Organometallic Reaction Mechanism. IX. Evidence for the Detailed Nature of the Alkyl Transfer Step in the Addition Reaction of Trimethylaluminum with Benzophenone[1]

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Abstract: Rate data for the addition of trimethylaluminum to benzophenone at several ratios and at several temperatures in benzene and diethyl ether have been obtained, and the activation parameters for each case have been calculated. Critical examination of the activation parameters for diethyl ether and the 1:1 reactant ratio in benzene indicate a common transition state, which arises from the reactants being held in a solvent cage, followed by bimolecular reaction of trimethylaluminum with the ketone. The reaction of excess trimethylaluminum with benzophenone in benzene proceeds *via* a different transition state; the activation parameters indicate a rigid cyclic transition state whose structure is discussed.

A study of the kinetics of the addition of trimethylaluminum to benzophenone in benzene has been recently presented.[3] The reaction in benzene was found to proceed through two distinct mechanistic paths depending on the ratio of reactants. In this solvent, the reactants, $Al(CH_3)_3$ and ketone, form a complex whose formation is nearly complete. When the ratio of $Al(CH_3)_3$ to ketone is 1:1 or less, the product is formed by a relatively slow rearrangement of the complex. When this ratio is greater than 1:1, rapid formation of product results from attack on the complex by a second molecule of monomeric trimethylaluminum. The half-life of the complex is about 2900 sec when it is present alone at 0.0883 *M* concentration, but decreases to about 50 sec when trimethylaluminum is also present at the same concentration.

The rate of addition of trimethylaluminum to benzophenone in diethyl ether has also been investigated.[4] This study showed that the reaction is first order in aluminum alkyl and first order in ketone. Although some complexation between reactants occurs, it is small enough to warrant a steady-state treatment of the rate data. The reaction in diethyl ether is much slower than in benzene. When 0.254 *M* trimethylaluminum reacts with 0.234 *M* benzophenone in diethyl ether, the half-life is 8.6×10^5 sec, and, when the concentration of trimethylaluminum is increased, only a normal rate enhancement is observed.

The difference in behavior in the two solvents can be explained partially by the position of equilibrium 1.

$$(C_6H_5)_2C{=}O + (CH_3)_3Al\cdot\text{solvent} \rightleftharpoons (C_6H_5)_2C{=}O\cdot Al(CH_3)_3 + \text{solvent} \quad (1)$$

In benzene this equilibrium lies almost completely to the right, whereas in diethyl ether the equilibrium lies almost completely to the left due to the competition between solvent molecules and ketone for the organoaluminum compound. This competition, of course, does not exist in benzene. Product is formed in diethyl ether by only a single reaction path. The path involving a bimolecular reaction of complex with monomeric $Al(CH_3)_3$, which was preferred in benzene when the ratio of $Al(CH_3)_3$ to ketone was greater than 1, is not observed in diethyl ether regardless of the ratio of reactants, due to the fact that the trimethylaluminum which is not complexed with benzophenone is complexed strongly to diethyl ether.

A major unresolved area concerning alkylation of ketones by organometallic compounds is the exact nature of the alkyl transfer step. In reactions in which the transition state has the same composition as the complex, the question is whether reaction occurs by direct intramolecular rearrangement of complex or by bimolecular collision involving the initially separated species.[5] It is impossible to distinguish between the two reaction paths on the basis of the rate law since the mathematical expressions describing both cases are essentially the same.[5a,e] The reaction of trimethylaluminum with benzophenone in a 1:1 ratio in benzene, where the reactants are initially present almost completely as complex, and in diethyl ether, where the reactants are initially present almost totally as separated species, affords a unique opportunity for the study of this unresolved aspect of organometallic reaction mechanisms.

Experimental Section

Materials. Trimethylaluminum was obtained from Texas Alkyls Inc. The batch analytical report received showed that triethylaluminum was present to the extent of 0.1%. No other impurities were reported. This material was further purified by distillation through a 1-ft packed column, taking the center cut for kinetic studies.

Eastman's reagent grade benzophenone was distilled twice *in vacuo*. The middle portion (mp 48.2-49.0°) of the second distillation was used in the kinetic studies. The benzophenone was stored in a glove box and shielded from light. Diethyl ether solutions of benzophenone were stored in tinted volumetric flasks in a glove box.

Eastman's reagent grade 1,1-diphenylethanol was used without further purification. Baker's reagent grade anhydrous diethyl ether was distilled under nitrogen from lithium aluminum hydride prior to use. Fisher reagent grade thiophene-free benzene was distilled from $NaAlH_4$.

Apparatus and Procedure. A Zeiss PMQ II single beam spectrophotometer was used for making kinetic measurements. A Cary

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(1) We are indebted to the National Science Foundation (Grant No. SP-14795) for partial support of this work.

(2) Union Camp Co. Predoctoral Fellow, 1970-1971.

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(4) E. C. Ashby and J. Laemmle, *J. Org. Chem.*, 33, 3398 (1968).

(5) (a) S. G. Smith and G. Su, *J. Amer. Chem. Soc.*, **88**, 3995 (1966); (b) J. Billet and S. G. Smith, *ibid.*, 90, 4108 (1968); (c) T. Holm, *Acta Chem. Scand.*, 20, 1139 (1966); (d) T. Holm, *ibid.*, 23, 579 (1969); (e) J. Laemmle, E. C. Ashby, and H. M. Neumann, *J. Amer. Chem. Soc.*, **93**, 5120 (1971).

Model 14 ultraviolet spectrophotometer was used for recording ultraviolet spectra. For glpc analysis, an F&M 720 gas chromatograph was employed using matched 6-ft Carbowax 20M columns.

All transfers of air-sensitive materials were performed under a nitrogen atmosphere in a specially constructed metal glove box. The atmosphere in the glove box was continuously circulated through a purification system consisting of two Dry Ice-acetone traps (−80°) in series, a 3-ft column containing MnO on vermiculite, and a 3-ft column containing molecular sieve 4a.[6]

Matched quartz 10-mm cells (Beckman Scientific Co.) and matched quartz 1-mm cells (Carl Zeiss, Inc.) were employed for obtaining ultraviolet spectra.

Temperature control for those reactions followed in the quartz cell was maintained by a Haake constant-temperature recirculator which pumped water through the jacket of the Zeiss cell compartment. For those reactions in which quenching techniques were used, a Sargent constant-temperature water bath was employed for controlling the temperature. Temperature readings were made using a calibrated thermometer reading to 0.1° (estimates possible to 0.02°).

Aluminum Analysis. Aliquots of trimethylaluminum solutions were hydrolyzed with 10% hydrochloric acid, and the organic layer was evaporated. Excess standard EDTA was added and the solution was titrated with standard zinc acetate using dithizone as an indicator.

Ultraviolet Spectra. The ultraviolet spectrum of benzophenone and the ultraviolet spectra of mixtures of benzophenone and trimethylaluminum in both benzene and diethyl ether have been previously described.[3,4]

Determination of Rate Constants. The kinetic techniques for determining reaction rates in diethyl ether have been previously described.[4] Rate constants were calculated from the second-order rate equation (eq 2), where $[A]_0$ and $[K]_0$ represent the initial concentrations of trimethylaluminum and benzophenone and [A] and [K] represent the concentrations at time t.[4]

$$k = \frac{1}{t([A]_0 - [K]_0)} \ln \frac{[K]_0[A]}{[A]_0[K]} \tag{2}$$

The average rate constant for each run was calculated from nine or ten sets of time-benzophenone concentration values. The values were obtained over the range from 10 to 75% reaction.

The kinetic techniques for determining reaction rates in a 1:1 reactant ratio in benzene have been previously described.[3] Rate constants were calculated from time *vs.* absorbancy data by use of the first-order rate equation (eq 3). The observed rate constant

$$k_{\text{obsd}} = \frac{1}{t} \ln \frac{A_0 - A_\infty}{A - A_\infty} \tag{3}$$

was divided by 2 to obtain the rate constant for the rate-determining step. This was necessary because the reaction product complexes trimethylaluminum so strongly that for every molecule of complex that reacts another is destroyed by the product.[3]

For the reaction using excess trimethylaluminum in benzene, the kinetic techniques employed are somewhat different from those previously described.[3] The sampling technique was essentially the same as that for the reaction in diethyl ether.[4] Since the reaction is rapid, it was initiated by injecting a small volume of standard ketone into a large volume of standard trimethylaluminum solution contained in a kinetic flask. Samples were withdrawn and rapidly quenched in 10% hydrochloric acid solution. The quenched samples were then dried over anhydrous magnesium sulfate. The concentration of benzophenone was determined by ultraviolet spectroscopy by measuring the absorbance in 1-mm cells at 274 mμ. Benzophenone has an extinction coefficient of 4520 at 275 mμ and obeys Beer's law over the measured concentration range at constant slit width of 0.2 mm.

Previous analysis of the data for reaction of excess trimethylaluminum in benzene[3] indicated that the composition of trimethyl aluminum was best described as a monomer-dimer equilibrium In the higher aluminum alkyl concentrations employed the predominant species was the dimer, while at the lower concentrations a considerable percentage of trimethylaluminum was present as monomer. In both cases, monomeric trimethylaluminum was shown to be the reactive species. To obtain the best value for the second-order rate constant for the reaction of complex with trimethylaluminum, it was desirable to have the initial concentration of uncomplexed trimethylaluminum as low as possible in order to maximize the portion present as monomer, and thus make valid the mathematical (monomer-monomer) analysis.[3] In the present study, the initial concentrations of uncomplexed trimethylaluminum are less than half the lowest values previously reported.[3] When trimethylaluminum exists as a monomer, and the monomer is the reactive species, the rate constant is given by

$$k = \frac{1}{t([A]_0 - 2[K]_0)} \ln \frac{[C]_0([C] + [A]_0 - 2[K]_0)}{[C]([C]_0 + [A]_0 - 2[K]_0)} \tag{4}$$

where $[A]_0$ and $[K]_0$ represent the values already stated and $[C]_0$ is the concentration of complex at zero reaction time. The rate constant at 25° is, as expected, higher than the value previously reported.[3] The values reported here for the second-order rate constant for the reaction of complex with trimethylaluminum were obtained at the lowest concentrations feasible.

Activation parameters for each of the three conditions studied were obtained by fitting of the appropriate equation: the activation energy and frequency factor from the Arrhenius equation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the "thermodynamic" Eyring equation.

Results and Discussion

Nature of the Complex. In order to understand the detailed nature of the alkyl transfer step in alkylation of ketones by aluminum alkyls, the exact nature of the organoaluminum-ketone complex which precedes alkylation must be discussed. The existence of a 1:1 complex between $(CH_3)_3Al$ and benzophenone has been definitely established in benzene[3] and seems probable in diethyl ether.[4] Mulliken has classified a number of electron acceptors and donors into various types.[7] Trimethylaluminum was classified as a vacant orbital acceptor and ketones were classified as onium donors which contain a relatively easily ionized atomic lone pair of electrons. Thus, the complex between trimethylaluminum and benzophenone is expected to be a σ complex. Evidence that this is correct is shown by examination of the ultraviolet spectra of benzophenone and of mixtures of trimethylaluminum and benzophenone. Figure 1 illustrates the spectrum of a 5.1×10^{-5} M solution of benzophenone in diethyl ether and the spectrum of a solution of 5.1×10^{-5} M benzophenone and 0.5 M trimethylaluminum. The concentration of ketone is such that the peak characteristic of the $\pi \rightarrow \pi^*$ transition ($\lambda_{\max}$ 249 mμ, ϵ 1.8×10^4) is shown. The spectra are identical within the accuracy of addition except that the trough occurring at 236 mμ in the mixture solution is not so deep as that of the ketone solution due to end absorption by $(CH_3)_3Al$ which occurs at 240 mμ. Theoretical considerations show that if the $(CH_3)_3Al$ were complexed to the π electrons, the $\pi \rightarrow \pi^*$ maximum should increase in intensity and be shifted to longer wavelengths consistent with properties characteristic of charge transfer complexes.[7,8] This spectral change is not observed, indicating that complexation of the aluminum alkyl to the π electrons is not important. Figure 2 illustrates the spectrum of a 3.3×10^{-3} M solution of benzophenone as well as a solution of a mixture of 3.3×10^{-3} M benzophenone and 0.274 M trimethylaluminum in diethyl ether. The concentration of ketone is such that the ketone peak characteristic of the $n \rightarrow \pi^*$ transition ($\lambda_{\max}$ 344.5 mμ, ϵ 119) is shown. The $n \rightarrow \pi^*$ absorption spectrum characteristic of pure benzophenone disappears upon addition of trimethylaluminum and a new

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[6] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).

[7] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[8] (a) R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951); (b) *J. Amer. Chem. Soc.*, **74**, 811 (1952).

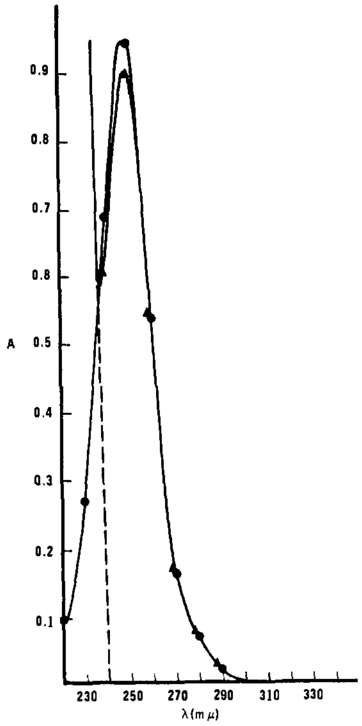


Figure 1. The ultraviolet spectrum of diethyl ether solutions of: (●) 5.1 × 10^{-5} M benzophenone, (▲) 5.1 × 10^{-5} M benzophenone + 0.5 M trimethylaluminum, and (------) 0.5 M trimethylaluminum.

absorbance occurs which increases in intensity as the concentration of trimethylaluminum is increased. This change in the n → π^* spectrum of benzophenone upon addition of trimethylaluminum indicates that the nonbonding electrons on the carbonyl oxygen are being affected, as would be expected by formation of a σ complex.

In benzene, complexation between benzophenone and trimethylaluminum is so strong that the n → π^* spectrum characteristic of pure ketone completely disappears and a strong absorption occurs in the visible spectrum.[3] Although the $\pi \rightarrow \pi^*$ spectrum of benzophenone in benzene could not be investigated because the solvent itself absorbs strongly at wavelengths shorter than 280 mμ, there is no reason to believe that the nature of the complex formed in benzene is different from that formed in ether.

Results analogous to those described above were obtained from spectra of mixtures of $MgBr_2$ with 2-methylbenzophenone in diethyl ether.[9]

Further evidence that ketones form σ complexes rather than π complexes with vacant orbital donors is the fact that the heats of reaction of $SbCl_5$ with ketones are almost the same as the heats of reaction with ethers.[10] Since ethers have no π electrons available, only σ complexes can be formed. Complexes between ketones and $SbCl_5$ are relatively strong[10] indicating that they are σ complexes.[7] Complexes between π donors and vacant orbital acceptors are expected to be weak and not very stable.[7]

The geometry of the complex would then be expected to be that in which the aluminum is bonded to a sp^2 hybrid orbital of the carbonyl oxygen. Thus, the unit A lies in a plane (with bond angles about 120°)

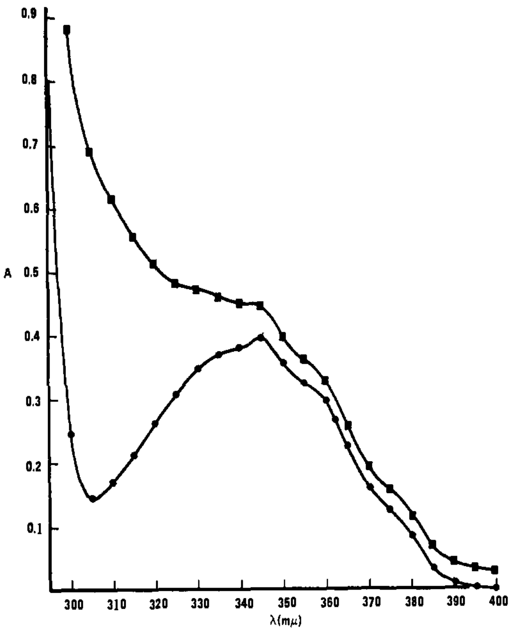
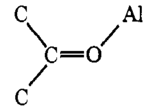
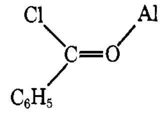


Figure 2. The ultraviolet spectrum of diethyl solutions of (●) 3.3 × 10^{-3} M benzophenone and (■) 3.3 × 10^{-3} M benzophenone + 0.274 M trimethylaluminum.



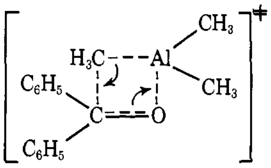
A

with the p orbitals on the carbonyl carbon and oxygen perpendicular to the plane. This is the structure observed in the aluminum chloride–benzoyl chloride complex.[11] The unit B is planar; the C–O–Al bond angle is about 150°, and the other angles are about 120°.



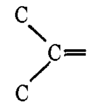
B

Possible Rearrangement of Complex. The reaction of $Al(CH_3)_3$ with benzophenone in diethyl ether and the same reaction in 1:1 ratio in benzene will be discussed first. In these systems the transition state contains one ketone and one $Al(CH_3)_3$ molecule. The transition state C suggested for this reaction is



C

The geometry of this transition state is such that the



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[9] E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **94**, 5421 (1971).

[10] G. Olofsson, *Acta Chem. Scand.*, **22**, 377 (1968).

[11] S. R. Rasmussen and N. C. Brock, *ibid.*, **20**, 1351 (1966).

unit lies in a plane with the methyl carbon above the carbonyl carbon and the aluminum above the carbonyl oxygen. The complex previously described could rearrange to the transition state by rotation about the C–O bond. In doing this, however, the π bond is distorted and considerable energy would thus be required. An estimate of the magnitude of this energy requirement can be made as follows.

Measurements of the isomerization reaction of a variety of olefins show that the reaction is first order with activation energies of 40–46 kcal.[12] The mechanism of these reactions has not been clearly established (excitation to a biradical, followed by free rotation, is a possibility), so that the energy necessary for rotation is probably not less than 40 kcal. The energy of the π bond in C=C can be taken as 65 kcal (*i.e.*, the difference between bond energies of 148 kcal for C=C and 83 kcal for C–C). The energy of the π bond in C=O can be taken as 87 kcal (*i.e.*, the difference between the bond energies of 169 kcal for C=O and 82 kcal for C–O).[13] These data suggest that rotation about the C–O bond should require in excess of 40 kcal, while the activation energies for the 1:1 benzene case and the diethyl ether case are only about one-half this magnitude. This comparison suggests that serious consideration should be given to the possibility that passage from complex to transition state can be accomplished with a smaller expenditure of energy by first dissociating the complex, followed by attack of trimethylaluminum from a slightly different direction.

Thermodynamics of $Al(CH_3)_3$ in Benzene. In the gaseous state, the equilibrium 5 exists with the dimer

$$Al_2(CH_3)_6 \overset{K_D}{\rightleftharpoons} 2Al(CH_3)_3 \qquad (5)$$

being the more abundant form at 25°. Quantitative measurements[14] of the equilibrium have been made over the temperature range 70–150°, leading to a value of ΔH of 20.40 ± 0.34 kcal. Extrapolation to 25° by use of their equation relating K_D and T, and conversion to concentration units, gives the following values:[15] $K_D(\text{gas}) = 5.1 \times 10^{-9}$, $\Delta G° = 11.3$ kcal, and $\Delta S° = 30.6$ eu.

Equilibrium 5 is important in benzene and affects the kinetic behavior when benzophenone reacts with excess trimethylaluminum. In this case, product is formed by reaction of $Al(CH_3)_3$ monomer with the 1:1 complex.[3] At sufficiently high concentrations, trimethylaluminum is present predominantly as dimer and the characteristic constant is $kK_D^{1/2}$. The best value of this constant[3] at 25° appears to be 0.26. At low trimethylaluminum concentrations, the monomer becomes predominant and the kinetic constant is k.[3] As previously stated, the value of k obtained in this work is our best possible value and leads to a value of 0.0035 l. mol^{-1} for K_D in benzene.

The thermodynamic quantities for the dimerization reaction in benzene are obtained as follows. $\Delta G°$ can be calculated directly from K_D. Since no experimental data for $\Delta H°$ are available, the assumption is made that $\Delta S°$ is the same in benzene as in the gaseous state. The validity of this assumption is supported by the measured entropy for the triethylaluminum equilibrium in *n*-hexadecane, $\Delta S° = 32.19$ eu,[16] a value very close to the gaseous $\Delta S°$ for trimethylaluminum (30.6 eu). From the assumption $\Delta S°(\text{gas}) = \Delta S°(\text{benzene})$, it follows that $\Delta H(\text{benzene}) = 12.4$ kcal.

These values of ΔH are also pertinent to the activation energies observed in nmr experiments for the exchange of bridge and terminal methyl groups in the $Al(CH_3)_3$ dimer.[17] There is general agreement[17b,c] that the rate of exchange in toluene is determined by the rate of dissociation of the dimer. Reported activation energies for exchange are 15.6 ± 0.2 kcal in cyclohexane[17a] and 15.4 ± 2 kcal in toluene.[17b] The latter value would be expected to be about the same as the ΔH for equilibrium in benzene. Thus, at first our estimate of 12.4 kcal may seem too low. However, Jeffery and Mole[17c] have pointed out the difficulty of accurate temperature measurements in these nmr experiments; their data indicate an activation energy in toluene of about 11 kcal.

The solvation energy of the trimethylaluminum monomer in benzene is a further quantity of interest. The solvation energy of a species X is the enthalpy change for the process 6. If the solvation energy of

$$X(\text{in the gas phase}) \longrightarrow X(\text{in solution}) \qquad (6)$$

the dimer is small, then the solvation energy of the monomer is $^1/_2(12.4 - 20.4) = -4.0$ kcal.

Thermodynamics of Complex Formation. The enthalpy change for the reaction

$$Al(CH_3)_3 + (C_2H_5)_2O \longrightarrow (C_2H_5)_2O \cdot Al(CH_3)_3 \qquad (7)$$

has been measured in hexane solvent and the value is −20.21 kcal.[18] The assumption is made that the same value will apply in diethyl ether solvent. The equilibrium will be so far to the right, of course, that almost no free $Al(CH_3)_3$ is present in the medium.

An important equilibrium was that given by eq 1. Measured values for ΔH for such equilibria are not available for $Al(CH_3)_3$; however, good estimates can be made based on a comparison of enthalpies for the adduct formation of other Lewis acids with ethers and ketones. In a qualitative thermochemical study,[19] it was shown that the relative heat effects on adduct formation in ethylene chloride solvent are, for $SbCl_5$, $(CH_3)_2CO = CH_3COOC_2H_5 = (C_2H_5)_2CO = (C_2H_5)_2O$; and for $SnCl_4$, $(CH_3)_2CO = CH_3COOC_2H_5 > (C_2H_5)_2CO = (C_2H_5)_2O$. In a later quantitative study, the values shown in Table I were obtained with $SbCl_5$ in the same solvent.[10]

Exhibiting the same trend are the values[20] for adduct formation with BF_3 in the gas phase. Values of −13.7 and −12.8 kcal were obtained with dimethyl ether and ethyl acetate, respectively.

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[12] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 254–257.

[13] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 100.

[14] C. H. Henrickson and D. E. Eymann, *Inorg. Chem.*, **6**, 1461 (1967).

[15] All stated numerical values for equilibrium constants will be in concentration units and at 25°. Thermodynamic properties are stated for 25° using standard states defined on a molarity basis.

[16] M. B. Smith, *J. Phys. Chem.*, **71**, 364 (1967).

[17] (a) K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Borchert, *ibid.*, **69**, 3418 (1965); (b) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 5460 (1966); (c) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **22**, 1129 (1969).

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Table I. Heats of Reaction of $SbCl_5$ with Ketones and Ethers in Ethylene Chloride[10]

Ketone	ΔH, kcal	Ether	ΔH, kcal
$(CH_3)_2CO$	-17.03	$C_3H_7OCH_3$	-18.09
$(C_2H_5)_2CO$	-16.53	$(C_3H_7)_2O$	-17.84
$(i\text{-}C_3H_7)_2CO$	-16.20		
$(i\text{-}C_4H_9)_2CO$	-16.38		
$C_6H_{10}O$	-17.79		

All of these data indicate that ΔH values for ketones are slightly less negative than those for ethers. Since ΔH for eq 7 has been measured[18] to be -20.2 kcal, we assume a value 6% smaller, *i.e.*, $\Delta H = -19.0$ kcal, for eq 8.

$$Al(CH_3)_3 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_2CO \cdot Al(CH_3)_3 \quad (8)$$

In benzene or diethyl ether solvent, the trimethylaluminum monomer is solvated so the actual reactions in which complex is formed are, along with the calculated enthalpies

$$(C_2H_5)_2O \cdot Al(CH_3)_3 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_2CO \cdot Al(CH_3)_3 + (C_2H_5)_2O \quad (9)$$
$$\Delta H_E = +1.2 \text{ kcal}$$

$$(C_6H_6) \cdot Al(CH_3)_3 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_2CO \cdot Al(CH_3)_3 + C_6H_6 \quad (10)$$
$$\Delta H_B = -15.0 \text{ kcal}$$

These enthalpy values are consistent with the observed tendencies for formation of complex.[3,4] Assuming that $\Delta S° = 0$ for these reactions leads to equilibrium constants (as normally expressed without a solvent concentration term) for complex formation of 0.014 in ether and 10^{12} in benzene.

Activation Parameters. The rates at several temperatures for the addition reaction performed at the two conditions have been obtained, and the activation parameters for each case have been calculated. The values are shown in Tables II and III. Although the activation enthalpy (22.2 kcal) for the reaction in ether, Table II, is similar to the activation enthalpy in benzene (18.5 kcal), Table III, suggesting the same mechanism in both cases, the enthalpies are not immediately comparable. In ether the reactants are present as separated entities; in benzene the reactants are already combined in a complex.

Table II. Activation Parameters for the Addition Reaction of Trimethylaluminum to Benzophenone in Diethyl Ether

Temp, °C	10^6k, l. mol^{-1} sec^{-1}	
0.0	0.123	$E_a = 22.8$ kcal
20.0	2.19	Frequency factor = 2.22×10^{11} l. mol sec^{-1}
25.0	4.14^a	$\Delta H^{\ddagger} = 22.2$ kcal
30.0	7.88	$\Delta S^{\ddagger} = -8.6$ eu

[a] From ref 4.

Table III. Activation Parameters for the Addition of Trimethylaluminum to Benzophenone in Benzene in a 1:1 Reactant Ratio

Temp, °C	10^4k, sec^{-1}	
12.6	0.316	$E_a = 19.1$ kcal
20.0	0.607	Frequency factor =
25.0	1.20^a	1.27×10^{10} l. mol sec^{-1}
30.0	2.07	$\Delta H^{\ddagger} = 18.5$ kcal
40.0	5.95	$\Delta S^{\ddagger} = -14.1$ eu

[a] From ref 3.

Two pathways, both consistent with the rate law, have been suggested for organometallic alkylation of ketones. One suggested pathway is that complex formation is a nonproductive equilibrium and that reaction occurs by bimolecular collision of the reactants. The alternative is that product formation arises by internal rearrangement of the complex. The activation enthalpies were analyzed according to each possibility.

A bimolecular process is one in which the initially separated species undergo a collision in which rearrangement occurs smoothly to yield products. In both diethyl ether and benzene the trimethylaluminum monomer is solvated, and the bimolecular process can be represented as

$$S \cdot Al(CH_3)_3 + K \longrightarrow [S \cdot Al(CH_3)_3 \cdot K]^{\ddagger} \longrightarrow P \quad (11)$$

Since the rate constant in ether is a second-order constant, the measured enthalpy of activation (22.2 kcal) would be the activation enthalpy in the bimolecular step. In benzene, however, the observed rate constant is a first-order constant and the bimolecular constant, k_2, is related to it by $k_2 = k_{obsd}K$, and $\Delta H^{\ddagger}{}_2 = \Delta H^{\ddagger}{}_{obsd} + \Delta H_B = 18.5 - 15.0 = 3.5$ kcal. If this reaction is proceeding by a bimolecular mechanism, we note that the activation energy is almost the same as the energy required to dissociate $S \cdot Al(CH_3)_3$ (*i.e.*, 22.2 compared with 20.2 in ether, and 3.5 compared with 4.0 in benzene). Frequently in bimolecular reactions in which bond forming and bond breaking occur simultaneously, the activation energy is significantly lower than the dissociation energy of the bond being broken because of an energetic contribution due to the bond formation. In this case, there appears to be no contribution from the latter. Thus, assumption of a bimolecular process leads to a transition state in which $Al(CH_3)_3$ is adjacent to both a solvent molecule and a ketone molecule but is bonded to neither.

If direct rearrangement of complex is the mechanistic path, $\Delta H^{\ddagger}$ for the rearrangement step in benzene is 18.5 kcal. In ether the observed rate constant is a second-order constant and the unimolecular constant k_1 is related to it by $k_1 = k_{obsd}/K$, and $\Delta H^{\ddagger} = \Delta H^{\ddagger}{}_{obsd} - \Delta H_E = 22.2 - 1.2 = 21.0$ kcal. Thus, the activation energy for rearrangement of complex in each case is almost the same as the energy required to dissociate complex $(C_6H_5)_2CO \cdot Al(CH_3)_3$ (18.5 and 21.0 kcal compared with 19.0 kcal). The transition state indicated consists of a free $Al(CH_3)_3$ in the immediate proximity of the ketone. Again there is no indication of an energy contribution associated with a forming carbon–carbon bond in the transition state.

Thus, both arguments lead to the same transition state configuration, suggesting that the system is better described according to the following kinetic formalism.

$$\begin{tikzcd}
A + K \arrow[r, shift left, "k_1"] & (A - K) \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[d, "k_3"', "\Delta H_3^{\ddagger}"] & C \arrow[l, shift left, "k_{-2}"] \\
& P &
\end{tikzcd}$$

The symbol (A – K) indicates the species A and K are

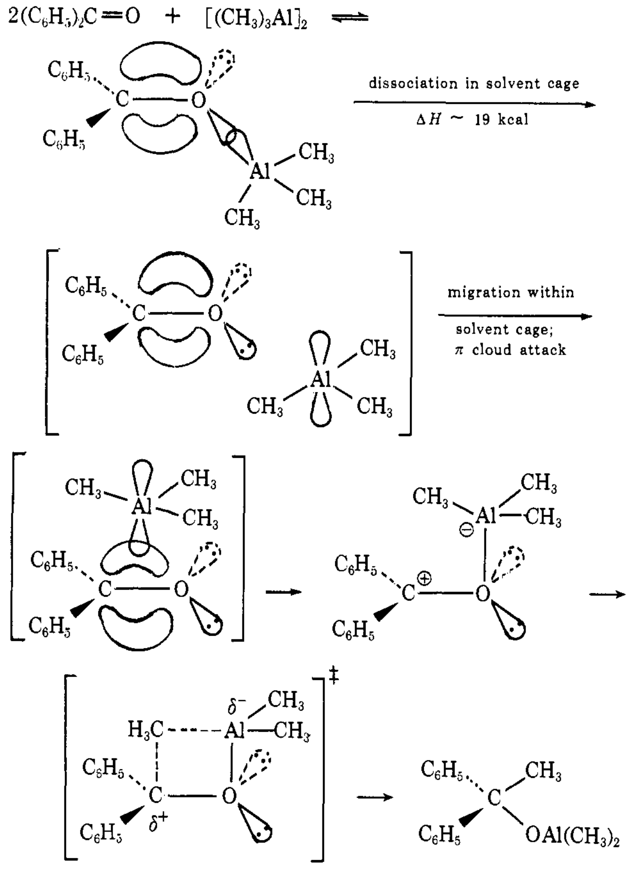

Figure 3. Illustration of the detailed sequence of transformations leading from reactants to product in the alkylation of benzophenone by trimethylaluminum in diethyl ether and in 1:1 reactant ratio in benzene. The brackets represent a cage of solvent molecules.

not chemically combined but held together briefly in a "cage" of solvent molecules. The steady-state treatment can be conveniently used to obtain a mathematical expression for the observed rate.

$$\frac{d[P]}{dt} = \frac{k_3(k_1[A][K] + k_2[C])}{k_{-1} + k_2 + k_3}$$

In ether, where the reactants are present predominantly as the separated species

$$k_{obsd} = \frac{k_1k_3[(k_{-1} + k_2)/k_{-1}]}{k_{-1} + k_2 + k_3} \simeq (k_1/k_{-1})k_3$$

$$\Delta H^{\ddagger}{}_{obsd} = 22.2 \simeq 20.2 + \Delta H^{\ddagger}{}_3((C_2H_5)_2O)$$

$$\Delta H^{\ddagger}{}_3((C_2H_5)_2O) \simeq 2.0 \text{ kcal}$$

In benzene, where the reactants are present combined in a complex

$$k_{obsd} = \frac{k_{-2}k_3[(k_{-1} + k_2)/k_2]}{k_{-1} + k_2 + k_3} \simeq (k_{-2}/k_2)k_3$$

$$\Delta H^{\ddagger}{}_{obsd} = 18.5 \simeq 19.0 + \Delta H^{\ddagger}{}_3(C_6H_6)$$

$$\Delta H^{\ddagger}{}_3(C_6H_6) \simeq -0.5 \text{ kcal}$$

Because of the uncertainties in the thermodynamic values used in calculating $\Delta H^{\ddagger}{}_3$, we regard $\Delta H^{\ddagger}{}_3((C_2H_5)_2O) = \Delta H^{\ddagger}{}_3(C_6H_6)$. The value is most likely a small positive number of about 1 or 2 kcal.

Figure 3 illustrates the detailed path by which benzophenone is alkylated by trimethylaluminum in diethyl ether and in the 1:1 reactant ratio in benzene. The separated species held in a cage of solvent molecules can be approached by dissociation of the complex or directly from the reactants. Bonding is depicted as occurring initially between the aluminum and the π-electron cloud near the carbonyl oxygen, followed by bonding of a methyl group with the carbonyl carbon. This sequence of transformations from reactants to products is most reasonable for two reasons: (1) the initial interaction which brings the reactants together on a product forming path is the electrostatic attraction between the aluminum and the carbonyl π-electron cloud, and (2) bond formation between the aluminum and the carbonyl oxygen occurs at a greater distance than bonding between a methyl and carbonyl carbon. Just which configuration in this sequence corresponds to the transition state of increased energy $\Delta H^{\ddagger}{}_3$ is, of course, unknown.

The transition states in diethyl ether and in the 1:1 case in benzene are probably very similar, so that the entropies of activation (−8.36 eu in ether, and −14.1 eu) reflect the fact that the initial conditions are different. The $\Delta S^{\ddagger}$ in benzene is the difference in entropy of the complex and the transition state. The decrease in entropy indicates a decreased freedom of motion in the transition state. In ether, $\Delta S^{\ddagger}$ is the difference in the entropy of the initial reactants (free ketone plus trimethylaluminum bound to an ether) and the transition state condition. Although freedom of motion is lost in forming the transition state proper, there is some compensation in the freedom of motion gained by the released ether molecule.

Recently, evidence has been accumulating that radical mechanisms may be important in certain reactions of this type. If reaction proceeds through formation of a radical in the solvent cage, the activation energy will be determined by the energy necessary to break the metal–carbon bond homolytically. Although limited thermodynamic data are available for this kind of consideration, the result in the case of $Al(CH_3)_3$ seems quite clear. The average bond energy for Al–C in the gaseous $Al(CH_3)_3$ monomer has been determined[21] to be 64.5 ± 2.0 kcal/mol. Although this value would probably be smaller in any complex, it is unlikely that it would be decreased to the point (*i.e.*, to about 20 kcal) where the radical mechanism would be competitive with the mechanism described in this paper.

Reaction in Excess Trimethylaluminum. The activation parameters for the reaction of benzophenone with excess trimethylaluminum are given in Table IV.

Table IV. Activation Parameters for the Addition Reaction of Excess Trimethylaluminum to Benzophenone in Benzene

Temp, °C	k, l. mol^{-1} sec^{-1}	
10.0	1.76	E_a = 11.1 kcal
15.0	2.54	Frequency factor =
20.0	3.53	6.19 × 10^8 l. mol^{-1} sec^{-1}
25.0	4.40	$\Delta H^{\ddagger}$ = 10.5 kcal
30.0	6.57	$\Delta S^{\ddagger}$ = −21.1 eu

The transition state has a composition corresponding to addition of one $Al(CH_3)_3$ molecule to the complex.[3]

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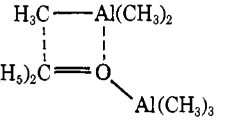
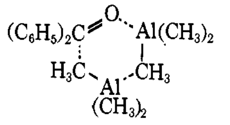
(21) C. T. Mortimer and P. W. Sellers, *J. Chem. Soc.*, 1978 (1963).

It is reasonable that attack of monomeric trimethylaluminum on the complexed ketone occurs in a way similar to the attack on uncomplexed ketone shown in the last part of Figure 3. Comparison of the enthalpies of activation is consistent with this view. The initial attack of a molecule of $(CH_3)_3Al$ on either complexed or uncomplexed ketone is at the cloud of π electrons which has its greatest density at the oxygen. In the complex, the electron density on the oxygen is decreased due to inductive withdrawal of electrons by the trimethylaluminum bond to the nonbonding electrons on the oxygen. As a result, bond formation with the attacking Al is energetically less favorable, and the activation enthalpy for attack of $(CH_3)_3Al$ on free ketone, $\Delta H^{\ddagger}_3$, is less than that for attack of $(CH_3)_3Al$ on complex, 10.5 kcal.

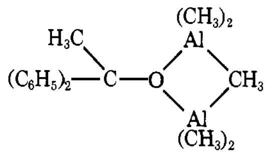
The transition states I and II have been suggested for this reaction in benzene[3,22] leading to the product "hemialkoxide" III. Structure I is more consistent with the description above; but examination of molecular models of both transition states I and II with reasonable bond distances and angles reveals an interesting feature. The arrangement of the atoms in what appears to be the most favorable six-membered ring II is rather like two planar four-membered rings fused at a common side with a dihedral angle of about 125°. In this structure, the four-membered ring containing the carbonyl (C=O) is not much different than the four-membered ring of transition state I. The major difference between the proposed transition states I and IV is that in structure I the trimethylaluminum molecule bound to the oxygen is free to rotate, while in structure IV rigidity is imposed by the bridging methyl group. The question is then whether or not a methyl bridge bond is formed as the free monomeric $(CH_3)_3Al$ attacks the complex. The formation of such a bond would be energetically favorable and an estimate of this effect can be made in the following way. The enthalpy change for the reaction $[Al(CH_3)_3]_2 \rightarrow 2Al(CH_3)_3$ in benzene was estimated above to be about 12.4 kcal. Since transition state IV contains one methyl bridge, it would be expected to be about 6 kcal more favorable than any transition state in which an aluminum–methyl bridge bond is not formed. The large negative entropy of activation, $\Delta S^{\ddagger} = -21.1$ eu, supports a fairly rigid cyclic transition state, such as IV.



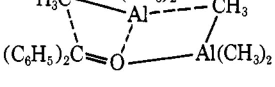
I



II



III



IV

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Rearrangements of Azidoquinones. X. Thermal Rearrangements of Monoazidoquinones to 2-Cyano-4-cyclopentene-1,3-diones[1,2]

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Abstract: The thermal decomposition of monoazido-1,4-quinones (**1**) is described. This reaction results in their high yield ring contraction to 2-cyano-4-cyclopentene-1,3-diones (**2**). The synthetic scope as well as the kinetics and mechanism of this rearrangement are discussed.

Azidoquinones constitute a synthetically versatile and readily available class of compounds. Depending upon their substitution pattern and the reaction conditions, a variety of very specific and high yield transformations can be accomplished. Monoazido-1,4-quinones stereospecifically rearrange to γ-cyano-alkylidene-$\Delta^{\alpha,\beta}$-butenolides when decomposed in cold concentrated sulfuric acid.[3] On the other hand, 4-azido-1,2-naphthoquinone ring expands to 4-hydroxy-1*H*-1-benzazepine-2,5-dione under the same reaction conditions.[4] Thermal decomposition of 2,5-diazido-1,4-benzoquinones induces their cleavage to two molecules of the corresponding cyanoketene,[5,6]

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[2] Based primarily upon the Ph.D. dissertation of Walter Weyler, Jr.

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[4] H. W. Moore, H. R. Shelden, and W. Weyler, *Tetrahedron Lett.*, 1243 (1969).

[5] H. W. Moore and W. Weyler, *J. Amer. Chem. Soc.*, 92, 4132 (1970).

[6] H. W. Moore and W. Weyler, *ibid.*, 93, 2812 (1971).