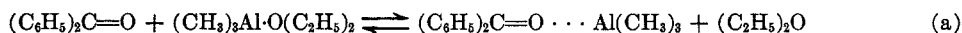


Mechanisms of Organometallic Alkylation Reactions. III. The Mechanism of Trimethylaluminum Addition to Benzophenone in Diethyl Ether

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The reaction of trimethylaluminum with benzophenone in diethyl ether has been used as a model system for the study of organometallic reaction mechanisms in polar solvents. A kinetic study of the reaction at 25° showed that the reaction obeys the second-order rate equation $d[P]/dt = k[A][K]$. The ultraviolet spectra of reacting mixtures showed that some complexation between reactants occurs but is small enough to warrant a steady-state treatment of the rate data. The mechanism of the reaction is expressed in steps a and b. A com-



parison of this mechanism observed in diethyl ether is made with the mechanisms observed in benzene solvent. Further comparison of this mechanism with Grignard alkylation mechanisms is also made.

Trialkyl- and triarylaluminum compounds have been reported by several workers to be monomeric in ether solution. Brown and Davidson² showed that trimethylaluminum dimethyl etherate is monomeric in solution. Mole³ reported that triphenylaluminum is monomeric in diethyl ether. Mole and Surtees⁴ reported that a solution of trimethylaluminum diethyl etherate is nearly monomeric in benzene. Nuclear magnetic resonance shows a single proton signal for a 20% solution of trimethylaluminum in diethyl ether both at room temperature and at -80°. Since nuclear magnetic resonance studies of trimethylaluminum in cyclopentane and toluene have shown that the methyl protons of dimeric trimethylaluminum are not equivalent at low temperature,^{6,7} one can only conclude that trimethylaluminum is monomeric in diethyl ether.

Little data is available on the reactions of organoaluminum etherates with ketones and no mechanistic work has been reported. Mole⁸ reported that triphenylaluminum in diethyl ether reacts with benzophenone only after several hours in a sealed tube at elevated temperatures. Mole and Surtees⁴ reported that trimethylaluminum diethyl etherate reacts readily with benzophenone in boiling benzene with a rapid release of diethyl ether.

The study of the addition reaction of trimethylaluminum to benzophenone was undertaken in the hope that the results would resolve some of the controversy surrounding organometallic alkylation reactions involving organometallic compounds containing metal atoms from groups I, II, and IIIA.⁹ This reaction is ideal for several reasons. First, trimethylaluminum is definitely monomeric in diethyl ether thus eliminating complex redistribution equilibria of the organometallic reactant which complicates the evaluation of kinetic data obtained using most organometallic compounds.

Normally only one aluminum-carbon bond is able to add to carbonyl compounds^{4,10} and the problem of competing reactions by various species is avoided. Furthermore, trimethylaluminum contains no β hydrogen and therefore will not reduce the ketone. Benzophenone, lacking an α hydrogen, cannot result in enolization. Therefore only an alkylation product should be observed.

Experimental Section

Materials.—Trimethylaluminum was obtained from Texas Alkyls, Inc. The Batch Analytical Report received showed that 0.1% triethylaluminum was present. 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 under vacuum. The middle fraction (mp 48.2–49.0°) of the second distillation was used in 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.

Apparatus and Procedure.—A Cary Model 14 recording spectrophotometer was used for recording all ultraviolet spectra. A Zeiss PMQ II single-beam spectrophotometer was used for obtaining Beer's law plots and making kinetic measurements at a single wavelength.

Matched quartz, 10-mm cells (Beckman Scientific Co.) were employed for obtaining 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.¹¹ The atmosphere in this glove box was such that neat triethylaluminum did not fume when exposed. All operations in the glove box involving kinetics were preceded by heating the equipment and placing it hot in the entry port, evacuating the entry port twice to at least 0.4 mm of pressure, and bleeding dry nitrogen back into the entry port before the door to the inner chamber was

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opened. Recirculation of the atmosphere through oxygen and water scrubbers was then allowed to proceed for at least 2 hr prior to exposure of solutions to the glove box atmosphere.

Calibrated syringes equipped with stainless steel needles were used for transfers of reagents. Deliveries could be reproduced with an average of $\pm 0.5\%$.

Ultraviolet Spectra.—In diethyl ether solution two major absorption bands were observed for benzophenone in the ultraviolet spectrum. The maximum representing the $n \rightarrow \pi^*$ transition occurs at $344.5 \text{ m}\mu$ with an extinction coefficient of 119. The maximum was found to obey Beer's law over the range of concentrations from $7.6 \times 10^{-4} \text{ M}$ to $8.09 \times 10^{-3} \text{ M}$. A much stronger maximum representing the $\pi \rightarrow \pi^*$ transition occurs at $251 \text{ m}\mu$ with an extinction coefficient of 1.8×10^4 . A trough occurs at $305 \text{ m}\mu$. Benzophenone does not absorb at wavelengths longer than $400 \text{ m}\mu$. 1,1-Diphenylethanol showed no absorbance at wavelengths longer than $300 \text{ m}\mu$.

A 0.4352 M solution of trimethylaluminum in diethyl ether showed no absorbance at wavelengths longer than $241 \text{ m}\mu$.

Spectra of mixtures of trimethylaluminum and benzophenone were obtained in the following way. Matched 10-mm quartz ultraviolet cells were taken into the glove box. The reference cell was filled with 3 ml of dry diethyl ether. The sample cell was filled with 1.5 ml of standard ketone solution and 1.5 ml of standard trimethylaluminum solution. Standard benzophenone spectra were obtained by using 1.5 ml of pure diethyl ether in the sample cell in place of standard trimethylaluminum solution for comparison purposes. The solutions were removed from the glove box and spectra were recorded immediately and at appropriate time intervals. Owing to the extreme sluggishness of the reaction between trimethylaluminum and benzophenone in diethyl ether, spectra recorded within several hours of mixing represented accurately the spectra at zero reaction time.

A mixture of 1.5 ml of $6.19 \times 10^{-3} \text{ M}$ benzophenone and 1.5 ml of $6.2 \times 10^{-3} \text{ M}$ trimethylaluminum gave an ultraviolet spectrum identical with that of benzophenone. At a trimethylaluminum concentration of 0.1 M , a slight absorbance was noted in the $400\text{--}450\text{-m}\mu$ region and the benzophenone maximum at $305 \text{ m}\mu$ was not quite so deep. When 1.5 ml of $6.19 \times 10^{-3} \text{ M}$ benzophenone is added to 1.5 ml of 0.548 M trimethylaluminum, the benzophenone maximum at $344.5 \text{ m}\mu$ appears as a shoulder, the trough at $305 \text{ m}\mu$ disappears completely, and a strong absorbance occurs. The absorbance at $400 \text{ m}\mu$ in this mixture is about 0.02. The relative absorbance at $344.5 \text{ m}\mu$ of mixtures is the same as that of pure benzophenone solution.

The benzophenone maximum at $251 \text{ m}\mu$ is not affected by a large excess of trimethylaluminum. When 1.5 ml of 10^{-4} M benzophenone was mixed with 1.5 ml of 0.435 M trimethylaluminum, the spectrum is identical with that of the pure ketone except that the maximum at $251 \text{ m}\mu$ decreases over a period of several days.

Kinetics.—An all-glass, round-bottom reaction flask was used for kinetic studies. The only opening to the flask was through a 2-mm-bore three-way Teflon stopcock which was used for adding reagents and withdrawing samples. Because of the slowness of the reaction it was convenient to add both reagents to the reaction flask inside the glove box. The reaction flask was then transferred to a constant-temperature bath at $25 \pm 0.02^\circ$. One side arm of the Teflon stopcock was connected to a nitrogen line. The stopcock was kept tightly sealed except when samples were withdrawn and then a strong flow of nitrogen was placed on the system.

Two methods were used to analyze for unreacted benzophenone at appropriate times. When the concentration of the ketone was less than 0.01 M , samples withdrawn from the reaction flask were injected into nitrogen-flushed ultraviolet cells and a measurement of the benzophenone maximum at $344.5 \text{ m}\mu$ was made. Since the relative absorbance of benzophenone at $344.5 \text{ m}\mu$ in diethyl ether is not affected significantly by trimethylaluminum, the concentration of benzophenone at any time could be determined from Beer's law.

In those runs in which the concentration of benzophenone was greater than 0.05 , gas chromatography was employed to determine the extent of reaction. The samples were quenched in water; concentrated hydrochloric acid was added directly to the diethyl ether layer with stirring. The concentrated hydrochloric acid was necessary to convert 1,1-diphenylethanol completely into 1,1-diphenylethylene. In quenched mixtures which were not treated with hydrochloric acid only partial conversion of the alcohol into the olefin occurred.

The areas under the peaks corresponding to unreacted benzophenone and to 1,1-diphenylethylene were measured with a planimeter. The combined areas of the olefin and ketone peaks were taken as proportional to the unreacted starting material and product.

Mixtures of benzophenone and 1,1-diphenylethanol in four different ratios were prepared by weighing out the reagents in volumetric flasks and diluting to the mark. The weight and mole per cent of the reagents in each flask were calculated and an aliquot from each solution was treated in the same manner as kinetic samples. The areas under the peaks corresponding to benzophenone and to 1,1-diphenylethylene were measured with a planimeter. The area per cent of each peak agreed better than one per cent to the mole per cent of each reagent. The agreement of the rate constants in which the concentration of benzophenone was determined by ultraviolet analysis and those in which the benzophenone concentration was determined by glpc substantiates the validity of the latter method. No product other than 1,1-diphenylethanol was found for this reaction.

Calculations.—Standard mixtures of benzophenone were prepared for these studies by carefully weighing out an appropriate amount of the ketone in a volumetric flask and diluting to volume. Standard trimethylaluminum solutions were prepared by dilution of an appropriate volume with diethyl ether.

Appropriate amounts of standard trimethylaluminum and benzophenone solutions were mixed in the kinetic flasks and the concentration of each reagent at zero reaction time was calculated from the dilution factor. The concentration of trimethylaluminum was determined for the standard solutions and for the kinetic solutions after mixing by decomposing aliquot samples with dilute hydrochloric acid and mixing with an excess of standard EDTA. Excess EDTA was then titrated with a standard zinc acetate solution using dithiazone as an indicator. The analyzed concentration of trimethylaluminum in the kinetic flask agreed within 0.5% of the concentration calculated by the dilution factor.

Rate constants were calculated from the second-order rate equation

$$k = \frac{2.3}{t([A]_0 - [K]_0)} \log \frac{[K]_0[A]}{[A]_0[K]}$$

where $[A]_0$ and $[K]_0$ represent the initial concentrations of trimethylaluminum and benzophenone and $[A]$ and $[K]$ represent the concentrations at time, t . 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.

Results and Discussion

The reaction of trimethylaluminum and benzophenone was found to proceed very slowly in diethyl ether in a single reaction to produce on hydrolysis the expected alcohol, 1,1-diphenylethanol. In a product study a reaction between 0.3 M trimethylaluminum and 0.3 M benzophenone resulted in an 82% yield of 1,1-diphenylethanol after 35 days at room temperature. A material balance indicated only unreacted benzophenone in addition to 1,1-diphenylethanol. There is no evidence that 100% yield of product cannot be realized if the reaction is allowed to proceed a sufficient length of time.

The ultraviolet spectra of reacting mixtures demonstrate that complexation between reacting species occurs to a very small extent. Thus a solution 0.00305 M in benzophenone and 0.00305 M in trimethylaluminum gave an ultraviolet spectrum identical with that of a solution of pure 0.00305 M benzophenone. When the trimethylaluminum concentration was increased to 0.274 M , a 90-fold excess of the aluminum alkyl, the ultraviolet spectrum showed a slight absorbance in the $400\text{--}450\text{-m}\mu$ region. In addition, the trough at $305 \text{ m}\mu$, characteristic of uncomplexed benzophenone, disappeared and a strong absorbance occurred at this wave-

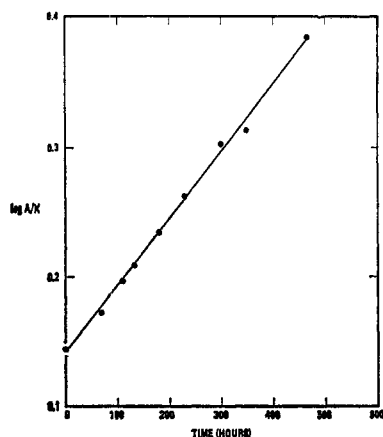


Figure 1.—Plot demonstrating second-order reaction of trimethylaluminum and benzophenone in diethyl ether at 25° (run no. 4, Table I).

length. The relative absorbance at the benzophenone maximum (344.5 $m\mu$) in this mixture remained unchanged when compared with a standard 0.00305 M benzophenone spectrum. The solution at this concentration appeared clear to the unaided eye. This behavior is in marked contrast to the behavior of benzophenone and trimethylaluminum in benzene.^{10a} In the nonpolar solvent a mixture of the aluminum alkyl and benzophenone resulted in a deep yellow color attributed to the formation of complex in high concentration. In addition, the ultraviolet spectra of reacting mixtures in benzene displayed no bands characteristic of benzophenone and showed a strong absorbance in the 400–500- $m\mu$ region even when the initial concentration of each reactant was only 0.006 M . In diethyl ether at concentrations of both the aluminum alkyl and benzophenone above 0.05 M the yellow color characteristic of the trimethylaluminum–benzophenone complex^{4,10a} becomes visible and deepens as the concentrations of each are increased. The fact that the ultraviolet spectral changes and the appearance of a yellow color are immediate when trimethylaluminum and benzophenone are mixed in diethyl ether, indicates that the equilibrium between reactants to form a complex is rapid.

The method used to study the reaction of trimethylaluminum with benzophenone kinetically proved to be very satisfactory. Reaction mixtures which were allowed to remain in the constant-temperature bath for several weeks, showed no signs of hydrolysis or loss of diethyl ether due to evaporation.

The reaction between trimethylaluminum and benzophenone in diethyl ether was found to be first order in each reactant and second order over-all. Table I summarizes the results obtained. The average rate constant is 0.0148 ± 0.0005 l. mol⁻¹ hr⁻¹ at 25°. The second-order behavior was observed between 10 and 75% reaction. Furthermore, the rate constant was found to be independent of the reactant ratio and of the initial concentration of either reactant. Thus the value of the rate constant did not vary with trimethylaluminum to benzophenone ratios of 0.517:1 to 18.8:1, initial benzophenone concentrations of 0.00681 to 0.3867 M , and with initial trimethylaluminum concentrations of 0.0246 to 0.3833 M . Data from a typical run is graphically illustrated in Figure 1 (data from run 4, Table I).

TABLE I
RATE CONSTANTS FOR THE REACTION OF TRIMETHYLALUMINUM WITH BENZOPHENONE IN DIETHYL ETHER AT 25.0°

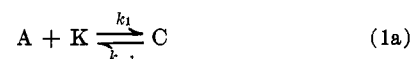
Run	(CH ₃) ₃ Al, <i>M</i>	(C ₆ H ₅) ₂ CO, <i>M</i>	(CH ₃) ₃ Al/ (C ₆ H ₅) ₂ CO	<i>k</i> , l. mol ⁻¹ hr ⁻¹
1	0.2003	0.3865 ^a	0.517	0.0153
2	0.2240	0.3250 ^a	0.658	0.0133
3	0.2540	0.2340 ^a	1.09	0.0162
4	0.2710	0.1950 ^a	1.39	0.0151
5	0.3415	0.1546 ^a	2.21	0.0151
6	0.2940	0.1300 ^a	2.26	0.0148
7	0.3538	0.1288 ^a	2.74	0.0138
8	0.2060	0.0651 ^a	3.16	0.0147
9	0.0246	0.00731 ^b	3.37	0.0154
10	0.0313	0.00681 ^b	4.59	0.0144
11	0.3833	0.07026 ^a	5.45	0.0159
12	0.1189	0.00632 ^b	18.8	0.0149 ^c

Average 0.0148 ± 0.0005

^a Benzophenone concentration determined by glpc analysis.

^b Benzophenone concentration determined by ultraviolet analysis. ^c Rate constant calculated from pseudo-first-order rate constant of 0.00177 hr⁻¹.

The monomeric nature of the reactants, trimethylaluminum and benzophenone, and the fact that the ultraviolet spectra of reacting mixtures show that the equilibrium to form complex is rapid and lies largely to the left, allowed the kinetic data to be easily interpretable in terms of a specific reaction mechanism. The mechanism (eq 1a and b) is consistent with all the observations. The rate expression for the appearance of product for the mechanism in eq 1 is given by eq 2.



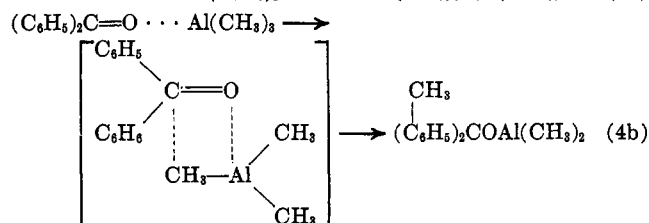
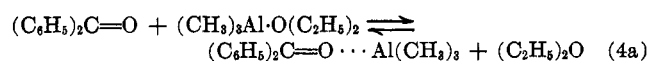
$$\frac{dP}{dt} = k_2[C] \quad (2)$$

In eq 1 the symbols represent the following species: A = aluminum alkyl (trimethylaluminum), K = ketone (benzophenone), and P = product (dimethylaluminum 1,1-diphenylmethylcarbinolate) formed by an intramolecular rearrangement of the complex, C. Assuming that the concentration of complex in the reacting mixture is so small that the steady-state approximation is valid, eq 3 demonstrates that second-order

$$\frac{dP}{dt} = \frac{k_2 k_1 [A][K]}{k_{-1} + k_2} = k[A][K] \quad (3)$$

kinetics should be observed for the proposed mechanism. The ultraviolet spectra of reacting solutions indicate that the concentration of complex is indeed small enough to make the steady-state approximation valid.

The detailed mechanism by which trimethylaluminum and benzophenone react in diethyl ether is given in eq 4a and b.



The contrast of the mechanism of addition of trimethylaluminum to benzophenone in diethyl ether to the recently described mechanisms for this reaction in benzene^{10a} is worth examining. The reaction in benzene was found to proceed through two distinct mechanistic paths depending on the ratio of the reactants (Table II). In these mechanisms A = aluminum

1:1	1:2
$A_2 \rightleftharpoons 2A$	$A_2 \rightleftharpoons 2A$
$K + A \rightleftharpoons C$	$K + A \rightleftharpoons C$
$C \rightarrow P'$	$C + A \rightarrow P$
$P' + A \rightleftharpoons P$	$P \rightleftharpoons P' + A$

alkyl [(CH₃)₃Al], K = ketone (benzophenone), C = complex [(C₆H₅)₂C=O ··· Al(CH₃)₃], P' = initial product [(C₆H₅)₂CCH₃OAl(CH₃)₂], P = final product [(C₆H₅)₂CCH₃OAl(CH₃)₂ · Al(CH₃)₃]. In both mechanisms complex formation between the reactants was nearly complete. When the ratio of the reactants, (C₆H₅)₂C=O to (CH₃)₃Al was 1:1 or less, the product was formed by a relatively slow intramolecular rearrangement of the complex. When the reactant ratio was greater than 1:1, a rapid attack on the complex by a second molecule of monomeric trimethylaluminum resulted in the formation of product.

The reaction in diethyl ether is much slower than in benzene. The half-life of a reaction of trimethylaluminum with benzophenone in benzene is about 5 hr when the concentration of each reactant is about 0.0083 M and about 1 min when the concentration of trimethylaluminum is doubled. In contrast, when 0.254 M trimethylaluminum is allowed to react with 0.234 M benzophenone in diethyl ether, the half-life is 9.7 days. This difference in reaction rate can be explained partially by the position of equilibrium (eq 1a). In benzene this equilibrium lies almost completely to the right whereas in diethyl ether the equilibrium lies almost completely to the left owing to the competition between solvent molecules and ketone for the organoaluminum compound. This competition of course does not exist in benzene. Secondly it was found that the reaction of complex to produce product was rather slow in benzene ($k_2 = 1.2 \times 10^{-4} \text{ sec}^{-1}$ at 25°). This is the only path by which the product can be formed in diethyl ether. The path (C + A → P) which was preferred in benzene is not possible in diethyl ether owing to the fact that trimethylaluminum which is not complexed with benzophenone has its vacant orbital satisfied by diethyl ether. Thus product formation by the consecutive bimolecular mechanism is impossible in diethyl ether regardless of the stoichiometry of reactants. Since formation of the product in diethyl ether is possible only by a slow rearrangement of a complex that exists in very small concentration, it is easy to see why the reaction is so slow in diethyl ether.

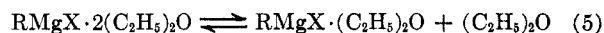
An interesting aspect of the reaction of trimethylaluminum with benzophenone in benzene is that the initially formed carbinolate complexed a molecule of trimethylaluminum and made it unavailable for further reaction. This did not occur in diethyl ether. Thus the relative basicities of diethyl ether, dimethylaluminum 1,1-diphenylmethylcarbinolate, and benzo-

phenone toward trimethylaluminum are in the following order: (C₂H₅)₂O > (C₆H₅)₂CCH₃OAl(CH₃)₂ > (C₆H₅)₂C=O.

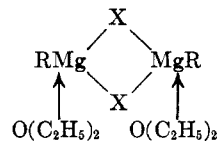
It is interesting to note that in both benzene and diethyl ether the intramolecular rearrangement of complex to product in the reaction of (C₆H₅)₂C=O with (CH₃)₃Al is very slow. On the other hand, when (CH₃)₃Al in benzene is used in excess, the reaction is extremely fast, pointing out the distinct preference for a consecutive bimolecular reaction compared with a simple first-order rearrangement of the complex. That is of course when the organometallic metalating agent is not complexed with ether such that it cannot easily participate in a consecutive bimolecular reaction. This point is very important in considering the reaction of Grignard reagents with ketones in that the crucial point in this mechanism concerns whether or not a consecutive bimolecular reaction is involved (mechanism A)¹² or a simple first-order disappearance of the complex in an intramolecular rearrangement (Table III,

Mechanism A	Mechanism B
$K + G \rightleftharpoons C$	$K + G \rightleftharpoons C$
$C + G \rightarrow P$	$C \rightarrow P'$
$P \rightleftharpoons P' + G$	

mechanism B).¹³ Although the Grignard reagent is solvated in diethyl ether, it is believed that this does not necessarily prevent the consecutive bimolecular mechanism because the second ether molecule attached to magnesium is not held very tightly. This con-



clusion is based on two observations: (1) typical magnesium compounds [C₂H₅MgBr, (C₂H₅)₂Mg, and MgBr₂] are isolated as monoetherates from solution by vacuum drying at room temperature; and (2) the fact that Grignard compounds associate in diethyl ether whereas aluminum alkyls do not indicate that the Grignard compounds are best represented in diethyl ether solution by eq 5. This is so because dissociation to a monoetherate containing a vacant orbital is necessary to form an associated species such as that shown.



Thus the monoetherate, possessing a vacant orbital, can participate in a consecutive bimolecular mechanism described by mechanism A.

Registry No.—Trimethylaluminum, 75-24-1; benzophenone, 119-61-9; diethyl ether, 60-29-7.

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