Mechanisms of Organometallic Alkylation Reactions. II.[1] Kinetics of Trimethylaluminum Addition to Benzophenone in Benzene. An Example of a Change in Mechanism with Stoichiometry[2]

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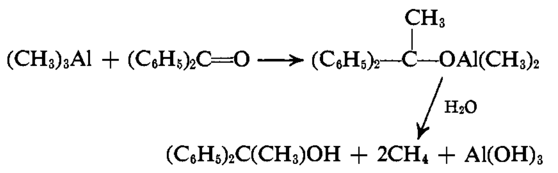
Abstract: The reaction of trimethylaluminum with benzophenone has been used as a model system for the study of reaction mechanisms describing organometallic alkylation reactions. The reaction of trimethylaluminum with benzophenone in benzene solvent in 1:1, 2:1, and higher ratios was studied kinetically and was found to proceed through two distinct mechanistic paths depending upon the ratio of aluminum alkyl to ketone. In both cases the reactants immediately form a complex whose formation is governed by a very large equilibrium constant [$(CH_3)_3Al + (C_6H_5)_2C{=}O \rightleftarrows (C_6H_5)_2C{=}O\cdots Al(CH_3)_3$]. Rates of reaction were followed by disappearance of both the complex band during reaction and the ketone band after hydrolysis. When the aluminum alkyl to ketone ratio is 1:1 or less, the addition product [$(C_6H_5)_2CCH_3OAl(CH_3)_2$] is formed by a relatively slow rearrangement of the complex as evidenced by the first-order disappearance of the complex. An unusual aspect of this reaction is that the addition product, as it is formed, complexes trimethylaluminum originally held in complex formation with benzophenone, thus releasing benzophenone from the complex into solution. Thus at 50% reaction the product consists mainly of an almost equimolar mixture of free benzophenone and a complex of the addition product with trimethylaluminum. Further alkylation of benzophenone after the addition product-$Al(CH_3)_3$ complex is formed does take place, but at a much slower rate than the first 50% of the reaction. Thus the mechanism is expressed in the following series of steps: (1) $A_2 \rightleftarrows 2A$, (2) $A + K \rightleftarrows C$, (3) $C \rightarrow P'$, (4) $P' + A \rightleftarrows P$, where A = aluminum alkyl [$(CH_3)_3Al$], K = ketone (benzophenone), C = complex [$(C_6H_5)_2C{=}O\cdots Al(CH_3)_3$], P′ = initial product [$(C_6H_5)_2CCH_3OAl(CH_3)_2$], and P = final product [$(C_6H_5)_2CCH_3OAl(CH_3)_2\cdot Al(CH_3)_3$]. When excess trimethylaluminum is allowed to react with benzophenone, a much faster reaction takes place. The complex initially formed is rapidly attacked by monomeric trimethylaluminum to form the alkylation product in a consecutive bimolecular reaction. The mechanism of reaction is expressed in the following steps: (1) $A_2 \rightleftarrows 2A$, (2) $A + K \rightleftarrows C$, (3) $C + A \rightarrow P$, (4) $P \rightleftarrows P' + A$.

The mechanisms of organometallic alkylation reactions involving organometallic compounds containing metal atoms from groups I, II, and IIIA have been the subject of considerable study and controversy for a number of years.[4] The mechanism receiving the most attention in the past few years has been the one describing the reaction of Grignard compounds with ketones in ether solvent.[4a] The major problem in this area has been the evaluation of kinetic data in terms of a mechanism involving redistribution equilibria in several steps of the reaction. Examination of reactions involving aluminum alkyls indicates that some of the complicating redistribution equilibria observed in Grignard (or organolithium) reactions should not be encountered when aluminum alkyls are the alkylating agents. Thus an accurate mechanistic evaluation of a group I, II, or IIIA organometallic alkylation reaction might be most easily attainable through a kinetic study of the reaction of an aluminum alkyl with some substrate such as a ketone. The reaction most appropriate for such a study is shown below. Trimethylaluminum containing no β-hydrogen will not produce any reduction of the ketone and benzophenone having no α-hydrogen will not result in the production of enolization product; thus only alkylation product should be observed.



$$(CH_3)_3Al + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_2\overset{CH_3}{\overset{|}{C}}{-}OAl(CH_3)_2 \quad (1)$$
$$\xrightarrow{H_2O} (C_6H_5)_2C(CH_3)OH + 2CH_4 + Al(OH)_3$$

Until recently, the reactions of organoaluminum compounds with ketones have received little attention. The reactive organoaluminum species in these reactions and the details of the reaction mechanisms are unknown. An understanding of the mechanism of the addition of organoaluminum compounds to ketones depends in part on knowledge of the composition of organoaluminum compounds in solution. Molecular weight determinations[5,6] of several organoaluminum compounds in benzene have been interpreted in terms of a monomer–dimer equilibrium in which the position of the equilibrium is a function of the nature of the alkyl group. Of the compounds reported, triisopropylaluminum was the least associated, being essentially monomeric in benzene, whereas trimethylaluminum was the most highly associated, being essentially dimeric in benzene.[6]

Pitzer[7] interpreted the infrared spectrum of trimethylaluminum in terms of a dimeric molecule pos-

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[1] Paper I in this series: E. C. Ashby, R. Duke, and H. M. Neumann, *J. Amer. Chem. Soc.*, **89**, 1964 (1967).

[2] This work was sponsored in part by the National Science Foundation and the Sloan Foundation. Portions of this work were taken from the M.S. thesis of J. Laemmle.

[3] To whom all inquiries should be sent.

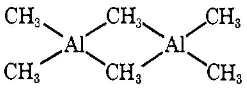
[4] (a) E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967), and references therein; (b) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 387 (1965).

[5] T. Mole, *Aust. J. Chem.*, **16**, 794 (1963).

[6] K. S. Pitzer and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **68**, 2204 (1946).

[7] K. S. Pitzer and R. K. Sheline, *J. Chem. Phys.*, **16**, 552 (1948).

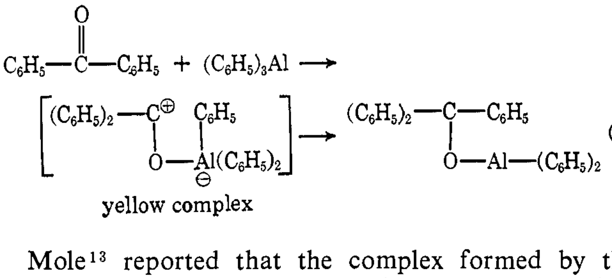
sessing a double alkyl bridge structure. Later X-ray determination of the structure of trimethylaluminum established the structure of the previously proposed



bridged dimer.[8]

Recent nuclear magnetic resonance studies by Muller[9] and Brown[10] show that trimethylaluminum in hydrocarbon solvent gives a single proton resonance signal at room temperature. As the temperature is lowered the signal shifts and broadens. At −65° two separate signals are found. These correspond to the protons of the bridging and terminal methyl groups. These results show that the trimethylaluminum dimer is undergoing very rapid exchange of terminal and bridging methyl groups at room temperature. Since dissociation to monomer and recombination is thought to be the mechanism for rapid exchange of alkyl groups,[10] it is clear that each dimer, as a stable entity, is very short lived. This indicates that although the amount of monomer present at any instant is very small, a very large amount of monomer is available for reaction in a relatively short period of time. Thus it seems reasonable to assume that either monomer or dimer or both may be the active organoaluminum species in ketone alkylation reactions.

Complexation between reacting species has been suggested as the pathway to products in the reactions of organoaluminum compounds with ketones. Wittig[11] reported that the reaction of triphenylaluminum with benzophenone proceeds through a yellow complex which forms immediately upon mixing the two reactants. The mechanism suggested by Wittig[12] is a stepwise reaction in which the complexation is followed by migration of a phenyl group.

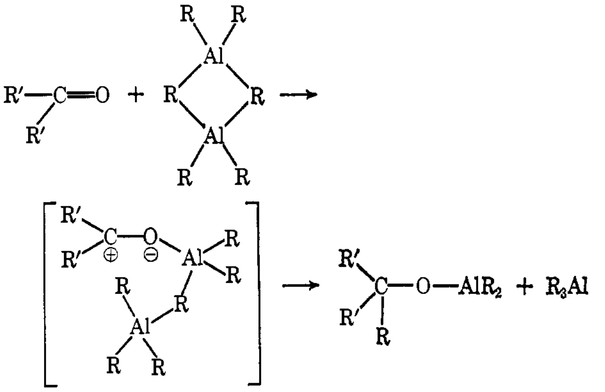


(2)

Mole[13] reported that the complex formed by the reaction of triphenylaluminum with benzophenone is a yellow oil. The yellow oil gave unchanged benzophenone upon hydrolysis, but upon heating yielded triphenylcarbinol.

Mole and Surtees[14] reported that the reaction of trimethylaluminum with benzophenone in benzene proceeds through a yellow complex. Ebulliometric measurements indicated the immediate formation of a monomeric complex, which then reacted to give a dimeric product in boiling benzene in about 5 min.

Pasynkiewicz and coworkers[15,16] have recently proposed mechanisms for the reaction of aluminum alkyls with ketones based on the results of product ratio studies in the reaction of triethylaluminum with diethyl ketone and trimethylaluminum with propiophenone. The reaction of the aluminum alkyl with the ketone in 1:1 ratio was proposed to proceed *via* a four-center transition state (eq 2) as suggested earlier by Wittig, and for the reactant ratio 2:1 *via* a six-center transition state (eq 3) in which participation of dimeric aluminum alkyl was assumed. On the other hand Mole and Surtees[14] suggested that when trimethylaluminum and benzophenone are allowed to react in 1:1 molar ratio the reaction is not first or second order with respect to complex $(C_6H_5)_2C{=}O\cdots Al(CH_3)_3$ and therefore alkylation does not proceed by intramolecular rearrangement of the complex (eq 2). These workers further reported that when the ratio of trimethylaluminum to benzophenone was 2:1 the reaction was immeasurably fast and kinetically complex.



(3)

Although the assumptions made concerning the mechanism of aluminum alkyl addition to ketones appear to be reasonable, there are no definitive data, kinetic or otherwise, to indicate the true mechanistic behavior of this reaction. Because of the fundamental nature of organometallic alkylation reactions and because of the obvious relationship of C–Al compounds to C–Mg compounds (Grignard reagents) and C–Li compounds, we have attempted a thorough kinetic study of the mechanism of trimethylaluminum addition to benzophenone. This study was purposely performed in a solvent (benzene) in which the aluminum alkyl used (trimethylaluminum) also is associated. This study has uncovered some very unusual aspects of this reaction which appear to have considerable significance in the basic understanding of organometallic alkylation reactions, since magnesium and lithium alkyls are associated in ether solvent. Thus the hope was that the results obtained in this study would be helpful in interpreting the more difficult systems involving Li and Mg alkyls.

Experimental Section

Materials. Trimethylaluminum was obtained from Texas Alkyls Inc. The Batch analytical report received with this chemical showed 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. The clear "water white" liquid was stored in a

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[8] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

[9] N. Muller and P. E. Pritchard, *J. Amer. Chem. Soc.*, **82**, 248 (1960).

[10] K. C. Williams and T. L. Brown, *ibid.*, **88**, 5460 (1966).

[11] G. Wittig, F. J. Meyer, and G. Gange, *Ann. Chem.*, **571**, 167 (1951).

[12] G. Wittig and O. Bud, *ibid.*, **566**, 113 (1950).

[13] T. Mole, *Aust. J. Chem.*, **16**, 807 (1963).

[14] T. Mole and J. R. Surtees, *ibid.*, **17**, 961 (1964).

[15] S. Pasynkiewicz and W. Arabas, *Rocz. Chem.*, **39**, 1393 (1965).

[16] S. Pasynkiewicz and E. Sliwa, *J. Organometal. Chem.*, **3**, 121 (1965).

round-bottomed flask fitted with a special joint containing a 2-mm bore Teflon stopcock. The stopcock was opened only when inside of the glove box.

Eastman's reagent grade benzophenone was distilled twice under vacuum. The middle fraction (mp 48.2–49.0°) of the second distillation was collected for further use. The benzophenone was stored in an inert atmosphere box and shielded from light. Benzophenone solutions were stored in tinted volumetric flasks in a glove box.

Eastman's reagent grade 1,1-diphenylethanol was used without further purification. Fisher certified thiophene-free benzene was distilled from sodium aluminum hydride under a nitrogen atmosphere 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 Beers' law plots and making kinetic measurements at a single wavelength. Matched quartz, 10-mm cells (Beckman Scientific Co.), were used for obtaining ultraviolet spectra.

All transfers involving 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 vermiculite, and a 3-ft column containing Molecular Sieve 4A.[17] The atmosphere in this glove box was such that pure triethylaluminum did not smoke when exposed. All operations in the glove box were preceded by bringing all needed equipment for a specific operation into the entry port, evacuating the entry port, and bleeding dry nitrogen back into the entry port before the door to the inner chamber was opened. After the contents were removed from the entry port to the glove box, recirculation of the atmosphere was allowed to proceed for at least 2 hr prior to exposure of trimethylaluminum and its solutions to the atmosphere.

Calibrated syringes equipped with stainless steel needles were used for transfer of reagents. Deliveries could be reproduced with an average of five parts per thousand.

The concentration of benzophenone in the product studies was determined by careful weighing of the ketone followed by accurate dilution. The concentration in the kinetic studies was determined by Beers' law with an extinction coefficient of 127 at 345 mμ.

The concentration of trimethylaluminum was determined 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 dithizone as an indicator.

Determination of Reaction Products. Product analysis was performed using an F & M Model 720 gas chromatograph with matched 2-ft Carbowax 20M columns. Product yields were determined by comparison of reaction mixtures with standard samples of benzophenone and 1,1-diphenylethanol in benzene.

Benzophenone (1.495 mmol) and trimethylaluminum (1.495 mmol) in 20 ml of benzene were allowed to react at reflux temperature for 24 hr. The mixture was hydrolyzed with a 50% hydrochloric acid solution. 1,1-Diphenylethanol was found in 96.5% conversion with 3.5% unreacted benzophenone recovered.

In a similar experiment benzophenone (0.748 mmol) and trimethylaluminum (1.495 mmol) in 15 ml of benzene were allowed to react at reflux temperature for 2 hr. The hydrolyzed mixture contained only 1,1-diphenylethanol.

In a further experiment benzophenone (1.459 mmol) and trimethylaluminum (0.748 mmol) in 15 ml of benzene were allowed to react at reflux temperature for 8 days. The hydrolyzed reaction mixture contained 48% 1,1-diphenylethanol and 52% benzophenone.

Effect of $(C_6H_5)_2CCH_3OAl(CH_3)_2$ on the Reaction of Trimethylaluminum with Benzophenone in Benzene. Dimethylaluminum 1,1-diphenylmethylcarbinolate was prepared by reaction of trimethylaluminum with benzophenone in benzene solvent in 1:1 ratio for 24 hr at reflux temperature. Analysis of the hydrolyzed reaction mixture by glpc showed that reaction was complete and that 1,1-diphenylethanol was the only product.

Benzophenone (0.647 mmol) was added to trimethylaluminum (1.291 mmol) in the presence of dimethylaluminum 1,1-diphenylmethylcarbinolate (0.647 mmol) in 25 ml of benzene. The mixture was allowed to react at room temperature for 1 hr accurately timed.

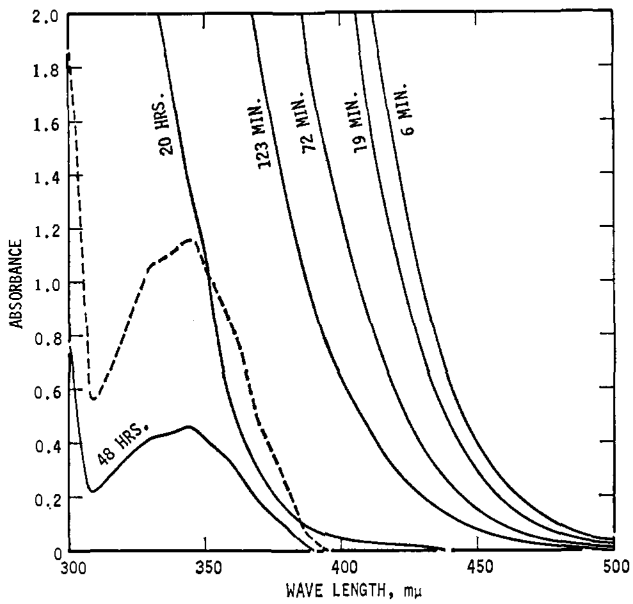

Figure 1. Spectra at various times of a solution 0.00911 *M* in benzophenone and 0.00911 *M* in trimethylaluminum. Dashed curve is spectrum of a solution containing only 0.00911 *M* benzophenone.

Analysis by gas chromatography of the hydrolyzed reaction mixture showed that 30.0% of the ketone had reacted.

Benzophenone (0.647 mmol) was allowed to react with trimethylaluminum (1.291 mmol) in 25 ml of benzene. Analysis after a reaction time of 1 hr showed that 97% of the ketone had reacted.

Benzophenone (0.647 mmol) was allowed to react with trimethylaluminum (0.646 mmol) in 25 ml of benzene for 1 hr. Analysis showed that 30.3% of the ketone had reacted.

Ultraviolet Spectra. In benzene solution only one absorption band for benzophenone can be observed in the ultraviolet spectrum. The maximum occurs at 345 mμ and has an extinction coefficient of 127. The maximum obeys Beers' law over the range of concentrations from 7.60×10^{-4} to 1.60×10^{-2} *M*. At wavelengths shorter than 270 mμ benzene itself absorbs so strongly that other bands characteristic of benzophenone cannot be obtained. Benzophenone has negligible absorption at wavelengths between 400 and 600 mμ. Neither 1,1-diphenylethanol nor trimethylaluminum absorbs over the entire range where spectra may be taken in benzene.

Spectra of mixtures of trimethylaluminum and benzophenone were otained in the following fashion. To a rubber-capped 10-mm quartz ultraviolet cell containing 3 ml of standard trimethylaluminum solution, 6–13 μl of standard ketone solution in dry benzene was added with a microsyringe. The cell was rolled to ensure mixing and placed in the cell compartment of a Cary 14 spectrophotometer. The spectrum was then recorded from 500 to 300 mμ.

When trimethylaluminum and benzophenone are mixed in an ultraviolet cell in 1:1 stoichiometry, a strong absorbance appears over the entire range from 270 to 500 mμ. This absorption completely obscures any absorption by the ketone. A typical experiment is illustrated in Figure 1. In this experiment, 13 μl of standard benzophenone solution was added to 3.0 ml of trimethylaluminum solution in a quartz cell bringing the initial concentration of each component to 0.00911 *M*. The spectrum of the solution, which had turned yellow immediately on mixing, was scanned from 500 mμ to shorter wavelengths. The absorbance exceeded the limit of the instrument (2.0) at 400 mμ. The absorption between 400 and 500 mμ gradually decreased until after 20 hr the yellow color had disappeared and the absorbance was zero at 400 mμ. A strong absorbance was still found in the 400–300-mμ region after 20 hr. After 48 hr, the strong absorbance had completely disappeared and the benzophenone spectrum reappeared. The benzophenone spectrum at this time indicated that about 35% of the ketone still remained. The ketone spectrum continued to decrease very slowly over the next several days. It is apparent that at 1:1 stoichiometry quantitative measurements of the rate can be made by observing directly in the uv cell the disappearance of the ketone–aluminum alkyl complex.

When trimethylaluminum in excess of a 1:1 stoichiometry was employed, the complex band disappeared so rapidly that accurate

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[17] We are indebted to Professor T. L. Brown of the University of Illinois for suggestions prior to construction of the recirculation system.

spectral measurements could not be made. Thus the kinetics under these conditions were studied by a different technique.

Kinetics of the Reaction by Direct Measurement of the Complex Band. All manipulations were performed in the inert atmosphere glove box described earlier. The reference cell was filled with 3 ml of freshly distilled benzene. The sample cell was filled with 3 ml of freshly prepared trimethylaluminum solution. The cells were tightly fitted with rubber caps. A 50-μl syringe was then filled to about 40 μl with a standard benzophenone solution, and the cells together with the 50-μl syringe were removed from the glove box. The cells were then placed in the cell chamber of the Zeiss PMQ II spectrophotometer. The cell chamber was maintained at 25 ± 0.1° by means of a Huake constant-temperature recirculator. The temperature was monitored in the water reservoir of the Huake recirculator.

After a suitable amount of time was allowed for the cells to come to temperature equilibrium, the cell chamber was opened briefly and an appropriate amount of benzophenone (*i.e.*, 6–13 μl) was injected into the sample cell. The sample cell was quickly removed from the cell chamber and rolled once to ensure proper mixing of the reactants and the cell was placed back in the chamber. The instrument was maintained in such a fashion that a reading could be taken immediately. The total time between the initial injection and the first reading was 5–10 sec. The first reading was taken to be the absorbance of the complex at zero reaction time. Measurements were made at 412 mμ, a wavelength at which neither benzophenone nor trimethylaluminum absorbs.

Kinetics of Reaction at 1:1 Stoichiometry by Quenching. A 100-ml round-bottomed flask with a 24/40 ground glass female joint was fitted with a 24/40 ground glass male joint attached to a three-way Teflon stopcock. The stopcock was designed so that a strong flow of nitrogen could be maintained on the system when adding reagents or withdrawing samples. To this flask, in a glove box, was added an exact volume of standard trimethylaluminum solution. The Teflon stopcock was closed thereby sealing the system. The flask was then removed from the glove box and placed in a constant-temperature bath which maintained the temperature at 25 ± 0.02°. A nitrogen line was attached to one opening of the three-way stopcock. After sufficient time had been allowed for the reaction flask and its contents to reach temperature equilibrium with the bath, an appropriate amount of benzophenone solution (*i.e.*, 0.5–1 ml) was added to the reaction flask under a heavy nitrogen flow. The flask was shaken lightly to ensure mixing of the reactants and the timer was started. An 8-ml sample was withdrawn immediately and quenched in a test tube containing 10 ml of 10% hydrochloric acid. The test tube containing the quenched sample was labeled and tightly stoppered. The time between the injection of the ketone and the quenching of the first sample was about 50 sec. After the first sample had been quenched, the Teflon stopcock was closed off, thereby resealing the system, and the nitrogen flow cut off. Other samples were quenched in the same manner at appropriate time intervals. Quenched samples were allowed to stand for 0.5 hr after which the benzene layer was removed and dried in test tubes containing Mallinckrodt analytical reagent grade magnesium sulfate. The benzene layer was then decanted into an ultraviolet cell and the absorbance at 345 mμ was recorded.

For ultraviolet analysis the reference cell contained a sample of trimethylaluminum solution which had been quenched and dried over anhydrous magnesium sulfate.

In order to calculate the initial concentration of benzophenone, additions of appropriate amounts of benzophenone were made to 100 ml of pure benzene in the exact fashion used in kinetic runs. This was repeated several times and the concentration of benzophenone calculated from Beers' law using the average absorbance. The value of the absorbance of the first quenched sample was within 1% of the average value of the absorbance found by the method just described. The value for the absorbance of the first quenched sample in a kinetic run was therefore taken to be the absorbance of benzophenone at zero reaction time.

Kinetics of the Reaction with Excess Trimethylaluminum by Quenching. A sampling method developed by Duke[18] in which individual reaction mixtures are initiated and quenched was used to study these very fast reactions.

Special reaction flasks were employed. These were 25-ml glass-stoppered volumetric flasks with a glass side arm between the stopper and the graduation mark. The side arm, about 20 mm in length and 10 mm in diameter, was tilted downward so that it formed an angle of about 60° with the neck of the flask. The glass stoppers had small glass hooks protruding from one side which allowed the stoppers to be held securely in the flask by rubber bands extending between the hooks and the side arms of the reaction flasks. In the glove box, an appropriate amount of benzophenone solution (15, 20, or 30 μl) was added to the side arm of the flasks using a 50-μl syringe. An 8-ml aliquot of standard trimethylaluminum solution was then transferred by syringe to the lower portion of each reaction flask taking care to prevent the organoaluminum compound from getting into the side arm containing the benzophenone. The ground-glass stoppers were then securely seated in the necks of the flasks and fastened in place with rubber bands. After the transfers were complete, the reaction flasks were removed from the glove box.

All but two of the reaction flasks were placed in a constant-temperature bath at 25 ± 0.02°. Just the lower bulbs of the flasks were immersed, leaving the necks and the ground-glass stoppers above water in order to carry out subsequent operations. The contents of the two remaining reaction flasks, one of which did not contain benzophenone, were hydrolyzed with 10% hydrochloric acid. The sample containing the benzophenone served as a measure of the initial ketone concentration at zero reaction time, and the other was employed in the reference ultraviolet cell to compensate for the absorbance of the solvent.

After adequate time had elapsed for the reactants to come to thermal equilibrium, a reaction was initiated by repeated inversions of the flask. The electric stopclock was started at the same time the reactants were mixed. The reactions were quenched by adding 10 ml of a 10% solution of hydrochloric acid from a syringe. The stopclock was stopped at the moment the syringe plunger was depressed. The entire operation of opening the reaction flask, quenching the reaction mixture, and stopping the stopclock could be accomplished in about 1 sec. Since the yellow color characteristic of the trimethylaluminum–benzophenone complex disappeared with the first small amount of hydrochloric acid solution, the reactions were probably effectively quenched in about 0.2 sec.

The benzene layer from each flask was removed and dried over anhydrous magnesium sulfate, in a manner previously described, in order to remove water from the benzene layer. The samples were carefully decanted from the test tubes containing magnesium sulfate into quartz ultraviolet cells. Ultraviolet readings of the benzophenone maximum at 345 mμ were made in a manner previously described.

In order to determine the concentration of benzophenone at zero reaction time, the kinetic flasks were taken into the glove box. Additions of standard benzophenone solution and standard trimethylaluminum solution were made in the exact manner as for a kinetic run. Without first initiating the reaction, each sample was quenched with 10% hydrochloric acid. The hydrolyzed benzene layer was then mixed with the benzophenone solution in the side arm. The samples were dried over anhydrous magnesium sulfate and ultraviolet readings were made. From the average absorbance of these samples, the concentration of benzophenone at zero reaction time was calculated from Beers' law. When an actual kinetic run was made, one reaction flask was hydrolyzed prior to the mixing of the reactants. The value of the concentration of benzophenone in this flask never varied by more than 1% from the average concentration of benzophenone at zero reaction time.

Calculations. For each experiment in which the disappearance of the complex was measured, rate constants were calculated from 25 sets of time–absorbance values plus the infinity readings. The values were obtained over the range 10–75% reaction.

For each experiment in which the disappearance of the ketone carbonyl maximum was measured and in which equivalent amounts of benzophenone and trimethylaluminum were used, rate constants were calculated from eight sets of time–benzophenone concentration values. Although determinations were made through 75% reaction experimentally, rate constants could be calculated for only the first half of the reaction for reasons discussed fully in the Discussion section.

For each experiment in which the disappearance of the ketone carbonyl maximum was measured and in which trimethylaluminum was in excess, rate constants were calculated from nine or ten sets of time–benzophenone concentration values. The values ranged from 10 to 80% reaction.

Results and Discussion

Benzophenone and trimethylaluminum react to form the expected alkylation product dimethylaluminum

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[18] R. Duke, Ph.D. Thesis, The Georgia Institute of Technology, Atlanta, Ga., 1967.

1,1-diphenylmethylcarbinolate[$(C_6H_5)_2CCH_3OAl(CH_3)_2$] in high yield without the side reactions of enolization or reduction. Previous workers have pointed out[13,19] that only one methyl group is available for alkylation. Because of the importance of this point, trimethylaluminum and benzophenone were allowed to react in benzene in 2:1, 1:1, and 1:2 ratios. When the reactants were mixed in 2:1 ratio, reaction proceeded rapidly to produce the alkylation product in 100% yield. In 1:1 ratio the alkylation product was also produced in 100% yield; however, the reaction was much slower, requiring refluxing conditions for 24 hr to produce complete reaction. When the reactants were mixed in 1:2 ratio and allowed to reflux for 8 days, the final product after hydrolysis contained approximately equal amounts of benzophenone and 1,1-diphenylethanol. This shows that the dimethylaluminum carbinolate is unreactive toward benzophenone. It also appears unlikely that equilibrium 4 leads to a detectable concentration of trimethylaluminum.

$$2(CH_3)_2AlOC(C_6H_5)_2CH_3 \rightleftarrows (CH_3)_3Al + CH_3Al(OC(C_6H_5)_2CH_3)_2 \quad (4)$$

The immediate formation of a yellow color and strong absorbance over the range from 270 to 500 mμ when trimethylaluminum and benzophenone are mixed are strongly indicative of complex formation. Similar ultraviolet spectral changes have been equated to complex formation when organometallic compounds are added to ketones.[20] The relative positions and intensities of the spectra of benzophenone and the complex (see Figure 1) are such that the extent of complex formation cannot be estimated from the spectral data. The ebulliometric data of Mole[14] indicate that complex formation between trimethylaluminum and benzophenone is quantitatively complete within the limits of the measurement. Our kinetic results, described below, are consistent with the equilibrium being strongly in the direction of complex formation.

General Features of Rate Studies. The reaction of trimethylaluminum with benzophenone in benzene was studied in two ways: (1) by following directly the disappearance of the complex band at 412 mμ, and (2) by quenching the reaction mixture with acid and then measuring the carbonyl group absorbance at 345 mμ. The reaction was studied at trimethylaluminum–ketone ratios ranging from 0.855:1 to 3.76:1. This was the widest range allowed by the nature of the reaction. The aluminum alkyl and ketone concentrations were varied over a range of severalfold. The rate data were recorded generally between 10 and 80% reaction for each individual run.

A drastic increase in rate occurs when trimethylaluminum is used in excess of a 1:1 stoichiometry. A reaction mixture with an initial ketone concentration of 8.17×10^{-3} M and an initial trimethylaluminum concentration of 8.23×10^{-3} M had an experimental half-life of about 20,000 sec at 25°. By contrast, a reaction mixture with an initial trimethylaluminum concentration of 15.15×10^{-3} M and an initial ketone concentration of 7.55×10^{-3} M had an experimental half-life of about 58 sec at 25°. When the ratio of trimethylaluminum to benzophenone was 1.5:1, the reaction proceeded rapidly until 50% of the ketone had reacted, after which the reaction became very slow. In general, when a fractional excess of trimethylaluminum is used the reaction is fast until the excess has reacted. This type of behavior excludes the possibility of simple first-, second-, or third-order kinetics. What it does suggest is that upon addition of reactants a complex is formed immediately, which then reacts with further trimethylaluminum to give product in a rate-controlling reaction step. It also suggests that the product formed from the reaction of the complex with a further molecule of trimethylaluminum does not readily release trimethylaluminum.

Since the behavior is different for the two cases, reactions in which the amount of benzophenone is equal to or in excess of that of trimethylaluminum will be considered separately from cases in which excess trimethylaluminum is used. The mathematical analyses of the two cases are quite different, although three assumptions are common to both cases. The first assumption is that the stoichiometry of the complex is one trimethylaluminum to one benzophenone. The second assumption is that the complex forms extremely rapidly. (The manner in which the complex comes into being is not important so long as its formation is immediate.) The third assumption is that the equilibrium constant for formation of the complex is very large.

In writing mechanism and equations, the following symbolism will be used for compounds: A_2 represents the trimethylaluminum dimer; A represents the trimethylaluminum monomer; K represents the ketone benzophenone; C represents a complex containing one K and one A; P′ represents a product containing one K and one A; and P represents a product containing one K and two A's. The quantities $[K]_0$ and $[A]_0$ are the concentrations that benzophenone and trimethylaluminum would have if no reaction or complex formation occurred.

Detailed Kinetics of Reaction with Excess Trimethylaluminum. It has already been pointed out that trimethylaluminum in benzene solvent consists of an equilibrium mixture of monomer and dimer molecules with the equilibrium predominantly favoring the dimer in the concentration range where association measurements have been made. In the present kinetic studies the experimental data were analyzed in three ways. In the first method the aluminum alkyl was considered to be predominantly dimeric with the dimer reacting to give product. This method is referred to as the dimer–dimer analysis. In the second method the aluminum alkyl was considered to be predominantly dimeric with the monomer reacting with the complex to give product. This method is referred to as the dimer–monomer analysis. Owing to certain trends in the data it was recognized that at very low aluminum alkyl concentrations the solution may contain a considerable proportion of trimethylaluminum monomer. Thus in the last method of analysis the aluminum alkyl was considered to be predominantely monomeric with the monomer reacting with the complex to give product. This method is referred to as the monomer–monomer

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[19] K. Ziegler in "Organometallic Chemistry," K. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 5.

[20] (a) S. G. Smith, *Tetrahedron Lett.*, 7, 409 (1963); (b) S. G. Smith and G. Su, *J. Am. Chem. Soc.*, **86**, 2750 (1964); (c) S. G. Smith and G. Su, *ibid.*, **88**, 3995 (1966); (d) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1962).

analysis. It should be noted that the designations for these methods of analysis are such that the predominant species is indicated first and the reactive species is indicated second. It should be noted that in the presence of excess trimethylaluminum the formation of complex is essentially complete, and the amount of uncomplexed ketone is negligible. Thus the experimental measurement of the benzophenone concentration in the quenched reaction mixture gave a direct determination of the concentration of complex in the reaction mixture at the time of quenching. For this reason the differential equations derived for the three methods of analysis express the rate in terms of the disappearance of complex.

The Dimer–Dimer Analysis. The reaction of trimethylaluminum with benzophenone to give product by the trimethylaluminum dimer attacking the complex is represented by mechanism 5

$$A_2 \rightleftharpoons 2A \text{ (rapid)} \tag{5a}$$

$$A + K \rightleftharpoons C \text{ (rapid)} \tag{5b}$$

$$C + A_2 \xrightarrow{k_d} P + A \text{ (rate controlling)} \tag{5c}$$

The differential equation expressing the disappearance of the complex is given by eq 6

$$\frac{d[C]}{dt} = \frac{k_d}{2}[C]([C] + [A]_0 - 2[K]_0) \tag{6}$$

where [C] is the concentration of complex at time t. The solution to eq 6 is given by eq 7

$$k_d = \frac{2.303(2)}{t([A]_0 - 2[K]_0)} \log \frac{[C]_0([C] + [A]_0 - 2[K]_0)}{[C]([C]_0 + [A]_0 - 2[K]_0)} \tag{7}$$

where $[C]_0$ is the concentration of complex at zero reaction time. For the special case where $[A_0] = 2[K]_0$, the differential equation expressing the disappearance of complex is given by eq 8.

$$\frac{d[C]}{dt} = \frac{k_d}{2}[C]^2 \tag{8}$$

The solution to eq 8 is given by eq 9.

$$k_d = \frac{2}{t}\left(\frac{1}{[C]} - \frac{1}{[C]_0}\right) \tag{9}$$

Values of k_d obtained by applying this analysis of the data are shown in Table I.

The Dimer–Monomer Analysis. The reaction of trimethylaluminum with benzophenone to give product *via* attack by monomeric trimethylaluminum on the initial complex is represented by mechanism 10.

$$A_2 \overset{K_D}{\rightleftharpoons} 2A \text{ (rapid)} \tag{10a}$$

$$A + K \rightleftharpoons C \text{ (rapid)} \tag{10b}$$

$$C + A \xrightarrow{k} P \text{ (rate controlling)} \tag{10c}$$

The assumptions in analyzing the data according to mechanism 10 are the same as those made in analyzing the data according to mechanism 5 except that the rate-controlling step involves the attack of monomeric trimethylaluminum on the complex to form the product. Fitting the data to mechanism 10 does not allow calculation of a unique value of the rate constant k, but instead leads to the product $k\sqrt{K_D}$, where K_D is the dissociation constant of dimeric trimethylaluminum, $K_D = [A]^2/[A_2]$.

Table I. "Constants" from the Dimer–Monomer Analysis Compared to "Rate Constants" from the Dimer–Dimer Analysis

$(C_6H_5)_2$-CO, $M \times 10^3$	$(CH_3)_3$-Al, $M \times 10^3$	$(CH_3)_3Al/(C_6H_5)_2$-CO	Dimer–dimer k_d, l. mol^{-1} sec^{-1}	Dimer–monomer $k\sqrt{K_D}$, l.$^{1/2}$ mol$^{-1/2}$ sec^{-1}
11.30	17.41	1.54	5.00 ± 0.30[a]	0.227 ± 0.024[c]
7.55	12.64	1.68	4.90 ± 0.28[a]	0.219 ± 0.013[c]
7.55	13.21	1.75	5.18 ± 0.32[a]	0.235 ± 0.007[c]
7.55	15.15	2.00	4.82 ± 0.32[b]	0.226 ± 0.018[d]
7.55	15.34	2.03	4.10 ± 0.30[b]	0.203 ± 0.020[d]
11.30	22.86	2.02	4.12 ± 0.34[b]	0.255 ± 0.006[d]
5.68	11.70	2.06	4.48 ± 0.26[b]	0.208 ± 0.019[e]
11.30	25.28	2.21	4.32 ± 0.26[a]	0.281 ± 0.019[e]
7.55	18.93	2.50	3.72 ± 0.30[a]	0.246 ± 0.007[e]
5.68	16.26	2.93	3.54 ± 0.12[a]	0.251 ± 0.008[e]
7.55	22.97	3.04	3.44 ± 0.10[a]	0.275 ± 0.008[e]
5.68	21.38	3.76	3.24 ± 0.22[a]	0.276 ± 0.016[e]

[a] Calculated from eq 7. [b] Calculated from eq 9. [c] Calculated from eq 13. [d] Calculated from eq 15. [e] Calculated from eq 12.

The differential equation for the disappearance of complex according to mechanism 10 is given by eq 11.

$$\frac{d[C]}{dt} = \frac{-k\sqrt{K_D}}{2}[C]([C] + [A]_0 - 2[K]_0)^{1/2} \tag{11}$$

There are three solutions to eq 11. When $[A]_0$ is greater than $2[K]_0$ the solution is given by eq 12.

$$k\sqrt{K_D} = \frac{2.3\sqrt{2}}{t\sqrt{([A]_0 - 2[K]_0)}} \times \log \frac{\left(\sqrt{[C]_0 + [A]_0 - 2[K]_0} - \sqrt{[A]_0 - 2[K]_0}\right)\left(\sqrt{[C] + [A]_0 - 2[K]_0} + \sqrt{[A]_0 - 2[K]_0}\right)}{\left(\sqrt{[C]_0 + [A]_0 - 2[K]_0} + \sqrt{[A]_0 - 2[K]_0}\right)\left(\sqrt{[C] + [A]_0 - 2[K]_0} - \sqrt{[A]_0 - 2[K]_0}\right)} \tag{12}$$

When $[A]_0$ is less than $2[K]_0$ the solution is given by eq 13.

$$k\sqrt{K_D} = \frac{2\sqrt{2}}{t\sqrt{2[K]_0 - [A]_0}} \times \left(\tan^{-1}\sqrt{\frac{[C]_0 + [A]_0 - 2[K]_0}{2[K]_0 - [A]_0}} - \tan^{-1}\sqrt{\frac{[C] + [A]_0 - 2[K]_0}{2[K]_0 - [A]_0}}\right) \tag{13}$$

For the special case where $[A]_0$ equals $2[K]_0$, the proper differential equation for the disappearance of the complex is given by eq 14.

$$\frac{d[C]}{dt} = -\frac{k\sqrt{K_D}}{\sqrt{2}}[C]^{3/2} \tag{14}$$

The solution to eq 14 is given by eq 15.

$$k\sqrt{K_D} = \frac{2\sqrt{2}}{t}\left(\frac{1}{\sqrt{[C]}} - \frac{1}{\sqrt{[C]_0}}\right) \tag{15}$$

Table II. "Constants" from the Dimer–Monomer Analysis Compared with "Rate Constants" from the Monomer–Monomer Analysis

$(C_6H_5)_2CO$, $M \times 10^3$	$(CH_3)_3Al$, $M \times 10^3$	Initial free $(CH_3)_3Al$, $M \times 10^3$	Monomer–monomer k, l. mol^{-1} sec^{-1}	Dimer–monomer $k\sqrt{K_D}$, l.$^{1/2}$ mol$^{-1/2}$ sec^{-1}	Dimer–monomer $k\sqrt{K_D}$,[a] l.$^{1/2}$ mol$^{-1/2}$ sec^{-1}
7.55	12.64	5.09	2.45 ± 0.14[b]	0.219 ± 0.013[d,g]	0.240 ± 0.010[d]
7.55	13.21	5.66	2.59 ± 0.16[b]	0.235 ± 0.017[d,g]	0.250 ± 0.009[d]
7.55	15.34	5.79	2.05 ± 0.15[c]	0.203 ± 0.020[f,g]	0.222 ± 0.014[f]
5.68	11.70	6.02	2.24 ± 0.13[c]	0.208 ± 0.019[e,g]	0.226 ± 0.010[e]
11.30	17.41	6.11	2.50 ± 0.15[b,h]	0.227 ± 0.024[d,g]	0.247 ± 0.015[d]
7.55	15.15	7.60	2.41 ± 0.16[c,h]	0.226 ± 0.018[f,g]	0.243 ± 0.011[f]
5.68	16.26	10.58	1.77 ± 0.06[b,h]	0.251 ± 0.008[e]	
11.30	22.86	11.56	2.06 ± 0.17[c,g]	0.255 ± 0.006[f]	
7.55	18.93	12.38	1.86 ± 0.15[b,g]	0.246 ± 0.007[e]	
11.30	25.28	13.98	2.16 ± 0.13[b,g]	0.281 ± 0.019[e]	
7.55	22.97	15.42	1.72 ± 0.05[b,g]	0.275 ± 0.008[e]	
5.68	21.38	15.70	1.62 ± 0.11[b,g]	0.276 ± 0.016[e]	

[a] Averaged from values constituting 50% reaction or less. [b] Calculated from eq 18. [c] Calculated from eq 20. [d] Calculated from eq 13. [e] Calculated from eq 12. [f] Calculated from eq 15. [g] Drift in constants with reaction time during individual run. [h] Slight drift in constants with reaction time during individual run.

Values of $k\sqrt{K_D}$ obtained by applying the dimer–monomer analysis to the data are shown in Tables I and II.

The Monomer–Monomer Analysis. At very low concentrations of trimethylaluminum the solution may contain a considerable proportion of monomer. Certain trends in the rate data indicated that this occurs when the concentration of trimethylaluminum is less than 0.005 M.

Mechanism 16 represents the reaction of trimethylaluminum with benzophenone to give product *via* attack by monomeric trimethylaluminum on the initial complex. It should be noted that mechanism 16 is the same as mechanism 10, but the mathematical analysis is different because of the assumption that the predominant trimethylaluminum species is monomer.

$$A_2 \rightleftharpoons 2A \text{ (rapid)} \tag{16a}$$

$$A + K \rightleftharpoons C \text{ (rapid)} \tag{16b}$$

$$C + A \longrightarrow P \text{ (rate controlling)} \tag{16c}$$

The differential equation expressing the disappearance of the complex according to mechanism 16 is given by eq 17.

$$\frac{d[C]}{dt} = -k[C]([C] + [A]_0 - 2[K]_0) \tag{17}$$

The solution to eq 17 is given by eq 18.

$$k = \frac{2.3}{t([A]_0 - 2[K]_0)} \times \log \frac{[C]_0([C] + [A]_0 - 2[K]_0)}{[C]([C]_0 + [A]_0 - 2[K]_0)} \tag{18}$$

For the special case where $[A]_0 = 2[K]_0$ the differential equation expressing the disappearance of complex is given by eq 19.

$$\frac{d[C]}{dt} = k[C]^2 \tag{19}$$

The solution to eq 19 is given by eq 20.

$$k = \frac{1}{t}\left(\frac{1}{[C]} - \frac{1}{[C]_0}\right) \tag{20}$$

Values of k obtained by applying the monomer–monomer analysis to the data are shown in Table I.

Conclusion

The "constants" calculated from the dimer–dimer analysis and from the dimer–monomer analysis are compared in Table I. The values of k_d calculated from the dimer–dimer analysis were found to be dependent on the trimethylaluminum to benzophenone ratio. As the ratio of trimethylaluminum to benzophenone increases, the values decrease. At the lowest $(CH_3)_3Al$:$(C_6H_5)_2CO$ studied, 1.54:1, the average value is 5.00 ± 0.30 l. mol^{-1} sec^{-1}, while at the highest ratio studied, 3.76:1, the average value is only 3.24 ± 0.22 l. mol^{-1} sec^{-1}. This unmistakable trend toward lower values with higher aluminum alkyl to ketone ratios suggests that the dimer–dimer analysis does not properly describe the system.

The average "constants" $k\sqrt{K_D}$, calculated from the dimer–monomer analysis, showed no marked trend with the trimethylaluminum to benzophenone ratio. The average values were somewhat smaller when the $(CH_3)_3Al$ to $(C_6H_5)_2CO$ ratio was less than 2:1 than those calculated for the reactant ratios greater than 2:1. At $(CH_3)_3Al$ to $(C_6H_5)_2CO$ ratios of exactly 2:1, the values were smaller at lower initial trimethylaluminum concentrations and larger at higher initial trimethylaluminum concentrations. In those cases in which a smaller average " constant" was found, a trend toward decreasing constants with reaction time was found for individual runs. Thus for the initial portion of the run the constants were the same as those calculated for reactant ratios greater than 2:1 but toward the end of the run the values had decreased. This behavior is evident in Figure 2. (The functions plotted correspond to eq 12 for the lower set of data, and to eq 13 for the upper set of data; in either case the dimer–monomer analysis indicates a straight line of slope $-k\sqrt{K_D}$.) The lower curve shows the data corresponding to the eleventh experiment of Table II. The linearity shows that the dimer–monomer analysis properly describes this experiment. The upper curve shows the data corresponding to the second experiment of Table II. It can be seen that although the dimer–monomer analysis does not describe the entirety of the experiment, the initial slope is the same as for the lower curve.

The trend found for constants calculated from the dimer–monomer analysis suggests that at low tri-

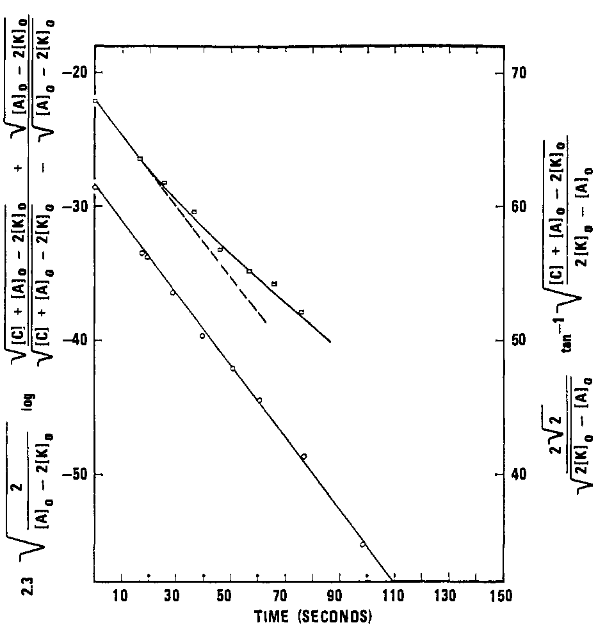


Figure 2. Evaluation of two runs by dimer–monomer analysis.

methylaluminum concentration, a considerable proportion of trimethylaluminum exists as monomer. In experiments in which the stoichiometry is 2:1 or less, the amount of free trimethylaluminum at zero time may be small, since it never exceeds that of the complex. As the reaction proceeds the concentration of free trimethylaluminum decreases further, and the proportion of monomer must increase. Near the end of the reaction the proportion of monomer may be quite large. In such an experiment the dimer–monomer analysis would not describe the data perfectly. By examining the data in individual runs it is possible to note the concentration of aluminum alkyl in which the amount of monomer is significant enough to cause decreasing constants. The constants calculated from the dimer–monomer analysis are quite consistent for trimethylaluminum concentrations above 0.005 *M*. Below 0.005 *M* the constants begin to decrease but the effect is not serious (*i.e.*, constants lower than 0.200) until the concentration of free trimethylaluminum is lower than 0.003 *M*.

Table II compares "constants" calculated from the dimer–monomer analysis (*i.e.*, $k\sqrt{K_D}$) with "constants" calculated from the monomer–monomer analysis (*i.e.*, *k*). The data in Table II are arranged according to increasing initial free trimethylaluminum concentration. An average value is designated by a superscript *g* or *h* if the calculated "constant" showed a trend with reaction time for the run. It should be noted that the last six experiments in Table IV show no drift in values of $k\sqrt{K_D}$. (The lower curve of Figure 2 is typical of these runs.) The sixth row of figures in Table II represents constants calculated from the dimer–monomer analysis using data only up to 50% reaction for those runs in which decreasing constants with increasing reaction time were found. (The upper curve of Figure 2 is such a run.) These "constants" compare favorably with those calculated for runs which show no trends.

The rate "constant" calculated from the monomer–monomer analysis showed a tendency to increase with reaction time when the ratio of trimethylaluminum to benzophenone is 2:1 or greater and when the initia concentration of free trimethylaluminum is 0.006 *M* or greater. The average rate constants from the monomer–monomer analysis also decreased with increasing ratio due to the high proportion of dimer at high reactant ratio. It should be noted that rate constants calculated from the dimer–dimer analysis are exactly twice those calculated from the monomer–monomer analysis. Thus these two cases are kinetically indistinguishable. It is unreasonable, however, that analysis by the dimer–dimer mechanism should best fit the data at very low aluminum alkyl concentrations where a relatively large proportion of monomer exists and not fit the data at higher aluminum alkyl concentrations where the predominant trimethylaluminum species is the dimer. It is perfectly reasonable for the monomer–monomer analysis to fit the data in such a fashion, however.

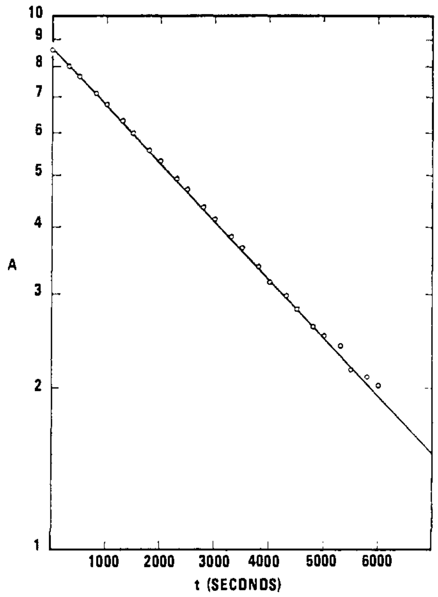


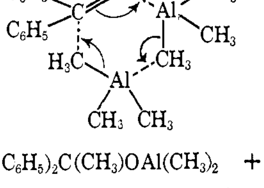
Figure 3. Disappearance of complex at 25°.

Further, it appears clear that at high free aluminum alkyl concentrations, the predominant aluminum alkyl species is the dimer and at low aluminum alkyl concentration the aluminum alkyl exists largely as monomer. Regardless of the trimethylaluminum monomer–dimer ratio, the rate-controlling step of the reaction is an attack of monomeric trimethylaluminum on the complex. This is indeed the preferred reaction path when it is operative. The details of this mechanism are represented by eq 21a–d.

$$2(CH_3)_3Al \rightleftharpoons [(CH_3)_3Al]_2 \qquad (21a)$$

$$(C_6H_5)_2C{=}O + (CH_3)_3Al \rightleftharpoons \underset{\text{I}}{(C_6H_5)_2C{-}O\cdots Al(CH_3)_3} \qquad (21b)$$

$\text{I} + (CH_3)_3Al \longrightarrow$



$\longrightarrow$

$$\underset{\text{II}}{(C_6H_5)_2C(CH_3)OAl(CH_3)_2} + Al(CH_3)_3 \qquad (21c)$$

$$\text{II} \rightleftharpoons (C_6H_5)_2C(CH_3)OAl(CH_3)_2 \cdot Al(CH_3)_3 \qquad (21d)$$

Detailed Kinetics of Reaction at 1:1 Stoichiometry. When trimethylaluminum and benzophenone are allowed to react in 1:1 stoichiometry, the complex band at 412 mμ (followed until 75% reaction) disappeared in a first-order fashion. A typical example is shown in Figure 3. First-order rate constants were calculated from eq 22 for each absorbance reading

$$k_{\mathrm{obsd}} = \frac{2.3}{t} \log \frac{A_0 - A_\infty}{A - A_\infty} \qquad (22)$$

where A is the absorbance at time t, A_0 is the absorbance at zero reaction time, and A_∞ is the absorbance at infinite reaction time. The absorbance at infinite reaction time was always within 0.003 absorbance unit of the base line. The average values for 12 separate experiments are shown in Table III.

Table III. Rate Constants for Disappearance of the Complex Band at 25°

$(C_6H_5)_2CO$, $M \times 10^3$	$(CH_3)_3Al$, $M \times 10^3$	$k_{\mathrm{obsd}} \times 10^4$, sec^{-1}
6.58	6.60	2.44 ± 0.09
6.58	6.60	2.55 ± 0.03
6.58	6.60	2.49 ± 0.07
6.91	6.90	2.32 ± 0.05
6.91	6.90	2.35 ± 0.05
6.91	6.90	2.41 ± 0.04
9.11	8.90	2.33 ± 0.04
9.11	8.90	2.50 ± 0.04
9.11	8.90	2.43 ± 0.03
4.44	4.15	2.42 ± 0.03
4.44	4.15	2.41 ± 0.11
4.44	4.15	2.41 ± 0.12
		Av 2.41

The kinetics of the reaction of trimethylaluminum with benzophenone in 1:1 ratio was also followed by quenching the reaction mixture in 10% hydrochloric acid, and then measuring the absorbance at 345 mμ. Since the quenching destroys the complex and regenerates ketone, the experimental reading of the absorbance at 345 mμ after quenching measures the sum of uncomplexed ketone and unreacted complex in the reaction at the time of quenching. In these experiments the experimental variable is [X] = [K] + [C].

The decrease of [X] with time was found to be more complex and slower than the decrease of [C]. In the initial stages of a reaction d[C]/dt is about twice d[X]/dt. The conclusion follows that [K] is increasing during this stage of the reaction. These observations suggested mechanism 23.

$$A_2 \rightleftharpoons 2A \text{ (rapid)} \qquad (23a)$$

$$A + K \rightleftharpoons C \text{ (rapid)} \qquad (23b)$$

$$C \xrightarrow{k_1} P' \text{ (rate controlling)} \qquad (23c)$$

$$P' + A \longrightarrow P \text{ (rapid and complete)} \qquad (23d)$$

The reappearance of ketone is attributed to the strong tendency of the alkylation product P′, *i.e.*, dimethylaluminum carbinolate, to combine with trimethylaluminum in the last step of the mechanism. The net reaction corresponding to this mechanism is

$$2C \longrightarrow P + K$$

In order to provide further evidence that P′ and A do indeed interact to form P, the following experiments were performed. When trimethylaluminum and benzophenone were allowed to react in 2:1 ratio for 1 hr the reaction was complete. When the ratio was 1:1 the reaction was only 30% complete in 1 hr. However, when trimethylaluminum and benzophenone were allowed to react in 2:1 ratio after the two parts of trimethylaluminum were added to one part of dimethylaluminum 1,1-diphenylmethylcarbinolate (P′), the reaction was exactly 30% complete in 1 hr. This experiment indicates that each molecule of P′ ties up one molecule of trimethylaluminum and makes it unavailable for reaction except at a much slower rate than the initial reaction.

Mechanism 23 predicts that the complex should disappear in a first-order manner with $k_{\mathrm{obsd}} = 2k_1$. It also predicts the relation between [X] and t given by eq 24. The rate constants calculated from quenching

$$k' = 2k_1 = \frac{2.3}{t} \log \frac{[X]_0 - [K]_0 + {}^1\!/_2[A]_0}{[X] - [K]_0 + {}^1\!/_2[A]_0} \qquad (24)$$

experiments by use of eq 24 are given in Table IV.

Table IV. Rate Constants from Quenching Experiments at 1:1 Stoichiometry

$(C_6H_5)_2CO$, $M \times 10^3$	$(CH_3)_3Al$, $M \times 10^3$	$k' \times 10^4$, sec^{-1}
8.15	8.08	1.78 ± 0.12
8.17	8.28	1.42 ± 0.09
8.35	8.28	1.51 ± 0.07
15.71	15.82	1.90 ± 0.07
16.05	16.00	2.08 ± 0.14
16.05	13.72	2.09 ± 0.08

A further test of the validity of mechanism 23 is a comparison of k_{obsd} and k', since each should equal $2k_1$. The average value of k_{obsd} from the experiments of Table III is 2.41×10^{-4} sec^{-1}. The average value of k' from the experiments of Table IV is 1.80×10^{-4} sec^{-1}. The comparison suggests that mechanism 23 is nearly correct but requires some modification.

It should be emphasized that the spectrum generated by the complex when trimethylaluminum and benzophenone are allowed to react in 1:1 ratio gradually disappears and regenerates the ketone spectrum. The absorbance of the benzophenone maximum after the complete disappearance of the complex band indicates that approximately 65% of the ketone has reacted. The benzophenone maximum then continues to disappear very slowly, indicating that mechanism 23 is not entirely accurate. The regeneration of the benzophenone spectrum must be due to the reaction of the alkylation product, dimethylaluminum carbinolate (P′), with trimethylaluminum. Since trimethylaluminum is not complexed to the ketone, it must be complexed to the initially formed product.

A mechanism which is better able to account for our observations, but which is more difficult to handle mathematically, is

$$A_2 \rightleftharpoons 2A \text{ (rapid)} \qquad (25a)$$

$$A + K \rightleftharpoons C \text{ (rapid)} \qquad (25b)$$

$$C \xrightarrow{k_1} P' \text{ (rate controlling)} \qquad (25c)$$

$$P' + A \rightleftharpoons P \text{ (rapid)} \qquad (25d)$$

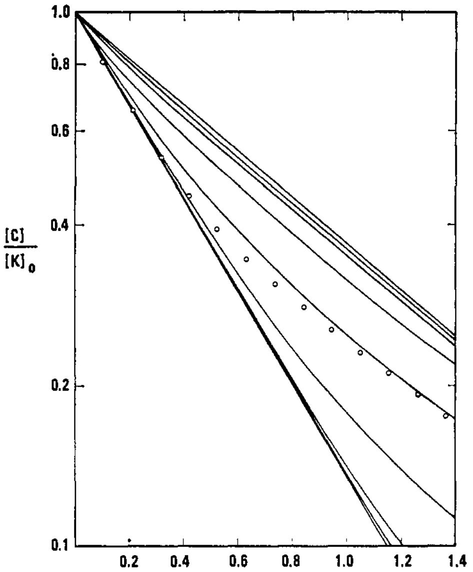


Figure 4. Calculated behavior of [C] for mechanism 25 for various values of R. Curves from top to bottom are for values of $R = \infty$, 10^3, 10^2, 10, 1, 10^{-1}, 10^{-2}, 10^{-3}, and 0. Points are experimental values at 30°.

In this mechanism both P and P′ appear as products in measurable amount.

The differential rate expression for [C] for this mechanism can be set up easily in terms of the equilibrium constant $R = [P'][C]/[P][K]$, which expresses the relative ability of P′ and K to combine with A. The resulting differential equation is

$$\frac{R([K]_0/[C]) - 2(R - 1) + 2(R - 1)\sqrt{1 + R([K]_0/[C])} - R}{2R\sqrt{1 + R([K]_0/[C])} - R}\,\frac{d[C]}{dt} = -k_1[C]$$

There is no general simple integral rate expression for this equation. For the two limits, $R = 0$ and $R = \infty$, the complex will disappear according to a first-order law. For $R = 1$, the rate will be two-thirds order in complex. For other values of R the differential equation can be solved by numerical methods. In Figure 3 are shown solutions for various values of R. It can be seen that for small values of R the behavior will appear to be first order for a considerable extent of reaction, and that the rate constant can be evaluated from the initial slope. It can be seen from Figure 3 that the behavior will be indistinguishable from first-order behavior up to 50% disappearance of complex when $R = 0.1$, and up to 75% disappearance of complex when $R = 0.01$. Since, in fact, first-order disappearance of the complex is observed for the first 75% of the reaction at 25°, it would appear that the product P′ does indeed complex trimethylaluminum to a considerably greater degree than does benzophenone.

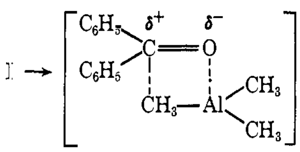
The superiority of mechanism 25 over mechanism 23 is more evident at 30° than at 25°. The average results from three experiments at 30° have been plotted in Figure 4, the time scale being adjusted to fit the initial slope of the data points to the initial slope of the theoretical curves. At this temperature the behavior is indistinguishable from first-order behavior only up to about 40% disappearance of complex. The behavior over-all suggests that $R \simeq 0.8$ at this temperature.

Interpreting the data (obtained by direct measurement of complex) in terms of mechanism 25 gives a value of k_1 of 1.20×10^{-4} sec^{-1} at 25°, and a value of 2.10×10^{-4} sec at 30°. The activation energy is then about 20 kcal.

The following equations show in detail the mechanism by which trimethylaluminum is thought to react with benzophenone when the ketone is equal to or in excess of the aluminum alkyl. The structure proposed for

$$2(CH_3)_3Al \rightleftharpoons [(CH_3)_3Al]_2 \quad (26a)$$

$$(C_6H_5)_2C{=}O + (CH_3)_3Al \rightleftharpoons \underset{\text{I}}{(C_6H_5)_2C{=}O\cdots Al(CH_3)_3} \quad (26b)$$



$$\rightarrow \underset{\text{II}}{(C_6H_5)_2C(CH_3)OAl(CH_3)_2} \quad (26c)$$

$$\text{II} + (CH_3)_3Al \rightleftharpoons (C_6H_5)_2C(CH_3)OAl(CH_3)_2{\cdot}Al(CH_3)_3 \quad (26d)$$

P is similar to one suggested earlier by Ziegler and coworkers[21] as an intermediate in the alkyl exchange of the system $R_3Al\text{–}R'OAlR_2$.

Thus the mechanism satisfies the major observations, namely, the first-order disappearance of the complex throughout most of the reaction, the appearance of the ketone as the complex band disappears, the complexation of aluminum alkyl with the product, and the further slow reaction of ketone after the complex has diminished to negligible concentrations.

General Conclusions

It appears clear from this work that trimethylaluminum reacts with benzophene by two distinct mechanistic paths depending on the stoichiometry of the reaction. These mechanisms involve (1) a first-order disappearance of complex (four-center transition state, 1:1 stoichiometry, eq 26) and (2) reaction of a molecule of complex with an additional molecule of alkylating agent (six-center transition state, 1:2 stoichiometry, eq 21). Because of the similarity of the Al–C, Mg–C, and Li–C bonds, it would appear that such mechanisms are also possible for the description of similar reactions involving organomagnesium and organolithium compounds.

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[21] K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Stendel, *Ann.* **629**, 53 (1960); K. Ziegler and W. R. Kroll, *ibid.*, **629**, 167 (1960).