

ORGANOMETALLIC REACTION MECHANISMS

XVIII *. CONCERNING THE NATURE OF THE TRANSITION STATE IN THE REACTION OF TRIALKYLALUMINUM COMPOUNDS WITH KETONES **

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Summary

$\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ (**1**) has been used as a mechanistic probe to determine the nature of the transition state in the reaction of two equivalents of a trialkylaluminum compound with a ketone in hydrocarbon solvent. **1** was prepared in benzene and the solution composition determined. Low temperature ^1H NMR data of **1** as the mono(diethyl etherate) indicate that the ether oxygen is simultaneously coordinated to both aluminum atoms. The reactions of **1** with 4-*t*-butylcyclohexanone in hydrocarbon solvent were compared to the reactions of triethylaluminum with the same ketone. The results support the importance of a bridging alkyl group described by the formation of a six-centered transition state when two equivalents of a trialkylaluminum compound are allowed to react with a ketone in hydrocarbon solvent. The results also argue against a transition state described by two moles of trialkylaluminum compound complexed to the carbonyl oxygen atom.

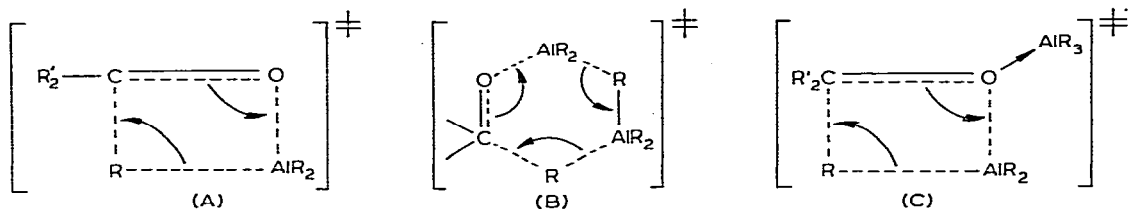
Introduction

The reaction of a trialkylaluminum compound with a ketone in hydrocarbon solvent proceeds via two distinct mechanistic pathways depending on the ratio of reagent to substrate [1]. When the trialkylaluminum compound and a ketone are mixed in 1/1 molar ratio, a bimolecular transition state results which can be

* For part XVII see ref. 16.

** Dedicated to Professor Henry Gilman, the Father of Organometallic Chemistry in the United States, in appreciation and total amazement of all of his contributions to Organometallic Chemistry.

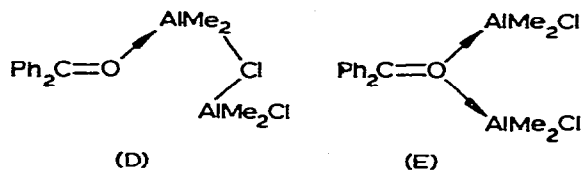
described as four centered A [2]. This mechanistic pathway is characterized by



predominant equatorial attack on 4-t-butylcyclohexanone and an activation energy which closely approximates the heat of formation of the σ -complex between the trialkylaluminum compound and the ketone. On the other hand, a different mechanistic pathway results on mixing a trialkylaluminum compound with a ketone in 2/1 ratio, respectively. The transition state is termolecular and the activation energy for the reaction is much less than for the reaction in 1/1 ratio [2]. Also a complete reversal in stereochemistry of alkylation of 4-t-butylcyclohexanone occurs when the reaction is carried out in 2/1 R_3Al /ketone ratio to give predominantly axial attack. The termolecular transition state has been described by a cyclic six-centered transition state [2,3] in which an alkyl group is bridged between two aluminum atoms (B). The relief of compression of the 2,6-diequatorial hydrogen atoms against the complexed carbonyl function during axial attack (as compared to equatorial attack) has been suggested by us to explain the stereochemistry of the very highly selective axial attack [3].

Mole [4] has described a transition state (C) which provides for the complexation of both molecules of the R_3Al compound to the carbonyl oxygen in the transition state. The stereochemistry of alkylation may now be explained as above in terms of a compression effect or via a deformation of the cyclohexanone ring to a half-chair conformation. Both of these transition states can explain the lowering of activation energy of the termolecular versus the bimolecular transition state in terms of a smaller ΔH^\ddagger and a large negative ΔS^\ddagger for the former [2].

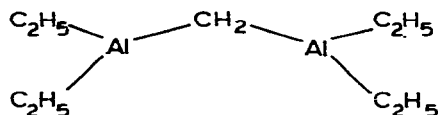
In order to resolve these diverse transition state configurations, we attempted to observe a termolecular complex involving two molecules of $(CH_3)_3Al$ and a Lewis base in hydrocarbon solvent [5]. No such complex was observed for the bases ether and benzophenone. Instead, a 1/1 complex of $(CH_3)_3Al$ and benzophenone resulted and one half of the starting amount of $(CH_3)_3Al$ dimer was recovered. However, a termolecular complex was observed by 1H NMR when two molar equivalents of $(CH_3)_2AlCl$ and benzophenone were allowed to react in toluene at $-80^\circ C$. Furthermore, this complex possessed two distinct types of methyl groups which are consistent with structure D, but not structure E. Unlike the observation of a termolecular complex for acetophenone and two



equivalents of $AlCl_3$ in benzene reported by Pasynekewicz [6], this termolecular

complex does proceed to methylation product. Furthermore, $(\text{CH}_3)_2\text{AlCl}$ alkylates 4-*t*-butylcyclohexanone in 2/1 ratio to give 90% axial methylation in hydrocarbon solvent, i.e., it behaves much like $(\text{CH}_3)_3\text{Al}$.

These results provide evidence that suggests the involvement of a six-centered termolecular transition state **B** with little contribution from transition state **C**. However, the strength of an alkyl bridging group is considerably less than that of a chlorine bridging group between two aluminum atoms. In order to document the importance of $\text{Al}-\text{CH}_3-\text{Al}$ bridge bonds in the transition state when two equivalents of a R_3Al compound are allowed to react with a ketone in hydrocarbon solvent, we undertook a study of the reaction of methylenebis(diethylalane) (**1**) with 4-*t*-butylcyclohexanone. This compound constrains two



(1)

aluminum atoms to a single bridging atom configuration and should serve as an excellent model for testing the importance of bridging in the reaction of two equivalents of $(\text{C}_2\text{H}_5)_3\text{Al}$ with 4-*t*-butylcyclohexanone.

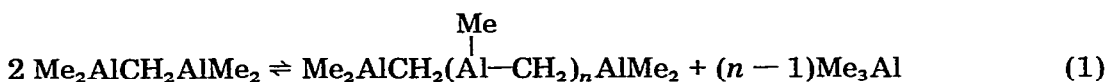
If the bridging of an alkyl group contributes significantly to the energetics of the transition state, then the following characteristics of the reaction of **1** and 4-*t*-butylcyclohexanone in 1/1 molar ratio in hydrocarbon solvent should be observed: (1) a predominance of axial ethylation, and (2) a rate of ethylation comparable to substituting two equivalents of Et_3Al for **1**. If the bridging of an alkyl group contributes insignificantly to the energetics of the transition state then the bridging constraint of **1** should noticeably alter the course of the reaction with 4-*t*-butylcyclohexanone compared to two equivalents of Et_3Al .

Results and discussion

Synthesis of methylenebis(dimethylalane) (2) in hydrocarbon solvent

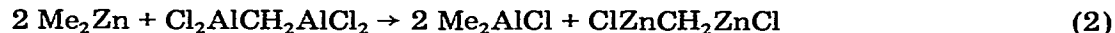
The use of (**2**) as a model compound would have distinct advantages over **1** since study of solution behavior by NMR spectroscopy would be less complicated with methyl groups than ethyl groups. **2** has been reportedly synthesized ether free by the reaction of a large excess of Me_3Al with $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ followed by the removal of Me_2AlCl by fractional distillation [7]. However, the evidence presented for the existence of this compound by the authors is weak, and indeed we were not able to repeat the work.

Our results suggest that **2** is unstable and is best described by eq. 1. This suggestion is analogous to a similar process involving tetraalkylaluminoxanes [8].



In order to overcome the problems associated with eq. 1 an attempt was

made to synthesize **2** via the metathesis of Me_2Zn with $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ in toluene. Unfortunately, exchange of zinc for aluminum gave $\text{ClZnCH}_2\text{ZnCl}$ as a white solid and Me_2AlCl was formed in solution according to eq. 2.



Although it appears that **2** is too unstable to prepare in hydrocarbon solvent, we can report that **2** was prepared by the reaction of CH_3Li with $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ in 4/1 molar ratio in diethyl ether at 0°C . The ambient temperature ^1H 60 MHz NMR showed two singlets, one at -1.09 and one at -2.11 ppm (from the diethyl ether triplet) with a ratio of 1/6 protons, respectively. The downfield singlet is assigned to the methylene protons in **2** and the upfield singlet is assigned to the methyl protons. A similar attempt to prepare **2** from $(\text{CH}_3)_2\text{Mg}$ and $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ was not successful.

Synthesis of methylenebis(diethylalane) (1) in hydrocarbon solvent

1 has been reportedly synthesized from $\text{Cl}_2\text{AlCH}_2\text{AlCH}_2$ and $\text{C}_2\text{H}_5\text{Li}$ in benzene according to eq. 3 [9]. We found that this reaction proceeds smoothly



provided the reaction mixture is stirred at 60°C for 4 h. The yield is quantitative and provides a solution which on hydrolysis exhibits a $\text{C}_2\text{H}_6/\text{CH}_4/\text{Al}$ ratio of 1.95/0.52/1.0. (calcd. for $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$: 2/0.5/1). Upon carefully removing the solvent from **1**, a glass-like material resulted which gave a weight % Al analysis of 29.50 (calcd. for **1**: 29.29). In addition mass spectral analysis of the gasses from hydrolysis of **1** by D_2O gave 97% ethane- d_1 and 100% methane- d_2 .

Solution composition of 1 in hydrocarbon solvent

The results of cryoscopic molecular weight measurements of **1** in benzene are shown in Fig. 1. The i value steadily increases from a value of 1.1 at 0.007 M to 1.7 at 0.127 M .

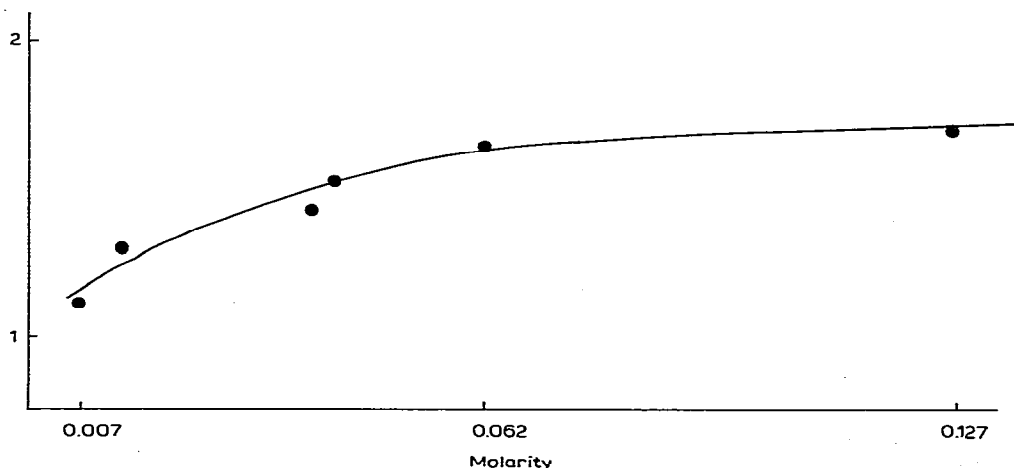


Fig. 1. Cryoscopic molecular association behavior of $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ in benzene.

TABLE 1

 ^1H 100 MHz NMR OF $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ AND Et_3Al IN TOLUENE AT -65°C

	Chemical shift relative to toluene methyl	Integration (Found (calcd.))	Assignment
$(\text{Et}_2\text{Al})_2\text{CH}_2$	-0.90 (t)	1.66 (1.5)	CH_3 of terminal ethyl
$(\text{Et}_2\text{Al})_2\text{CH}_2$	-1.21 (q)	1.00 (1.00)	CH_2 of bridging ethyl
$(\text{Et}_2\text{Al})_2\text{CH}_2$	-1.92 (broad)	1.58 (1.50)	CH_2 of terminal ethyl + AlCH_2Al
Et_3Al	-0.89 (t)	3.00 (3.00)	CH_3 of terminal ethyl
Et_3Al	-1.20 (q)	1.00 (1.00)	CH_2 of bridging ethyl
Et_3Al	-1.97 (q)	2.00 (2.00)	CH_2 of terminal ethyl

The correct formulation of **1** was revealed on inspection of the ^1H 100 MHz NMR spectrum of this compound at -65°C in toluene. Table 1 clearly shows that the chemical shifts of the ethyl group quartets and triplets for **1** are indistinguishable from those of triethylaluminum at -65°C [11]. The AlCH_2Al group gives a resonance that is at surprisingly low field. The position of this resonance is consistent with the low field position of the AlCH_2Al resonance of **2** in diethyl ether. The similarities between the ^1H NMR spectrum for **1** and $(\text{C}_2\text{H}_5)_3\text{-Al}$ indicate that **1** exists in hydrocarbon solvent as a mixture of triethylaluminum dimer and a variety of methylene bridged aluminum compounds. The formulation of **1** as a complex mixture is consistent with the molecular association data since as the concentration increases, association of the mixture through bridging alkyl groups should also increase, leading to a higher effective average molecular weight. Thus the formulation of **1** as a mixture in hydrocarbon solvent makes **1** unsatisfactory in hydrocarbon solution as a model system for our mechanistic investigation. However, this problem was remedied by the results of complexation of **1** by a Lewis base discussed in the next section.

Interaction of 1 with the Lewis base diethyl ether

When one molar equivalent of diethyl ether was added to a solution of **1** in benzene, a molecular weight of 270 ± 13 was obtained (this value was independent of concentration from 0.03 to 0.11 M). A complex of **1** formulated as $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ and one molar equivalent of diethyl ether has a calculated molecular weight of 258. The nature of the complex promises to be unusual since addition of two molar equivalents of diethyl ether to **1** in benzene gives a molecular weight of 188 ± 10 and again independent of concentration from 0.04 to 0.1 M. If **1** had complexed both equivalents of diethyl ether a molecular weight of 332 would have been obtained. A calculation of the average molecular weight for $\text{Et}_2\text{AlCH}_2\text{AlEt}_2 \cdot \text{OEt}_2$ plus one equivalent of diethyl ether is 217. Thus **1** appears to complex one equivalent of diethyl ether very strongly but not a second equivalent. ^1H 100 MHz NMR at -65°C of **1** as the diethyl etherate in toluene shows only one type of ethyl group attached to aluminum.

TABLE 2

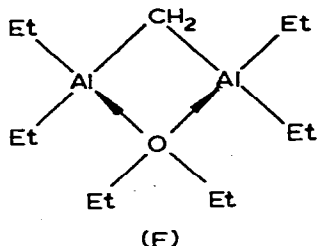
1H 100 MHz OF $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ AND Et_3Al DIETHYL ETHERATES AT -65°C IN TOLUENE

	Chemical shift relative to toluene methyl	Integration (Found (calcd.))	Assignment
$(\text{AlEt}_2)_2\text{CH}_2 + \text{Et}_2\text{O}$	-0.61 (t + s)	2.20 (2.30)	CH_3 ethyl + AlCH_2Al
$(\text{AlEt}_2)_2\text{CH}_2 + \text{Et}_2\text{O}$	-1.53 (t)	1.00 (1.00)	CH_3 of Et_2O
$(\text{AlEt}_2)_2\text{CH}_2 + \text{Et}_2\text{O}$	-1.88 (q)	1.30 (1.33)	CH_2 ethyl
$\text{Et}_3\text{Al} \cdot \text{OEt}_2$	-0.61 (t)	1.45 (1.50)	CH_3 ethyl
$\text{Et}_3\text{Al} \cdot \text{OEt}_2$	-1.47 (t)	1.16 (1.00)	CH_3 of Et_2O
$\text{Et}_3\text{Al} \cdot \text{OEt}_2$	-1.88 (q)	1.00 (1.00)	CH_2 ethyl
$(\text{AlEt}_2)_2\text{CH}_2 + 2\text{OEt}_2$	-0.61 (t + s)	1.67 (1.75)	CH_3 ethyl + AlCH_2Al
$(\text{AlEt}_2)_2\text{CH}_2 + 2\text{OEt}_2$	-1.25 (t)	1.52 (1.5)	CH_3 of Et_2O
$(\text{AlEt}_2)_2\text{CH}_2 + 2\text{OEt}_2$	-1.88 (q)	1.00 (1.00)	CH_2 ethyl

Table 2 shows that the chemical shift of this ethyl group is identical with that for triethylaluminum diethyl etherate. However, the position of the diethyl ether triplets is distinctly different. A ^1H NMR spectrum at -65°C for the mixture of 1 with two equivalents of diethyl ether shows no change in position of either the methylene signal of the ethyl groups attached to aluminum from that for $\text{Et}_2\text{AlCH}_2\text{AlEt}_2 \cdot \text{OEt}_2$. Surprisingly only one type of ethyl group is present for diethyl ether. This indicates that the free and the uncomplexed diethyl ether are rapidly exchanging.

In order to gain more information about this system, the ^1H 60 MHz NMR spectrum of $\text{Et}_2\text{AlCH}_2\text{AlEt}_2 \cdot \text{OEt}_2$ was obtained at temperatures between -65 and -91°C . Collapse of the diethyl ether resonances began at -80°C , but was not complete at -91°C . Spectra of this mixture were also obtained in 80% n-pentane/20% toluene- d_8 down to -110°C . In this solvent, collapse of the diethyl ether triplets began below -100°C and was not complete at -110°C .

The results of these complexation studies can be summarized as providing evidence for the representation of $\text{Et}_2\text{AlCH}_2\text{AlEt}_2 \cdot \text{OEt}_2$ by structure F. The



complexation of the diethyl ether with two aluminum atoms finds analogy with

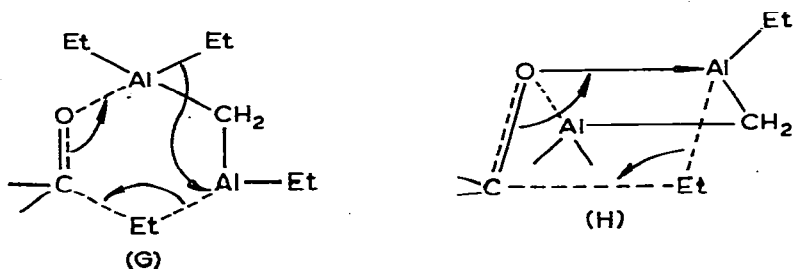
the complexation properties of aluminoxanes [8]. In the case of $\text{Et}_2\text{AlCH}_2\text{AlEt}_2 \cdot \text{OEt}_2$, the diethyl ether complexes with such a high formation constant that complexation of a second equivalent of diethyl ether is thermodynamically unfavorable. Part of this thermodynamic unfavorability may be due to steric congestion offsetting any energy gain from complexation of the second equivalent. However, even though the diethyl ether coordinates strongly, it appears from the results of ^1H low temperature NMR that $\text{Et}_2\text{AlCH}_2\text{AlEt}_2 \cdot \text{OEt}_2$ is very substitution labile.

$\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ as a mechanistic probe for the reaction: $2 \text{R}_3\text{Al} + \text{ketone}$ in hydrocarbon solvent

Although $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ exists as a complex mixture in hydrocarbon solvent, the addition of one equivalent of diethyl ether provides the $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ formulation. Diethyl ether has approximately the same base strength toward alkylaluminum compounds as does benzophenone. Thus, the addition of a ketone to a solution of 1 in hydrocarbon solvent should initially provide the $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ formulation complexed with the ketone.

Stereochemistry of 4-t-butylcyclohexanone ethylation by 1 in hydrocarbon solvent

Table 3 presents the stereochemical results of the reaction of Et_3Al and 1 with 4-t-butylcyclohexanone in benzene. A 1/1 molar ratio of 1 to 4-t-butylcyclohexanone gives 75% axial ethylation which is what is predicted for the involvement of a six-centered transition state as shown in G. The transition state



represented by H is also possible and relates to the transition state C. However, the Al—O distance in H would necessarily be longer than the Al—O distance in

TABLE 3

STEREOCHEMISTRY OF ETHYLATION OF 4-t-BUTYLCYCLOHEXANONE WITH $\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ AND Et_3Al IN BENZENE

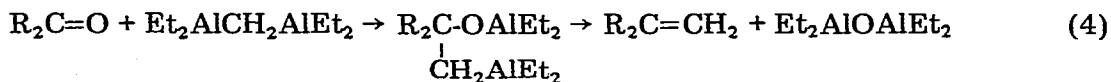
Aluminum compound	Ratio Al/ketone	% Ethylation	
		axial	equatorial
$\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ ^a	2/1 ^b	75	25
Et_3Al ^c	2/1	88	12
$\text{Et}_2\text{AlCH}_2\text{AlEt}_2$ ^a	1/1 ^b	20	80
Et_3Al ^c	1/1	21	79

^a 0.25 M in 4-t-butylcyclohexanone. ^b Actual molar ratios are one half of these values. ^c See reference 15.

C because of the constraint of the Al—CH₂—Al angle in the transition state. This increased Al—O distance should decrease the activation of the carbonyl group ascribed to complexation of two molar equivalents of alkylaluminum to the same carbonyl oxygen atom. Unfortunately, no prediction can be made as to the magnitude of the change comparing the ethylation stereochemistry of **1** versus two equivalents of Et₃Al with 4-*t*-butylcyclohexanone if the transition state of H is in operation. The decrease to 75% axial ethylation from 88% for Et₃Al (Table 3) may be reasonable for the increase in the Al—O bond length. At the very least, the similar stereochemistries of ethylation for **1** and two equivalents of Et₃Al imply similar transition states.

The reaction of **1** in 1/2 molar ratio with 4-*t*-butylcyclohexanone gave the same stereochemistry of ethylation as Et₃Al in 1/1 molar ratio. This can be ascribed to a similar four-centered transition state.

The reaction of 4-*t*-butylcyclohexanone with **1** gave in addition to ethylation and reduction products, 4-*t*-butyl-1-methylenecyclohexane in 36–43% yield. When **1** was mixed in any ratio with benzophenone in benzene a 100% yield of 1,1-diphenylethylene was obtained before or after hydrolysis. These observations are in agreement with the results obtained by Lehmkuhl [10] concerning the reaction of **1** with ethylene which results in ethylene insertion into the aluminum—ethyl bond. The appearance of Wittig type products before hydrolysis may be ascribed to the driving force provided by the formation of Et₂AlOAlEt₂ as shown in eq. 4.



*Rates of ethylation of triethylaluminum and 1 with 4-*t*-butylcyclohexanone in toluene*

Figure 2 shows the results of a rate study at 0°C in toluene for the reaction of: (1) two equivalents of Et₃Al; (2) one molar equivalent of **1**; and (3) one-half molar equivalent of **1** with 4-*t*-butylcyclohexanone. This rate study was carried out in order to compare the rates of the above reactions in order to determine if the reaction of Et₂AlCH₂AlEt₂ is proceeding via a 6-centered transition state in its reaction with 4-*t*-butylcyclohexanone. If **1** ethylates 4-*t*-butylcyclohexanone via a transition state similar to that for the reaction with two equivalents of Et₃Al, then the two reactions should show comparable rates. The half life of the reaction with two equivalents of Et₃Al is 56 s while that for one molar equivalent of **1** is 560 s. While this difference is considerable, the half life of the reaction with one equivalent of Et₃Al at 0°C in toluene is greater than 30 000 seconds [13]. Clearly a ten fold difference in rate is not too much to conclude that one molar equivalent of **1** ethylates 4-*t*-butylcyclohexanone via a transition state similar to that for two equivalents of Et₃Al. However, one half molar equivalent of **1** ethylates 4-*t*-butylcyclohexanone with a half life of 370 s. This result also indicates a transition state for ethylation similar to that formed with two equivalents of Et₃Al. This result now provides a dichotomy, since the stereochemistry of ethylation by one half molar equivalent of **1** parallels that for one equivalent of Et₃Al, when at the same time, the rate of

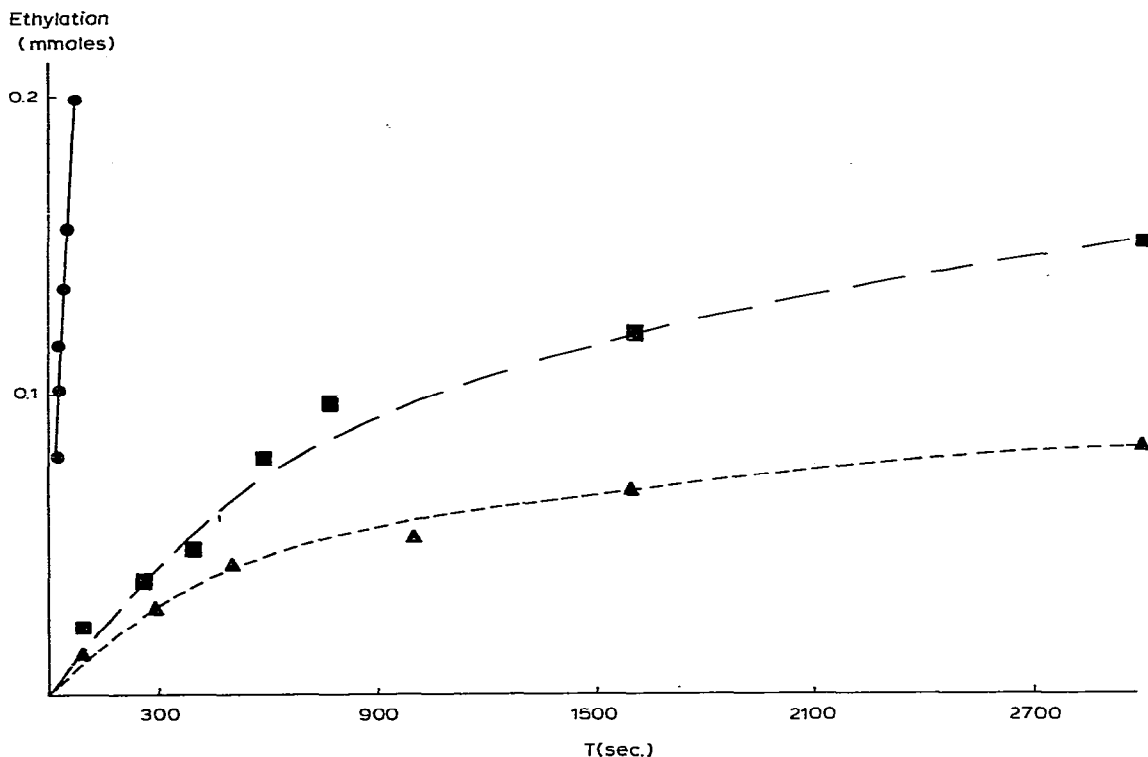


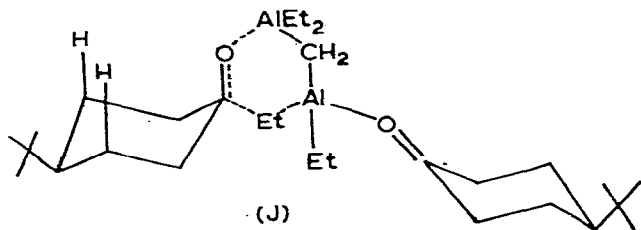
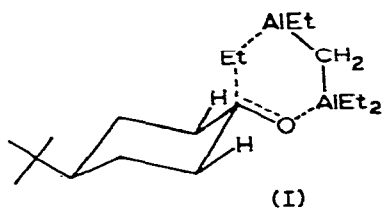
Fig. 2. Rates of ethylation at 0°C in toluene of ● 2 Et₃Al, ■ Et₂AlCH₂AlEt₂, ▲ 1/2 Et₂AlCH₂AlEt₂ with 4-t-butylcyclohexanone.

ethylation closely resembles that observed for two equivalents of Et₃Al.

Although only one equivalent of diethyl ether will complex 1 in benzene, 4-t-butylcyclohexanone should be a stronger Lewis base than benzophenone which has the same base strength as diethyl ether toward R₃Al compounds [2]. In addition, when 1 and 4-t-butylcyclohexanone are mixed in 1/1 ratio with one equivalent of diethyl ether in benzene a 55/45 ratio of axial to equatorial ethylation product is observed. This result is consistent with the notion that diethyl ether complexes a complex of 1 and 4-t-butylcyclohexanone, but not as strongly as a second equivalent of 4-t-butylcyclohexanone. Thus, it seems reasonable that when 4-t-butylcyclohexanone is added to 1 in a 2/1 molar ratio both equivalents of ketone complex 1 to give rise to stereochemistries of ethylation that are dependent on the ratio of 4-t-butylcyclohexanone to 1.

Now the dichotomy between rate and stereochemistry of ethylation observed in the reactions of 1 compared to Et₃Al may be resolved. When a ketone and a R₃Al compound are mixed in 1/1 molar ratio, alkyl bridging becomes impossible since the unoccupied orbital of aluminum is filled by donation from the lone pair of the carbonyl oxygen. Thus a four-centered transition state is the only pathway possible for alkyl transfer. However, with the complexation of each aluminum atom of 1 with ketone, the Et₂Al functionalities are still held in a bridging configuration by the methylene group. This fact still allows the six-

centered transition state to operate, but with no activation due to bis coordination of the carbonyl oxygen as in C. An inspection of transition state J shows that the predominance of equatorial ethylation is an indication that the steric effect of the 3,5 diaxial hydrogens with the attacking Et_2Al functionality complexed to 4-t-butylcyclohexanone, directs the stereochemistry equatorial in opposition to the compression effect. The compression effect directs the stereochemistry toward axial attack for one equivalent of 1 with 4-t-butylcyclohexanone as shown in transition state I.



Conclusion

The results demonstrate the power of a bridging alkyl group to form a six-centered transition state in the alkylation of ketones by two equivalents of a R_3Al compound in hydrocarbon solvent. Any activation of the carbonyl group by coordination of both equivalents of R_3Al compound must be minor.

Experimental

Materials

Diethyl ether (Fisher Anhydrous) was predried over Na wire and then subjected to distillation under nitrogen from LiAlH_4 or Na/benzophenone. Benzene and toluene were stirred overnight with concentrated H_2SO_4 , washed with H_2O , dried over MgSO_4 , stored over Na and distilled from NaAlH_4 or Na/benzophenone under nitrogen prior to use. Methylene chloride and bromide were purified by distillation under nitrogen from activated 3A molecular sieves, through a 2 ft by 1 inch column of sieves, onto molecular sieves. Ethyl bromide was prepared from ethanol by treatment with $\text{HBr}/\text{H}_2\text{SO}_4$, distilled twice and stored over anhydrous Na_2CO_3 under N_2 . Me_2Hg was obtained from Org Met and used without further purification. Li dispersion (Alpha) was repeatedly washed with diethyl ether in a glove box to remove the petroleum oil and the ether removed under vacuum prior to use. Zinc acetate dihydrate (Fisher) was

dried by suspending 20 g in 50 ml acetic anhydride and refluxing for 24 h. The anhydrous zinc acetate was collected by filtration and washed with 2–40 ml portions of glacial acetic acid and then subjected to vacuum overnight in order to remove traces of acetic acid.

4-t-Butylcyclohexanone (Frinton) was distilled under vacuum prior to use. *cis*- and *trans*-1-Ethyl-4-t-butylcyclohexanols were prepared by the reaction of ethylmagnesium bromide and 4-t-butylcyclohexanone in diethyl ether. The isomers were separated by preparative GLC using a 20 ft. 15% FFAP on Chromosorb W at 125°C and 103 ml/min. 4-t-Butyl-1-methylenecyclohexane was prepared from 4-t-butylcyclohexanone and triphenylmethylene phosphorane in DMSO. The product was distilled from the reaction mixture at 100 Torr and collected in a dry ice-acetone trap. The 4-t-butyl-1-methylenecyclohexane was further purified by preparative GLC on a 20 ft. FFAP at 125°C and 103 ml/min. ¹H 60 MHz NMR and mass spectrometry were used to establish the identity of the 4-t-butyl-1-methylenecyclohexane.

Analytical methods

Aluminum and magnesium were analyzed by EDTA titration. Chloride was analyzed by Vollhard titration. Methane and ethane were analyzed using a Toepler pump and by GLC on a 2 ft. Porapak Q with propene as the internal standard. Retention times relative to propene are: methane, 0.04; ethane, 0.195. Response factors were determined by adding a standard benzene solution, consisting of a mixture of Me₃Al and Et₃Al to a 200 ml round-bottomed flask containing 10 ml of dilute aqueous H₂SO₄. The flask was equipped with a serum cap and a stirring bar. Vigorous stirring was maintained for 15 min after introduction of 5 ml of propene gas and at least three separate response factor determinations were made and the average used for analysis of gases on hydrolysis of Et₂AlCH₂AlEt₂.

The products from the reaction of 4-t-butylcyclohexanone with ethylaluminum compounds were analyzed on a 20 ft., 15% FFAP on Chromosorb-W column at 125°C. The retention times relative to the internal standard 3,3,5-trimethylcyclohexanone were: 4-t-butyl-1-methylenecyclohexane, 0.38; 4-t-butylcyclohexanone, 3.10; *cis*-4-t-butylcyclohexanol, 4.00; *trans*-1-ethyl-4-t-butylcyclohexanol, 4.20; *trans*-4-t-butylcyclohexanol, 4.92; and *trans*-1-ethyl-4-t-butylcyclohexanol, 5.07.

Mass spectral analysis of methane and ethane for deuterium content were carried out in the following manner. Samples for a mixture of Et₃Al and Me₃Al were hydrolyzed with either D₂O or H₂O in a 200 ml round-bottomed flask equipped with a serum cap. 1 was similarly hydrolyzed with D₂O. The gas samples were then introduced via syringe onto a 4 foot by 2 mm Porapak Q column at room temperature employing a Varian 3700 series gas chromatograph interfaced with a Varian MAT 112S mass spectrometer with a Varian MAT SS200 Data System.

Reaction of 1 with 4-t-butylcyclohexanone. Stereochemistry of ethylation

1 in either toluene or benzene was placed in a 100 ml round-bottomed flask equipped with a serum cap; 4-t-butylcyclohexanone was then added in the appropriate molar ratio as a standard solution in either toluene or benzene. The

reaction was allowed to stir for 24 h and then hydrolyzed with a small amount of saturated ammonium chloride solution. The internal standard was added and an aliquot was then removed and dried over MgSO_4 prior to GLC analysis. When 1 and 4-*t*-butylcyclohexanone were mixed in 1/1 molar ratio, the following product distribution was obtained: 4-*t*-butyl-1-methylenecyclohexane, 43%; 4-*t*-butylcyclohexanone, 4.3%; *trans*-4-*t*-butylcyclohexanol, 15.3%; *cis*-4-*t*-butylcyclohexanol, 1.9%, *cis*-1-ethyl-4-*t*-butylcyclohexanol, 8.8%; *trans*-1-ethyl-4-*t*-butylcyclohexanol, 26.7%. When 1 and 4-*t*-butylcyclohexanone were mixed in 1/2 molar ratio, the product distribution was: 4-*t*-butyl-1-methylenecyclohexanol 36%; 4-*t*-butylcyclohexanone, 12.4%; *trans*-4-*t*-butylcyclohexanol, 23.2%; *cis*-4-*t*-butylcyclohexanol, 2.4% *cis*-1-ethyl-4-*t*-butylcyclohexanol, 24.6%; *trans*-1-ethyl-4-*t*-butylcyclohexanol, 3.6%.

Reaction of 1 with benzophenone

When 1 and benzophenone were mixed in toluene or benzene, the sole product in quantitative yield was 1,1-diphenylethylene, which was identified by comparison of the NMR spectrum with that of a known sample (Aldrich). Furthermore, this product was formed independently of the mole ratio of 1/benzophenone. In addition ^1H NMR of the reaction mixture showed 1,1-diphenylethylene to be present before hydrolysis. No aluminum salts of 1,1-diphenylethanol were present before hydrolysis.

*Kinetics of alkylaluminum compounds with 4-*t*-butylcyclohexane*

The kinetics studies were carried out in toluene at 0°C . 0.5 mmol of 4-*t*-butylcyclohexanone as a solution in toluene was added to a dry, nitrogen filled, 100 ml round bottomed flask equipped with a teflon stirring bar and a serum cap. Toluene was then added to give the desired concentration and the solution was allowed to come to thermal equilibrium for at least 15 min in a 0°C bath. A solution of the organoaluminum compound was then added. After a certain amount of time the reaction mixture was hydrolyzed with 5 ml of saturated ammonium chloride solution. The internal standard was then added, and the toluene solution was extracted into diethyl ether. The ether extract was dried over MgSO_4 and the solution was then carefully concentrated. The products were quantized by GLC analysis. Each data point was taken as an average of two runs with each run without 10% of the other. With the expectation of Et_3Al in 1/1 molar ratio with 4-*t*-butylcyclohexanone, each reaction was followed for at least two half lives. The organoaluminum compound was always added in 0.1 *M* concentrations.

Preparation of organometallic reagents

Ethyllithium. Ethyllithium was prepared under argon by adding 0.5 mol ethyl bromide in 100 ml benzene slowly to 2 mol (20 g) of freshly washed Li dispersion suspended in 400 ml of benzene at room temperature. The reaction was stirred overnight and filtered. The solution containing ethyllithium was analyzed (1) for ethane after hydrolysis on a vacuum line with aqueous HCl by use of a Toepler pump and (2) for total base.

Me_2Mg . Dimethylmagnesium was prepared by stirring 50 mmol (3.74 ml) of neat Me_2Hg with 5 g of magnesium (Ventron Chips) with the aid of a room

temperature water bath for 24 h. The gray metallic mixture was extracted with diethyl ether, and the resulting mixture analyzed for methane after hydrolysis on a vacuum line using a Toepler pump and magnesium by EDTA titration.

Dimethylzinc. Dimethylzinc was prepared by adding 100 ml of 1.98 M (198 mmol) Me_3Al (Ethyl Corp.) in dodecane slowly to 15.7 g (85 mmol) of anhydrous zinc acetate suspended in 50 ml of dodecane at room temperature [9]. After the addition was complete, the reaction mixture was subjected to slow distillation through a 40 cm vigreux column and the Me_2Zn was collected in toluene (b.p. 36–38°C). The resulting toluene solution of Me_2Zn was analyzed for methane after hydrolysis using a Toepler pump and for zinc by EDTA titration.

$\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$. $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ was prepared as described by Mottus [12] and Ort using Alcan grade MD202 aluminum powder. The reaction mixture was filtered to remove solids and the solvent of the resulting light brown solution was removed under vacuum to give a brownish solid. This solid was washed twice with fresh CH_2Cl_2 (150 ml/0.1 mol scale prep) to give an off-white solid with a $\text{CH}_3/\text{Al}/\text{Cl}$ analysis of 0.95/2/3.7. Analysis Found: Al, 25.5, Cl, 62.2. $\text{CH}_2\text{Al}_2\text{Cl}_4$ calcd.: Al, 25.7; Cl, 67.7%. NMR (diethyl etherate in C_6H_6), (δ from C_6H_6 singlet): -3.33 (q, 8 H), -6.2 (t, 12 H), -8.05 (s, 2 H).

Triethylaluminum and trimethylaluminum. Both of these compounds were generously supplied by the Ethyl Corp. and distilled in a dry box through a 20 cm Vigreux column. Solutions were prepared in the glove box and standardized via aluminum (EDTA) and gas (Toepler pump) analysis after hydrolysis,

Preparation of diethyl etherates in hydrocarbon solvent. The etherates of the hydrocarbon soluble alkylaluminum compounds were prepared by addition of a standard solution of diethyl ether in the desired hydrocarbon solvent to a standardized solution of the alkylaluminum compound in the same solvent with stirring at room temperature. The molarity of the resulting solution was determined by aluminum analysis with EDTA.

The bis(diethyl etherate) of $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ was prepared by adding a standard solution of diethyl ether in the desired solvent to a suspension of $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ in the same solvent at 0°C. No other cleavage by $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ occurred in two weeks at room temperature.

Molecular weight

The molecular weights were determined cryoscopically in benzene using an apparatus described elsewhere [14]. All measurements of solvent and alkylaluminum compounds were carried out by weight. Furthermore, known volumes of standardized alkylaluminum solutions were weighed so that the grams of solute and solvent could be calculated. The K_f of benzene had previously been determined [5] as 5.163.

NMR

Samples for 100 MHz proton NMR were prepared in a dry box by adding the organometallic solution of known concentration in toluene to an NMR tube equipped with a ground glass joint and adjusting the volume with toluene- d_8 (Aldrich) to 10% of the total volume. The samples were then degassed with freeze-pump-thaw cycles on a vacuum line and sealed under vacuum. The

samples were stored in a freezer until the spectra were recorded. A Jeol 100 MHz Fourier transform NMR equipped for low temperature operation at a constant temperature to within 0.1° was used to record the 100 MHz spectra.

The 60 MHz NMR spectra were recorded on a Varian T-60 NMR. The samples were prepared by adding the organometallic solution of known concentration to an NMR tube which had been flamed under vacuum through a needle and filled with nitrogen.

Synthesis of alkylaluminum compounds

Et₂AlCH₂AlEt₂ (II) in benzene. The procedure of Lehmkuhl and Schafer [10] was used by adding 251 ml of 0.78 M EtLi in benzene slowly to 9.0 g (48.9 mmol) of Cl₂AlCH₂AlCl₂ suspended in 50 ml of benzene at room temperature with stirring. After the addition was complete, the reaction pot was slowly warmed to 60°C with an oil bath and stirred at that temperature for 4 h. After cooling to room temperature the white solid in the reaction vessel was allowed to settle and the supernatant solution was siphoned under nitrogen pressure with a stainless steel cannula into a flask filled with nitrogen. 300 ml of fresh benzene was added to the solid in the reaction flask and stirred for 2 h at 60°C. Once the white solid had settled and the benzene had cooled to room temperature, the supernatant solution was siphoned into the flask containing the previous supernatant solution.

All volatile materials were removed from the white solid in vacuo overnight. The white solid gave a Li/Cl analysis of 1.3/1 and contained no aluminum. The yield of reaction product is essentially quantitative and only a trace of chloride was present in solution.

To prepare a toluene solution, the benzene was carefully removed at 0.5 Torr with the aid of a room temperature water bath to leave a viscous colorless liquid. The desired amount of toluene was then added and the solution analyzed for aluminum by EDTA titration for standardization purposes. Lehmkuhl [3] had reported that this compound decomposes on attempted distillation at 10^{-3} Torr, so care was taken in removing the solvent.

Me₂AlCH₂AlMe₂ in diethyl ether. To 23 ml of 0.218 M Cl₂AlCH₂AlCl₂ in diethyl ether at room temperature was added slowly 40.2 ml of cold 0.497 M MeLi in diethyl ether. A white precipitate appeared instantly upon addition of the MeLi and the reaction was allowed to stir for 4 h at room temperature after the addition of MeLi was completed. The reaction was filtered and the solid was washed with 20 ml of fresh diethyl ether. The solid contained only a trace of aluminum and all the chloride from Cl₂AlCH₂AlCl₂, and was presumed to be LiCl. The supernatant solution had a CH₄/Al analysis of 2.6/1. Calculated for Me₂AlCH₂AlMe₂, 2.5/1.

Reaction of excess Me₃Al with Cl₂AlCH₂AlCl₂. To 20 mmol of Cl₂AlCH₂AlCl₂ at 0°C in a 3-neck flask fitted with a dropping funnel and a 10 cm packed column was added slowly 160 mmol of Me₃Al as a 2.0 M solution in toluene. The volatile liquids were removed by distillation through the packed column at 30°C between 10 and 20 Torr. Again, 160 mmol of Me₃Al as a 2.0 M solution in toluene was added at 0°C and the volatile liquids were again removed by distillation at 30°C between 10 and 20 Torr to give a colorless viscous liquid. 100 ml of fresh toluene was added and the resulting solution gave a CH₄/Al/Cl

analysis of 2.8/1.0/0.05. Calculated for $\text{Me}_2\text{AlCH}_2\text{AlMe}_2$ 2.5/1.0/0. The -70°C ^1H 60 MHz NMR showed a substantial amount of Me_3Al in solution (2.07 ppm (s, 1 H) and -2.63 ppm (s, 2 H) from toluene methyl singlet) along with numerous other singlets between -1.0 and -3.0 ppm upfield from the toluene methyl singlet. The solution was then stripped under 0.5 Torr vacuum until only a viscous colorless liquid remained. Again 100 ml of toluene was added and the solution gave a $\text{CH}_4/\text{Al}/\text{Cl}$ analysis of 2.2/1/0.09. Calculated for $\text{Me}_2\text{AlCH}_2\text{Al}(\text{Me})\text{CH}_2\text{AlMe}_2$ 2.33/1/0. The toluene was again removed at 0.5 Torr and vacuum continued at room temperature for 24 h, after which time a glassy semi-solid mass remained. The toluene removed in vacuo contained Me_3Al as identified by -70°C ^1H 60 MHz NMR. The remaining material was dissolved in 100 ml of toluene and gave a CH_4/Al analysis of 2.1/1. Chloride was not analyzed.

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