaluminum with adamantanone at a molar ratio of two was carried out. It was found that the reactivity of this ketone was very low. Only a 20% conversion was observed in the reaction with trimethylaluminum at 0 °C for 4 hr. Adamantanone has so very rigid a cyclic system that it is difficult for the carbonyl plane to be distorted to the half-chair form. Table 4 summarizes the effects of hydrogens or methyl groups, which affect the direction of the attack of trimethylaluminum on cyclohexanone derivatives.

Temperature Dependence of the Product Distribution. In the case of 4-*t*-butylcyclohexanone, the product ratio (axial alcohol to equatorial alcohol) is not altered with the reaction temperature. However, it is affected by the reaction temperature in the cases of ketones containing 2-equatorial methyl substituents (listed in Table 3) or 3,3,5-trimethylcyclohexanone. Table 5 illustrates the results for 2,2,6-trimethylcyclohexanone, which showed the largest temperature dependence of the product distribution of all the ketones investigated.

A linear relationship is observed between the plot of log (-OHax./-OHeq.) *vs.* $1/T$ at Al/K=2. The dif-

Table 5. Reaction of 2,2,6-trimethylcyclohexanone with trimethylaluminum

Run	$AlMe_3$/K	[K]	Temp. (°C)	Conv. (%)	Product	
					-OHax. (%)	-OHeq. (%)
31	1.0	0.095	0	22.7	88.0	12.0
33	1.0	0.093	30	64.5	86.2	13.8
34	2.0	0.09	−30	~1	33.2	66.8
32	2.0	0.09	0	74.8	46.2	53.8
35	2.0	0.09	30	99.0	70.4	29.6
36	2.0	0.09	50	100	75.4	24.6
37	5.0	0.079	0	73.0	36.5	63.5
38	5.0	0.079	30	100	52.8	47.2

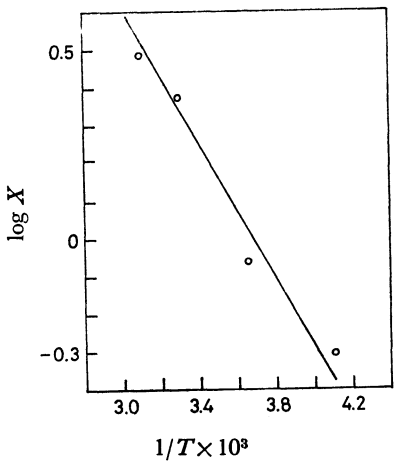

Fig. 8. log (−OHax./−OHeq.) *vs.* $1/T$ plot, Al/K=2.0.
Difference of activation energies; $E_{eq.}-E_{ax.}=4.06$ kcal/mol

ference between the activation energies was calculated to be about 4 kcal/mol. The difference in activation energy suggests a difference in mechanisms between axial and equatorial attacks. In addition, it should be noted that the results in $AlMe_3/K=2$ approach the results obtained at a molar ratio of one when the reaction temperature is elevated. From these two facts, it was considered that, in these ketones, the unimolecular reaction from the equatorial side contributed greatly even when the reactant ratio was two.

In these ketones, because of the large steric requirement, the rate of bimolecular axial attack decreased so as to be comparable with the rate of equatorial attack by the unimolecular process; therefore, the temperature dependence of the product distribution is observed.

On the other hand, in the case of 4-*t*-butylcyclohexanone, the rate of axial attack is sufficiently large and the temperature dependence is not observed.

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