Organometallic Reaction Mechanisms. VIII. A Detailed Description of the Mechanism of Methylmagnesium Bromide Addition to 2-Methylbenzophenone[1]

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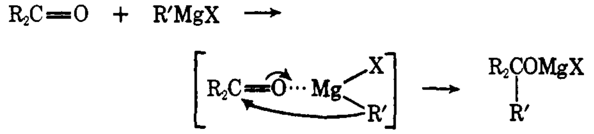
Abstract: The major areas of dispute concerning the mechanism of Grignard reagent addition to ketones have been the establishment of the reaction order of the Grignard reagent, the role of the reactive species (RMgX or R_2Mg), and the inability to evaluate kinetic data because of the presence of free ketyl in the reaction resulting in the formation of pinacol by-product. We report here, for the first time, satisfying answers to all of these questions for the reaction of methylmagnesium bromide with 2-methylbenzophenone. We have determined the reaction order of the Grignard reagent unequivocally by carrying out kinetic studies in excess ketone. The reaction proceeds by two paths, one first-order in CH_3MgBr and the other first-order in $(CH_3)_2Mg$. The order of the CH_3MgBr species was established by addition of sufficient $MgBr_2$ to shift the Schlenk equilibrium in the direction of this species. In the initial stages of the reaction both $(CH_3)_2Mg$ and CH_3MgBr were found to participate in the alkylation to comparable degrees. Although the reaction becomes more complicated beyond its initial stage, kinetic data from a variety of experiments revealed the series of steps and the nature of the intermediates that lead to the final product. Exchange studies involving magnesium bromide with all possible products arising from the reaction of ketone with dimethylmagnesium, *i.e.*, $(ROMgCH_3)_2$, $(ROMgCH_3 \cdot ROMgBr)$, show that these species have but fleeting existence in the reaction. Thus, the complexity is caused solely by the interaction of the product of CH_3MgBr addition to ketone, ROMgBr, with the species CH_3MgBr, $(CH_3)_2Mg$ and $MgBr_2$, and their respective ketone complexes. The amount of free 2-methylbenzophenone ketyl formed in the reaction is apparently very small since product studies under the actual conditions of the kinetics gave 100% yields of addition product. In addition, uv analysis shows that the rate of formation of the ketyl is much slower than the rate of alkylation. A detailed structural description of the mechanism of this reaction is shown in eq 21–27.

The mechanism of Grignard reagent addition to ketones has been the subject of controversy for some years.[3] Meisenheimer and Casper[4] suggested that a complex between the Grignard reagent and the ketone is converted to product by a unimolecular process (eq 1). Swain and Boyles[5] in 1951 suggested a third-order mechanism: first order in ketone and second order in Grignard reagent (eq 2). This mechanism was later supported by Anteunis[6] who reported that the reaction of Grignard reagents with ketones follows the third-order rate law. The Swain mechanism was criticized by several workers after 1957 when a convincing report appeared in which $R_2Mg \cdot MgX_2$ was proposed to represent the structure of Grignard reagents in ether solution.[7] Almost simultaneously Mosher, *et al.*, Bikales and Becker, and Hamelin and Hayes suggested a bimolecular mechanism involving 1 molecule of ketone and 1 molecule of unsymmetrical dimeric Grignard reagent (eq 3).[8]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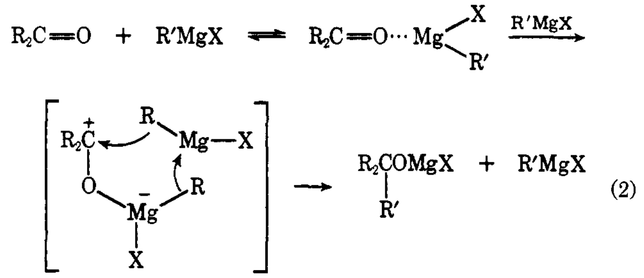
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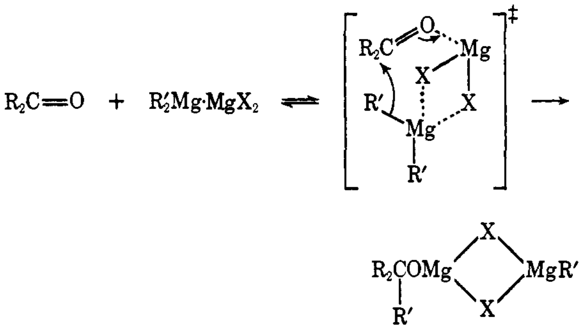
(3)

The dimer mechanism supported by Becker, Mosher, and Hamelin has been questioned more recently due to a better understanding of the composition of Grignard reagents in solution.[3b,9] However, work carried out in several laboratories since 1964 has been reported to support both the Swain and the Meisenheimer mechanisms.

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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 Company Predoctoral Fellow, 1970–1971.

(3) (a) M. S. Kharash and O. Reinmuth, "Grignard Reagents of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954; (b) E. C. Ashby, *Quart. Rev., Chem. Soc.*, 2, 259 (1967).

(4) J. Meisenheimer and J. Casper, *Chem. Ber.*, **54B**, 1655 (1921).

(5) C. G. Swain and H. B. Boyles, *J. Amer. Chem. Soc.*, 73, 870 (1951).

(6) M. Anteunis, *J. Org. Chem.*, **26**, 4214 (1961).

(7) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Amer. Chem. Soc.*, **79**, 3476 (1957).

(8) (a) J. Miller, G. Gregoriou, and H. S. Mosher, *ibid.*, **83**, 3955 (1961); (b) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1962); (c) R. Hamelin and S. Hayes, *C. R. Acad. Sci.*, **252**, 1616 (1961).

(9) (a) F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969); (b) E. C. Ashby and M. B. Smith, *ibid.*, **86**, 4363 (1964).

The Meisenheimer mechanism, which requires complex formation between the Grignard reagent and the ketone, has been strongly favored by Smith and coworkers.[10] Smith reported direct evidence for complex formation between various ketones and magnesium species. When dimethylmagnesium, methylmagnesium bromide, or magnesium bromide was added to certain hindered ketones, two bands were observed in the ultraviolet spectrum.[10a] The shorter wavelength maximum was a π–π^* carbonyl band of the ketone while the longer wavelength maximum was attributed to the shifted carbonyl band due to complex formation between ketone and magnesium species. In the cases where the ketones were 2,4-dimethyl-4′-methylmercaptobenzophenone[10b,c] and 4-methylmercaptoacetophenone,[10d] and the magnesium species was methylmagnesium bromide, the two bands were found to decrease with the same rate constant establishing that an equilibrium does exist between ketone and complex. The nature of the complex, whether it be a σ complex, charge transfer, solvent caged radical anion, etc., was not discussed.

Smith and coworkers base the interpretation of their kinetic data on the simple Meisenheimer mechanism and have described this mechanism by the following equations:[10]

$$\mathrm{K} + \mathrm{G} \overset{K}{\rightleftarrows} \mathrm{C} \tag{4}$$

$$\mathrm{C} \xrightarrow{k} \mathrm{P} \tag{5}$$

where K = ketone, G = Grignard, C = complex, and P = product. Their pseudo-first-order kinetic data are, in fact, consistent with the simple Meisenheimer mechanism only at Grignard concentrations below 0.2 M in the case 2,4-dimethyl-4′-methylmercaptobenzophenone[10c] and below 0.1 M in the case of 4-methylmercaptoacetophenone.[10d] The number of kinetic experiments in this range is small: four in the case of the first ketone, and two in the case of the second ketone. The majority of the experiments were performed at higher Grignard concentrations, where the pseudo-first-order rate constants are much larger than predicted by the simple Meisenheimer mechanism. Retention of the Meisenheimer mechanism, as the sole reaction path, could be accomplished by invoking a medium effect, linear in the concentration of titratable Grignard reagent. Although there are precedents for invoking medium effects to explain reaction rates, the proposal that the major effect of Grignard concentration on the rate is exerted *via* a medium effect, rather than on the way in which Grignard reagent enters the mechanism, is somewhat disconcerting.

In a second explanation for the behavior at high-Grignard concentration, a second path of reaction was assumed in addition to the Meisenheimer path.[10] In this case a dimeric Grignard species was assumed to exist in equilibrium with monomeric species. The dimer species was also assumed to form a complex with the ketone followed by rearrangement to form product. This suggestion, of course, supports the Swain mechanism involving 2 molecules of the Grignard reagent in the transition state at high Grignard reagent concentrations. To fit the data to this model the dimer complex must have a reactivity ten times greater than that of the monomer complex.

Holm[11] has obtained data of a similar pattern from other Grignard–ketone systems; again most of the kinetic data is at Grignard concentrations where association is appreciable. He favors a modified Meisenheimer mechanism (eq 6) at low Grignard concentrations, but suggests that at high Grignard concentrations, where most of the ketone is complexed, a bimolecular reaction of the complex with Grignard reagent is the most important reaction path.

$$\mathrm{P} \longleftarrow \mathrm{G} + \mathrm{K} \rightleftarrows \mathrm{C} \tag{6}$$

In our first kinetic study[12] we measured the rate of reaction of benzophenone with methylmagnesium bromide in diethyl ether using concentrations of the latter small enough that the reagent is predominantly monomeric, and at the same time sufficiently greater than the ketone concentration so that the concentration of Grignard reagent remains essentially constant during a given experiment. The functional dependence of the pseudo-first-order rate constant on Grignard concentration was used as a test of possible mechanisms, and it was found that the best fit to the experimental results was given by a mechanism similar to that originally suggested by Swain[5] (eq 2).

$$\mathrm{G} + \mathrm{K} \rightleftarrows \mathrm{C} \tag{7}$$

$$\mathrm{C} + \mathrm{G} \longrightarrow \mathrm{P}' \tag{8}$$

$$\mathrm{P}' \rightleftarrows \mathrm{P} + \mathrm{G} \tag{9}$$

The last equilibrium was suggested by us to account for the kinetic behavior at low ratios of Grignard to ketone; its existence or nonexistence would not affect the kinetic behavior when the Grignard reagent is in large excess. A quantitative test of this mechanism was a plot of [G] *vs.* $[\mathrm{G}]^2/k_{\mathrm{obsd}}$ which within experimental error is a straight line having the correct signs for the intercept and slope. We also tested our data against the Meisenheimer mechanism, the dimer mechanism and a simple bimolecular mechanism, and none gave a meaningful fit. More recently the Swain mechanism has also been supported by Tuulmets and coworkers.[13] These workers reevaluated earlier kinetic results obtained by themselves and by Smith, taking into account the concentrations of monomeric and polymeric species, and concluded[13b] that the Swain mechanism could account for the observed rate behavior up to concentrations of 1.2 M Grignard.

It is generally recognized that the two proposed mechanistic schemes (Swain and Meisenheimer mechanisms) are unrealistically simple. For example, the Grignard reagent (indicated simply as G) is not a single species even at low concentrations. Although all workers have recognized that $\mathrm{R_2Mg}$ is present in Grignard solutions, and that it is a more reactive species than RMgX, only Holm has attempted quantitative measurements to evaluate its importance in Grignard reactions: in the reactions of butylmagnesium bromide

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[10] (a) S. G. Smith, *Tetrahedron Lett.*, 7, 409 (1963); (b) S. G. Smith and G. Su, *J. Amer. Chem. Soc.*, **86**, 2750 (1964); (c) *ibid.*, **88**, 3995 (1966); (d) J. Billet and S. G. Smith, *ibid.*, **90**, 4108 (1968).

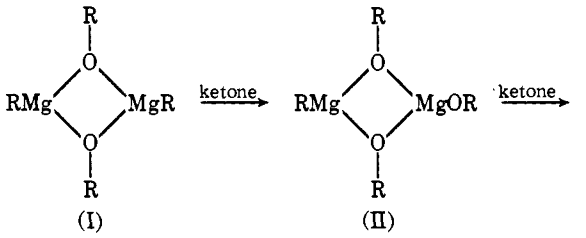
[11] (a) T. Holm, *Acta Chem. Scand.*, **19**, 1819 (1965); (b) *ibid.*, **20**, 1139 (1966); (c) *ibid.*, 21, 2753 (1967); (d) *ibid.*, 23, 579 (1969).

[12] E. C. Ashby, R. Duke, and H. M. Neumann, *J. Amer. Chem. Soc.*, **89**, 1964 (1967).

[13] (a) J. Koppel, L. Margua, and A. Tuulmets, *Reakts. Sposobnost Org. Soedin.*, 5, 1041 (1968); (b) A. Tuulmets, *ibid.*, 6. 854 (1969).

with acetone and methyl trifluoracetate,[11c] and in the reaction of methylmagnesium bromide with benzophenone.[11d] Unfortunately, the latter measurements were made at concentrations (0.4 and 0.568 *M*) at which the Grignard is associated. Recently in a study of the reaction of dimethylmagnesium with 2-methylbenzophenone[14] we have observed that the initial reaction leads to a series of intermediates (I and II), capable

$$R_2Mg + R_2C{=}O \longrightarrow RMgOR \longrightarrow$$



$$[Mg(OR)_2]_n \quad (10)$$

of acting as alkylating agents. If R_2Mg is an important reactant in the Grignard reaction, then the fate and/or role of these compounds in the reaction must be assessed.

The effect of impurities in the magnesium used to prepare the Grignard reagent has become a matter of concern, with respect to both net formation of by-products and effect on the measured rate of reaction. Both Smith and coworkers[10d] and this laboratory[15] have observed that rate constants obtained with benzophenone and excess methylmagnesium bromide show a dependence on initial ketone concentration. This is also true to a less marked extent with 2,4-dimethyl-4′-methylmercaptobenzophenone and 4-methylmercaptoacetophenone.[10d] In the case of benzophenone, rate constants obtained are much larger at high Grignard to ketone ratios when the Grignard concentrations are held constant. The high rate constants are accompanied by significant yields of nonaddition by-products, benzopinacol[10d,15] and benzhydrol.[16] We have found that at low methylmagnesium bromide to benzophenone ratios there is a 100% yield of addition product, and by-product formation in significant amounts occurs only in those cases in which large excesses of methylmagnesium bromide are used. The problem apparently occurs due to a small constant impurity in the Grignard reagent,[15,16] and can be reduced significantly by recrystallization of the Grignard reagent,[10d] or essentially eliminated by preparing the Grignard reagent from "ultra pure" magnesium[15] using special reaction conditions.

We have reproduced the rate data obtained in our initial studies[12] using Grignard reagent carefully prepared from triply sublimed magnesium (99.95% pure). However, it is now apparent that the triply sublimed magnesium used in our earlier studies is not sufficiently pure for the preparation of the Grignard reagent needed for these studies. Our recent report[15] that rate data can be obtained that are essentially independent of the initial ketone concentration when the Grignard reagent is prepared from an ultra pure source of magnesium (99.9995% pure) has provided information that is not consistent with our original proposal. Our position at the time was that parts per million of transition metal impurities were causing side reactions which could be completely avoided by the use of higher purity magnesium. As far as we know, all other workers in this field are using Grignard reagents in their kinetic studies prepared from triply sublimed magnesium or magnesium of lower purity.

Unfortunately, all mechanisms proposed by previous workers in this area leave much to be desired. More often than not mechanisms have been formulated in terms of species designated simply as G, C, and P, without further concern for their structures. Such a description does not provide a detailed understanding of the chemistry involved. For example, it would be more meaningful to be able to specify the nature of the reactive species in the Grignard reagent by a structural description rather than by the letter G so that the mechanism of this reaction can be helpful in resolving the stereochemical problems involving Grignard addition reactions, a subject of considerable interest at the present time. And finally, statements that other mechanisms can also be written that are consistent with the data[10c] do not leave one with the feeling that even the kinetic description is known with much certainty.

In a recent communication,[17] we reported initial rate studies concerning the reaction of methylmagnesium bromide, prepared from single crystal magnesium, with a large excess of 2-methylbenzophenone. These studies allowed us to determine directly and unequivocally, for the first time, the reactive organomagnesium species and their reaction orders in the addition of a Grignard reagent to a ketone. In the present study more detailed information concerning kinetic studies with ultra pure magnesium is presented, followed by a complete structural description of the entire reaction.

Experimental Section

Materials. Single crystal magnesium from Ventron Corp. (99.9995% pure) was milled with a carbide tool taking special precautions to maintain the purity of the magnesium. The turnings were washed several times with diethyl ether prior to use.

Eastman highest purity 2-methylbenzophenone was distilled under vacuum from Linde 4A molecular sieve. The middle fraction (bp 130° (0.03 mm)) was used in the kinetic studies. Glpc analysis of the distilled material showed it to be better than 99.9% pure. Diethyl ether solutions of 2-methylbenzophenone were stored in a glove box and carefully shielded from light.

Eastman reagent grade 9-fluorenone was used as a glpc standard without further purification. Fisher reagent grade anhydrous diethyl ether was distilled under nitrogen from $LiAlH_4$ prior to use. Methyl bromide (Matheson, 99.5% purity) was dried and purified by passing through a 30-cm tube of NaOH pellets and then through a 70-cm tube of Linde 4A molecular sieve. Baker reagent grade mercuric bromide was dried under vacuum for several hours prior to use.

Apparatus and Procedure. A Cary Model 14 recording spectrophotometer was used for recording visible spectra over a number of wavelengths. In the kinetic studies, a Zeiss PMQ II single-beam spectrophotometer was used for making absorbance measurements at a single wavelength. A Pyrex 10-mm sample cell was used in conjunction with a quartz 10-mm reference cell for obtaining visible spectra.

A F & M Model 700 flame ionization gas chromatograph equipped with dual 6 ft × 1/8 in. stainless steel, 10% Carbowax 20M columns was used to identify products.

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(14) J. Laemmle, E. C. Ashby, and H. M. Neumann, *J. Amer. Chem. Soc.*, **93**, 5120 (1971).

(15) E. C. Ashby, F. W. Walker, and H. M. Neumann, *J. Chem. Soc. D*, 330 (1970).

(16) S. E. Rudolph and S. G. Smith, *ibid.*, 1428 (1970).

(17) E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **93**, 4601 (1971).

All transfers of materials used in this study were performed in a glove box equipped with a recirculating system described elsewhere.[18] As an added precaution, a special line for prepurified nitrogen was added to the glove box and all materials were transferred in Schlenk tubes under a blanket of prepurified nitrogen.[19]

Calibrated syringes equipped with stainless steel needles were used for transfers of reagents. Deliveries could be reproduced to better than ±0.5%.

Solutions of 2-methylbenzophenone were prepared by adding a known amount of ketone from a calibrated syringe to a calibrated volumetric flask and diluting to the mark with diethyl ether. The concentration of 2-methylbenzophenone could then be easily determined from its density, 1.079, and the total volume of solution.

For obtaining visible spectra of reacting mixtures and for kinetic studies, accurate amounts of standard methylmagnesium bromide solutions were injected into known volumes of ketone solution with a Hamilton 100-μl syringe. The concentration of methylmagnesium bromide in the reacting solutions was determined by the dilution factor. For the product study, larger amounts of standard methylmagnesium bromide solutions were injected with a 1-ml syringe.

For kinetic studies involving excess magnesium bromide, standard solutions of mixtures of magnesium bromide and 2-methylbenzophenone were prepared. These solutions did not absorb at 410 mμ and were injected with known amounts of standard Grignard solutions.

For kinetic studies involving excess product, $CH_3(C_7H_7)(C_6H_5)COMgBr$, standard solutions of mixtures of product and 2-methylbenzophenone were prepared. These solutions did not absorb at 410 mμ and were injected with known amounts of standard Grignard solutions.

For exchange experiments involving $MgBr_2$ and $CH_3(C_7H_7)(C_6H_5)COMgCH_3$, standard solutions of mixtures of $MgBr_2$ and 2-methylbenzophenone were prepared. These solutions were injected with known amounts of CH_3MgOR and reaction of active methyl groups was followed by noting the change in absorbance at 410 mμ with time.

Preparations. To prepare methylmagnesium bromide, a Dry Ice-Acetone condenser and a 500-ml, round-bottomed flask containing an appropriate amount of single crystal magnesium turnings and a Teflon stirring bar were connected directly to a diethyl ether still. The apparatus was evacuated, flash flamed several times, and refilled with high purity nitrogen. The condensor was charged with Dry Ice and after distilling approximately 50 ml of ether into the reaction flask, methyl bromide was introduced through a side arm near the base of the condensor. After the reaction had been initiated, as evidenced by bubbling and heat release, stirring was started. The diethyl ether and methyl bromide were added at a rate to maintain gentle reflux of the solution without external heating. The methyl bromide was added until all of the magnesium was consumed, and the distillation of the ether was continued until the flask held approximately 300 ml of solution. After the flask had cooled to room temperature, the ether and excess methyl bromide were stripped from the Grignard reagent by means of gentle vacuum, and the white crystals of methylmagnesium bromide were subjected to 0.02 mm vacuum for 4 hr to remove the last traces of methyl bromide. After refilling the system with nitrogen, ether was distilled into the flask until it contained approximately 300 ml of solution. The reaction flask was removed from the assembly under a heavy flow of nitrogen, capped, and placed in the glove box. The Grignard solution was filtered through a glass frit under high purity nitrogen, with no exposure to the glove box atmosphere, and the filtered solution was stored in a flask in which the only entry was through a Teflon three-way stopcock. Analysis of the clear and colorless methylmagnesium bromide solution gave a C-Mg:Mg:Br ratio of 1.00:1.03:0.99.

The preparation of dimethylmagnesium has been previously described.[14] To prepare magnesium bromide, a water-jacketed reflux condensor and a 500-ml, round-bottomed flask containing an appropriate excess of single crystal magnesium turnings and a Teflon stirring bar were connected directly to the ether still. The system was evacuated and flamed. After refilling with nitrogen, an appropriate amount of mercuric bromide was added to the magnesium turnings. The system was again evacuated for 2 hr and gently flamed from time to time. Reaction was initiated by allowing diethyl ether to distill into the reaction flask. The mixture was stirred and after the desired volume of diethyl ether had been added, the solution was refluxed for 12 hr. The clear solution was drawn away from the residue by syringe and then filtered. Analysis by the EDTA and Volhard methods gave a Mg:Br ratio of 1:1.97. The magnesium bromide was stored in a glove box in a flask in which the only entrance was *via* a three-way Teflon stopcock.

Methylmagnesium 1-(2-methylphenyl)-1-phenylethoxide was prepared by mixing equal molar amounts of dimethylmagnesium and 2-methylbenzophenone in diethyl ether. The solution was stored in a flask containing a three-way Teflon stopcock. Glpc analysis on a hydrolyzed sample using 9-fluorenone as an internal standard showed no unreacted ketone and gave a $CH_3(C_7H_7)(C_6H_5)COH$:Mg ratio of 1.1:1.0.

Bromomagnesium 1-(2-methylphenyl)-1-phenylethoxide was prepared by mixing equal molar amounts of methylmagnesium bromide and 2-methylbenzophenone in diethyl ether. The solution was stored in a flask containing a three-way Teflon stopcock. Glpc analysis on a hydrolyzed sample using 9-fluorenone as an internal standard showed less than 2% unreacted ketone and gave a $CH_3(C_7H_7)(C_6H_5)COH$:Mg ratio of 1.1:1.0.

Visible Spectra and Kinetics. Diethyl ether solutions of 2-methylbenzophenone show negligible absorbance in the 400-600 mμ region of the visible spectrum, although concentrated solutions of the ketone absorb strongly at wavelengths shorter than 390 mμ. Diethyl ether solutions of methylmagnesium bromide show no absorbance in the visible spectrum.

Visible spectra of mixtures of methylmagnesium bromide with excess 2-methylbenzophenone were obtained in the following fashion. A Pyrex visible spectrum cell equipped with a 1-mm bore two-way Kimax micro Teflon stopcock was filled with a known volume of standard ketone solution in the glove box. The stopcock was closed and the cell was placed in the chamber of the Cary 14 spectrophotometer along with a reference quartz cell filled with diethyl ether. The spectrum of the ketone solution was then scanned between 400 and 600 mμ. The wavelength was then set at 400 mμ, the cell stopcock opened, and a small amount (15-45 μl) of standard methylmagnesium bromide injected. The cell was shaken rapidly to ensure mixing, and the spectrum was rapidly scanned between 400 and 600 mμ. When methylmagnesium bromide is mixed with solutions of excess 2-methylbenzophenone a strong absorbance appears in the 400-600 mμ region. The absorbance decreases with increasing wavelength. There is no absorbance maximum except in certain cases when a very small maximum occurs at 545 mμ after long reaction times. The absorbance at 410 mμ rapidly decreases with time. The reaction solutions appear yellow to the unaided eye and with time the yellow color fades directly to clear, or in some cases to a persistent pale pink color and then to clear.

The procedure for initiating reaction for the kinetic studies was similar to that for obtaining visible spectra. The reference and sample cells were placed in the jacketed cell holder of the Zeiss spectrophotometer. The cell chamber and cell holder were maintained at 20 ± 0.1° by means of a Haake constant-temperature recirculator. The temperature was monitored in the water reservoir of the recirculator.

After a suitable amount of time was allowed for the cells to come to temperature equilibrium, the sample cell was removed and a known small amount of standard organomagnesium solution was injected. The cell was rapidly shaken and placed in the chamber. The instrument was maintained in such a fashion that readings could be taken immediately. The total time between the initial injection and the first readings was generally 10 sec. Measurements were made at 410 mμ.

Product Analysis. The preparation of an authentic sample of 1-(2-methylphenyl)-1-phenylethylene has been previously described.[14] The glpc conditions necessary to separate 1-(2-methylphenyl)-1-phenylethylene, 2-methylbenzophenone, 1-(2-methylphenyl)-1-phenylethanol, and the internal standard 9-fluorenone have also been described.[14]

Ten reactions were run in which samples were withdrawn and quenched at appropriate intervals and after 24 hr. The concentrations of ketone and methylmagnesium bromide in many of these reactions were the same as those employed in selected kinetic runs which were followed spectroscopically. The purpose of these runs was to correlate the change of absorbance with time with product formation by following the appearance of product by glpc rather than by following the disappearance of complex by uv analysis. The reactions were set up in the following way. To a

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

[19] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

calibrated 50-ml volumetric flask, whose only entry was *via* a three-way Teflon stopcock, was added an appropriate amount of 2-methylbenzophenone, followed by dilution to the mark with diethyl ether. The flask was placed in a Sargent constant temperature bath at 20° and allowed to come to temperature equilibrium. An appropriate amount of methylmagnesium bromide was rapidly injected under nitrogen flow to bring the amount of each component to the desired concentration and the flask was rapidly shaken to ensure mixing. Samples were withdrawn under nitrogen flow at appropriate times and quenched in ether-saturated 10% H_2SO_4. The diethyl ether layer of each quenched sample was transferred to a quartz uv cell and about 20 μl of saturated solution of 9-fluorenone in diethyl ether added. The concentration of 9-fluorenone in each sample was determined by visible spectroscopy (λ 410 mμ, ϵ 144, slit $<$ 0.02 mm) and the samples were transferred to tubes containing anhydrous $MgSO_4$. A crystal of *p*-toluenesulfonic acid was added to each tube and the samples were vigorously shaken. The samples were then subjected to gas chromatography and 1-(2-methylphenyl)-1-phenylethylene, identified by comparison of its retention time with the authentic sample, was found to be the only product. The final yields for six of these reactions ranged between 97 and 104% and for the remaining four between 93 and 96%. The reaction is then quantitative within experimental error.

Kinetic Experiments. Ten visible spectrum kinetic runs were carried out at constant methylmagnesium bromide concentration and a tenfold variation of ketone concentration. Six experiments were carried out at a constant ketone concentration and a threefold variation of the Grignard concentration. Eight runs were carried out at two different excess ketone concentrations and a constant concentration of methylmagnesium bromide with added $MgBr_2$ in which the concentration of $MgBr_2$ was varied between 10 and 400% of the initial Grignard concentration. Two runs were carried out at two different excess ketone concentrations and a constant concentration of $ROMgCH_3$. Four runs were carried out at four different constant excess ketone concentrations and constant concentration of $ROMgCH_3$ with added $MgBr_2$ in which the initial concentration of $MgBr_2$ was equal to the initial concentration of $ROMgCH_3$. Two runs were carried out at two different constant excess ketone concentrations and constant $ROMgCH_3$ concentration with added $MgBr_2$ in which the initial concentration of $MgBr_2$ was one-half the initial concentration of $ROMgCH_3$. Two runs were carried out at two different constant excess ketone concentrations and a constant concentration of "mixed dimer" ($ROMgCH_3 \cdot ROMgBr$) prepared by the reaction of $ROMgCH_3$ with ROMgBr. One run was carried out at excess ketone concentration with mixed dimer and an amount of $MgBr_2$ equal to the mixed dimer concentration. Five kinetic runs were carried out at constant methylmagnesium bromide concentration and added reaction product, ROMgBr, in which the initial concentration of ROMgBr was equal to the initial concentration of Grignard reagent. Six kinetic runs were carried out at a constant excess ketone concentration and a constant methylmagnesium bromide concentration and a varied amount of added ROMgBr in which the initial concentration of ROMgBr was varied between 50 and 1830% of the initial Grignard concentration. The data in the above systems was gathered by noting the change in absorbance with time at 410 mμ.

Several duplicate runs were made in which the concentrations of Grignard reagent and ketone were identical. In one run the disappearance of the strong absorbance at 410 mμ attributed to CH_3MgBr-ketone complex was recorded. In the duplicate run, the change of absorbance with time at 545 mμ, attributed to ketyl,[10d] was recorded. In addition, in each run in which Grignard reagent and ketone were allowed to react, the absorbance at 545 mμ was recorded at long reaction times, in order to determine the relative amount of ketyl in each run.

In all runs involving measurement of the absorbance directly in the cell, approximately 30 individual points were taken.

Five kinetic runs were carried out at a constant methylmagnesium bromide concentration and a fivefold variation of ketone concentration in which the reaction mixture was quenched and the concentration of product directly determined. Five similar runs were carried out at a constant excess ketone concentration and a tenfold variation of Grignard reagent concentration. In those experiments involving quenching, eight or nine points were taken as well as an infinity reading after 24 hr.

Results and Discussion

Methylmagnesium bromide reacts with excess 2-methylbenzophenone to produce on hydrolysis the expected alcohol, 1-(2-methylphenyl)-1-phenylethanol, in quantitative yield with no indication of by-product formation.

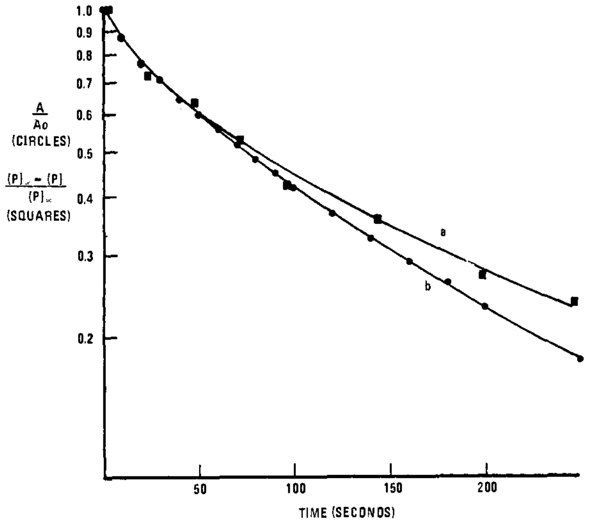
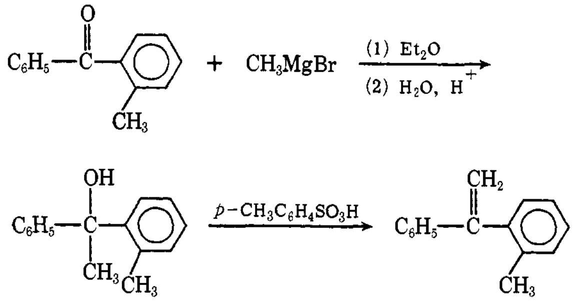


Figure 1. Normalized curves for the reaction of 0.56 *M* 2-methylbenzophenone with 0.0126 *M* methylmagnesium bromide illustrating (a) disappearance of active methyl groups and (b) disappearance of complex.



(11)

General Features of Rate Studies. The reaction of methylmagnesium bromide with excess 2-methylbenzophenone was studied in two ways, (1) by following directly the disappearance of the complex band at 410 mμ, and (2) by quenching reacting solutions with dilute acid and measuring the formation of product by glpc analysis.

Solutions of methylmagnesium bromide show no absorbance in the visible spectrum whereas concentrated solutions of 2-methylbenzophenone show a slight absorbance only in the 400–410-mμ region. Upon rapid mixing of solutions of methylmagnesium bromide and 2-methylbenzophenone, a strong absorbance immediately appears in the 400–600-mμ region. The absorbance decreases with increasing wavelengths with no maximum. Since mixtures of $(CH_3)_2Mg$ and 2-methylbenzophenone show little absorbance in the visible spectrum[14] and mixtures of $MgBr_2$ and 2-methylbenzophenone show no absorbance in the visible spectrum, the strong absorbance which occurs immediately upon mixing is attributed to a complex formed between CH_3MgBr and ketone. Methylmagnesium bromide reacts rapidly with 2-methylbenzophenone, and the complex rapidly disappears.

Figure 1 illustrates the disappearance of complex as determined by spectroscopy, and the reaction of active methyl groups (methyl groups bonded directly to Mg) as determined by the appearance of product. The rate of disappearance of complex is initially equal to the rate of disappearance of active methyl groups; however, at late reaction times the disappearance of complex has proceeded to a slightly greater extent than the disappearance of active methyl groups. The difference between the per cent product predicted by the disappearance of complex and that actually found by glpc analysis is never more than 5% at the longest reaction times and thus, Figure 1 shows that the rate of disappearance of the complex and of active methyl groups is essentially the same.

As illustrated in Figure 1, the total reaction is complex. Certain features in the rate data suggested that the initial rates, taken before significant product formation had occurred, could be treated in a pseudo-first-order fashion. Several experiments indicated that the complexity of the latter portion of the reaction was due to interaction of the product, ROMgBr, with the reactive species. Since the initial rate behavior is different than that found after significant amounts of product have formed, the treatment of the initial rate data will be considered separately from the latter portion of the reaction.

In certain kinetic runs, a very small absorbance maximum occurred at 545 mμ at long reaction times. This absorbance, attributed to Grignard–2-methylbenzophenone ketyl,[10d,20] was found to form slowly and persist long after the addition reaction was complete. Several duplicate runs were carried out in which the concentration of methylmagnesium bromide and ketone were identical. In one run the disappearance of complex was followed and in the duplicate run the behavior of the ketyl at 545 mμ was observed. The absorbance due to ketyl was initially low, then slowly increased to a maximum value at a time when the addition reaction was nearly complete, then very gradually decreased. This indicates that ketyl production is a minor side reaction not affecting the addition. In each run in which the complex was followed, the absorbance of ketyl at 545 mμ was recorded at long reaction times where ketyl absorbance is the greatest. The maximum absorbance at 545 mμ in each run is given in Tables I and II. The absorbancy value given is a measure of the relative amount of ketyl which occurred in each run. The data indicate that there is no simple relationship between the initial concentration of reactants and ketyl product, reinforcing the judgement that ketyl formation is a minor side reaction. The absolute amount of free ketyl formed in the reaction is apparently very small since product studies under the actual conditions of the kinetics gave 100% yield of addition product.

Table I. Initial Observed Rate Constants and Maximum Ketyl Absorbancies at Constant 0.445 M 2-Methylbenzophenone Concentration

$[G]_0$, M	Initial k_{obsd}, sec^{-1}	Ketyl A_{max}
0.0236	0.0101	0.112
0.0198	0.0101	0.023
0.0149	0.0093	0.061
0.00996	0.0097	0.014
0.00748	0.0108	0.003

Table II. Maximum Ketyl Absorbancies and Rate Constants, k_1, Calculated for the Reaction of 0.0124 M Methylmagnesium Bromide with 2-Methylbenzophenone

$[K]_0$, M	Initial k_{obsd}, sec^{-1}	k_1, l. mol^{-1} sec^{-1}	Ketyl A_{max}
0.128	0.00445	0.0284	0.017
0.230	0.00685	0.0253	0.026
0.343	0.00879	0.0215	0.029
0.448	0.0108	0.0213	0.010
0.563	0.0138	0.0245	0.022
0.668	0.0149	0.0222	0.016
	Av[a,b]	0.0239	
0.892	0.0217	0.0314	0.008
1.10	0.0262	0.0349	0.005

[a] The values of k_1 at the two highest ketone concentrations have been excluded from the averaging because they are inherently less accurate (due to faster rate) and for a reason indicated in the text. [b] Values calculated for k_1 are not greatly dependent on the numerical value of K_s. The average value of k_1 would be 0.0293 for K_s = 0.001, and would be 0.0213 for K_s = 0.003.

Smith and coworkers have reported pseudo-first-order kinetic studies involving benzophenone and excess methylmagnesium bromide.[10d] Their conclusion is the following: "because of the formation of what appears to be a radical species in the reaction of benzophenone with methylmagnesium bromide under the conditions used in these kinetic studies and our failure, to date, to completely eliminate the coupling reaction with dilute ketone solutions, a quantitative treatment of these data does not seem justified at this time." It is important to point out that in the system reported here the reaction is run in excess ketone and much higher purity magnesium is used to prepare the Grignard reagent. In our studies the formation of by-product is completely eliminated, the radical species has been shown to be unimportant, and therefore, a quantitative interpretation of the results is justified (Table I, Figure 7).

Evaluation of Equilibrium Constants. Four equilibria are known to be important in the reaction mechanism of methylmagnesium bromide with ketones. The first of these is the Schlenk equilibrium

$$CH_3MgBr \overset{K_s}{\rightleftarrows} (CH_3)_2Mg + MgBr_2$$

which defines the composition of methylmagnesium bromide in dilute diethyl ether solution.[3,9] The other three equilibria, which involve complexation between the various magnesium species defined by the Schlenk equilibrium and ketone, are represented by the following equations;

$$CH_3MgBr + K \overset{K_1}{\rightleftarrows} C_1 \qquad (12)$$

$$(CH_3)_2Mg + K \overset{K_2}{\rightleftarrows} C_2 \qquad (13)$$

$$MgBr_2 + K \overset{K_3}{\rightleftarrows} C_3 \qquad (14)$$

Evidence from previous work[14] indicated that K_2, the equilibrium constant for formation of complex between $(CH_3)_2Mg$ and ketone, is quite small relative to the magnitudes of K_1 and K_3 and can be considered zero in all of the data treatment. The values of K_1, K_3, and K_s were determined by the following methods.

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(20) K. Maruyama, *Bull. Chem. Soc. Jap.*, 37, 897 (1964).

Since the overall rate of change of absorbancy with time was found to have a value intermediate between first and second order, extrapolation of absorbancy values to zero reaction time was done algebraically both for first- and second-order behavior. At low ketone concentrations ($[K]_0 < 0.6$) the zero time absorbancies obtained from the first- and second-order extrapolation are the same within 1%; however, at high ketone concentration the second-order extrapolation gave a higher zero time absorbancy, as expected.

A value of the equilibrium constant, K_1, for complex formation between CH_3MgBr and 2-methylbenzophenone may be estimated from these data by means of a modification of the Scott equation[21] (eq 15). The

$$\frac{[K]_0[CH_3MgBr_0]}{FA_0} = \frac{[K]_0}{\epsilon_1 F} + \frac{1}{\epsilon_1 K_1} \qquad (15)$$

function F is equal to $[1 + 2\sqrt{K_s(1 + K_3[K]_0)}]$ and takes into account (1) the fact that only CH_3MgBr forms an absorbing complex with ketone, (2) the Schlenk equilibrium is defined by constant K_s, and (3) the fact that $MgBr_2$ forms a complex with 2-methylbenzophenone with equilibrium constant K_3 which has a significant value.

Figure 2 illustrates the modified Scott plot where the upper and lower limits shown indicate the values obtained from first- and second-order extrapolation, respectively. The value of the equilibrium constant is calculated to be 1.35 l. mol^{-1} and the value of the extinction coefficient of the complex is 109. For comparison purposes, the values of K_1 and ϵ_1 were also calculated from a normal Scott plot[10c,d,21] and gave values for K_1 of 1.35 l./mol^{-1} and for ϵ_1 of 101. Thus, the value for K_1 appears to be a totally reliable number.

The value of K_3, the equilibrium constant for complex formation between $MgBr_2$ and 2-methylbenzophenone, could not be evaluated in the media of high ketone concentration since mixtures of $MgBr_2$ and ketone do not absorb in the visible spectrum. However, mixtures of 0.00088 M ketone and 0.0232–0.116 M $MgBr_2$ absorb strongly at 312 mμ, the ketone trough. By relating the absorbancy values at 312 mμ to the reactant concentrations the value for the equilibrium constant K_3 was found to be 4 l. mol^{-1}.

The value of the Schlenk constant, K_s, was evaluated by adding large excess of $MgBr_2$ to reacting solutions at constant ketone and Grignard concentrations. Since only CH_3MgBr–ketone complex absorbs at 410 mμ, the increase in absorbance upon adding a large excess of $MgBr_2$ was taken to represent the increase in concentration of CH_3MgBr–ketone complex due to the shift in the Schlenk equilibrium involving the $(CH_3)_2Mg$ and $MgBr_2$ species as additional $MgBr_2$ is added. The increase in absorbance due to this cause is partially offset by the formation of complex C_3 between $MgBr_2$ and ketone, which lowers somewhat the concentration of free ketone. Using the known value of K_3, it is possible to take into account the decrease in ketone concentration and to effectively compare the zero time absorbance of the normal Grignard solution with that of the same solution containing sufficient amounts of $MgBr_2$ to convert the Grignard reagent completely to CH_3MgBr. Treatment of the data by this method yielded a value of 0.0022 for the Schlenk constant, K_s. Because of inherent limitations in the method, the numerical value of the constant is not established with great accuracy. However, the value compares well with literature values for methylmagnesium bromide, 0.0031, and ethylmagnesium bromide, 0.002,[22] and is consistent with the rate measurements described next.

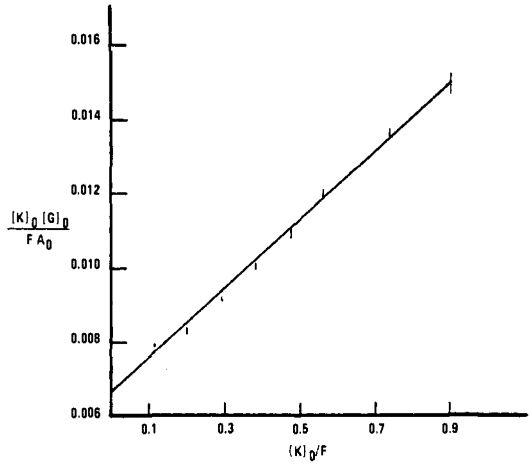

Figure 2. Modified Scott plot (eq 15) for the absorbance of CH_3-MgBr at 410 mμ in ether solutions of 2-methylbenzophenone at 20°.

Detailed Consideration of Initial Rates. Through quenching experiments it was shown that the initial rate of formation of the product was equal to the initial rate of disappearance of the absorption band at 410 mμ (Figure 1). Although the change in absorbance over the entirety of the reaction did not adhere to any simple integral order behavior, meaningful rate constants were obtained by treating the initial disappearance of complex in a pseudo-first-order fashion.

Initial rate constants were obtained in the following manner. The absorbancy at zero reaction time was determined by both first- and second-order extrapolation as previously noted. The average absorbancy value was taken to be the best value for the zero time absorbancy. The initial rate was then calculated using this value and the first measured value. The initial rate calculated at ketone concentrations equal to and below 0.448 M was identical with the initial rate calculated from the normal first-order extrapolation using the first two measured points. At higher ketone concentrations, where a larger per cent reaction had occurred at the same time interval, the initial rate was larger than that calculated by normal first-order extrapolation. Experiments with excess $MgBr_2$, to be discussed in detail later, show that this method gives correct values for the initial rates.

The validity of this first-order treatment is further supported by the constancy of initial rate constants obtained with varying concentrations of methylmagnesium bromide at constant excess ketone (Table I). The initial rate data were treated according to the model shown in Scheme I. In experiments in which the absorbance at 410 mμ is measured, it is assumed that in the initial stages of the reaction the absorption is due solely to C_1. According to this model the initial rate of

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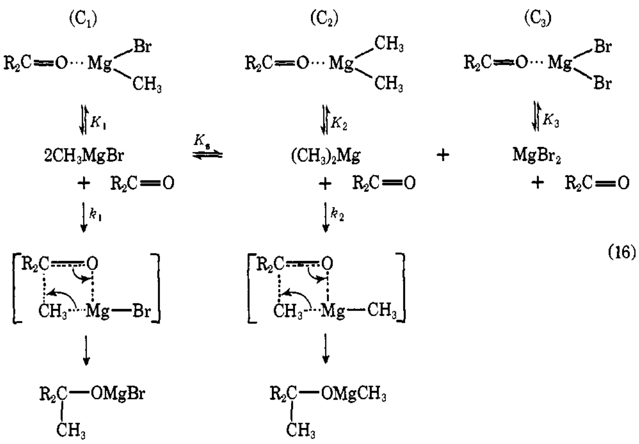
[21] R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, 75, 787 (1956).

[22] (a) T. Holm, *Acta Chem. Scand.*, 23, 579 (1969); (b) M. B. Smith and W. E. Becker, *Tetrahedron*, 22, 3027 (1966).

Scheme I



(16)

change of absorbancy is given by eq 17, where K_s, K_1,

$$\frac{d[C_1]}{dt} = \frac{(k_2\sqrt{K_s(1 + K_3[K])} + k_1)[K]}{(1 + K_1[K] + 2\sqrt{K_s(1 + K_3[K])})}[C_1]_0 \qquad (17)$$

and K_3 are the measured equilibrium constants previously given and k_2, the rate constant for the reaction of $(CH_3)_2Mg$ with 2-methylbenzophenone, was obtained from our previous work.[14]

Using the measured values for K_s, K_1, K_3, and k_2, k_1, the bimolecular rate constant for the reaction of CH_3MgBr with 2-methylbenzophenone,[23] was computed. A consistent value for k_1 should arise in separate experiments if the model properly describes the system and if all the constants employed are accurate. The results shown in Table II give a surprisingly consistent value for k_1 in experiments in which the ketone concentration is varied.

If this model is correct, it should be possible to obtain more directly an experimental value for k_1 by adding additional magnesium bromide to the reaction mixture, thus driving the Schlenk equilibrium far enough to the left so that the amount of dimethylmagnesium is insignificant. Several experiments, at two different ketone concentrations, were carried out in which $MgBr_2$ was added to the reaction mixture. In these experiments at additions of $MgBr_2$ higher than 20% of the initial Grignard concentration, magnesium bromide formed an insoluble compound with the reaction product at late reaction times, thus causing an interference with the absorbance readings due to scattering of light. In fact, at late reaction times when all complex had reacted, the absorbance values increased with time due to this light scattering. The consistent behavior of the absorbance readings at these very late times provided an empirical method for correcting for the scattering effect. The correction was made in the following way. A plot of absorbancy *vs.* time in this region of increasing absorbancy gave the appearance of a parabola displaced along the time axis. This suggested that plots of A *vs.* $\sqrt{t}$ in this region should be linear, and such proved to be the case. Extrapolation of such a plot to zero absorbancy indicated the time when light scattering became a factor. The line also provided the contribution of light scattering to the absorbancy at any time, and by subtracting this value from the total absorbancy, the absorbancy due to C_1 at any time could be determined. The light scattering interference occurred only at relatively late reaction times and reaction of C_1 was better than 80% complete before any interference was noted in the higher concentration ketone runs.

As magnesium bromide is increased in amount in a set of experiments at a constant excess of ketone, two effects are observed: (1) the observed initial rate constants decrease to a certain value, and (2) the first-order plots become linear. The results of two such sets of experiments are shown in Tables III and IV, and an individual run from Table IV is shown in Figure 3.

Table III. Reaction of 0.0124 *M* Methylmagnesium Bromide with 0.462 *M* 2-Methylbenzophenone in the Presence of Added Magnesium Bromide

$[MgBr_2]$, *M*	Initial k_{obsd}, sec^{-1}	Ratio of $MgBr_2$: Grignard		k_1, l. mol^{-1} sec^{-1}
0.0480	0.00680[a]	4:1		0.0251
0.0250	0.00672[a]	2:1		0.0243
0.0120	0.00672[b]	1:1		0.0239
0.00623	0.00693		Av	0.0244
0.00268	0.00872			
0.00156	0.00930			
0.000	0.0104			

[a] Corrected first-order plot linear >80% reaction. [b] Corrected first-order plot linear for 30% reaction.

Table IV. Reaction of 0.0124 *M* Methylmagnesium Bromide with 0.905 *M* 2-Methylbenzophenone in the Presence of Added Magnesium Bromide

$[MgBr_2]$, *M*	Initial k_{obsd}, sec^{-1}	Ratio of $MgBr_2$: Grignard		k_1, l. mol^{-1} sec^{-1}
0.0484	0.0137[a]	4:1		0.0343
0.0252	0.0120[a]	2:1		0.0297
			Av	0.0320

[a] Uncorrected first-order plot linear for 80% reaction.

The rate constant k_1 for the species CH_3MgBr was obtained with confidence from the first three experiments of Table III and from both experiments of Table IV by use of eq 18, in which [K] is a corrected value

$$k_1 = \frac{k_{obsd}(1 + K_1[K])}{[K]} \qquad (18)$$

which takes into account the ketone complexed by $MgBr_2$. Comparison of the average experimental value for k_1 from Table III, 0.0244 l. mol^{-1} sec^{-1}, with the average computed value from Table II, 0.0239 l. $mole^{-1}$ sec^{-1}, shows that agreement is good and the model is sound.

The average value for k_1 measured in 0.905 *M* ketone (Table IV), 0.0320 l. mol^{-1} sec^{-1}, is somewhat higher than either of these values. It is in excellent agreement with the computed value (Table II) for 0.892 *M* ketone, however. This excellent agreement between the computed and experimentally determined k_1 at the high ketone concentration is gratifying and demonstrates that the method of extracting initial rates, described

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(23) This does not imply that the reaction of CH_3MgBr with ketone occurs exclusively by bimolecular collision as this cannot be determined by kinetics. It is convenient for computational purposes to use the bimolecular constant. If reaction occurs by rearrangement of the complex, then the unimolecular constant $k_u = k_1/K_1$.

previously, is giving correct values. Thus, there appears to be a slight but real rate enhancement at very high ketone concentrations, probably due to gross changes in the nature of the solvent medium. This is not too surprising since at the highest ketone concentration employed, 1.1 *M*, one-fifth of the total solution by volume is ketone.

Detailed Consideration of the Later Stages of Reaction. When methylmagnesium bromide is allowed to react with excess 2-methylbenzophenone, the entirety of the reaction is complex and does not adhere to any simple integral order behavior. Deviation from simple pseudo-first-order behavior occurs rapidly and the apparent order of the reaction in Grignard species lies between first and second order. The change in absorbancy with time at 410 mμ parallels within a few per cent the disappearance of active methyl groups (Figure 1), indicating the change in absorbancy is directly related to product formation.

The rapid deviation from simple pseudo-first-order behavior as significant product formation occurs could have several possible causes, and the possibility of each cause and its effect was investigated in independent experiments.

The initial rate treatment demonstrated that both CH_3MgBr and $(CH_3)_2Mg$ react with 2-methylbenzophenone. The relative concentrations of CH_3MgBr and $(CH_3)_2Mg$ in the Grignard solution and the reaction rates of each with ketone are such that the reaction proceeds almost equally through both paths (40–55% *via* $(CH_3)_2Mg$ over the ketone concentration used). Thus, significant amounts of the product, $ROMgCH_3$, produced by the reaction of ketone with dimethylmagnesium must be formed.

If $ROMgCH_3$ undergoes little or no redistribution with $MgBr_2$, two effects would occur as the reaction proceeds, causing deviation from simple pseudo-first-order behavior. First, the reaction of $(CH_3)_2Mg$ with ketone would result in the buildup of $MgBr_2$ *via* the Schlenk equilibrium, thus decreasing the concentration of $(CH_3)_2Mg$ and thereby slowing down the reaction. Second, the methyl groups bonded to magnesium as CH_3MgOR would be relatively unreactive compared to $(CH_3)_2Mg$, thus slowing down the reaction.

The reaction product of the addition of dimethylmagnesium to 2-methylbenzophenone, $ROMgCH_3$, is a dimer in diethyl ether solution.[14] The reaction product of the addition of methylmagnesium bromide to 2-methylbenzophenone, ROMgBr, is also a dimer in diethyl ether solution (C = 0.041 m, i = 2.10; C = 0.072 m, i = 2.07).[24]

The exchange of $ROMgCH_3$ with $MgBr_2$ was investigated in several experiments. $ROMgCH_3$ was prepared by the reaction of dimethylmagnesium with 2-methylbenzophenone in a 1:1 ratio in diethyl ether. ROMgBr was prepared by the reaction of methylmagnesium bromide with 2-methylbenzophenone in diethyl ether. The following three experiments were carried out.

(1) Solutions of $ROMgCH_3$ were injected into solutions of excess 2-methylbenzophenone and the reaction was followed by noting the change in absorbancy at 410 mμ with time. This reaction was found to proceed in exactly the same fashion as the reaction in which $ROMgCH_3$ was produced *in situ* by the reaction of $(CH_3)_2Mg$ with 2-methylbenzophenone.[14]

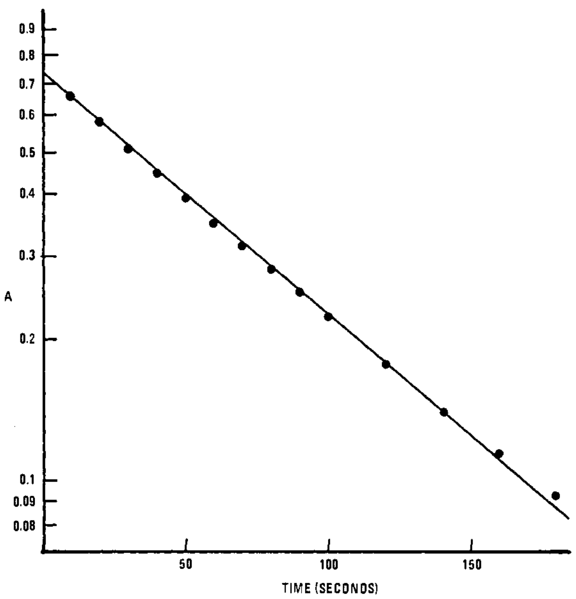

Figure 3. Uncorrected plot for the reaction of 0.905 *M* 2-methylbenzophenone with 0.0124 *M* methylmagnesium bromide in the presence of 0.0252 *M* magnesium bromide.

(2) Solutions of $ROMgCH_3$ were rapidly injected into solutions of $MgBr_2$ and excess 2-methylbenzophenone at several ketone concentrations. The concentration of $MgBr_2$ in these experiments was such that the initial ratio of $ROMgCH_3$ to $MgBr_2$ was 1:1. The reactions were followed by noting the change in absorbancy at 410 mμ with time.

(3) Solutions of methylmagnesium bromide were rapidly injected into solutions of ROMgBr and excess 2-methylbenzophenone at several ketone concentrations. The concentration of ROMgBr in these experiments was such that the initial ratio of Grignard reagent to ROMgBr was 1:1. The reactions were followed by noting the change of absorbancy at 410 mμ with time. A set of experiments at a particular ketone concentration is illustrated in Figure 4.

The reaction of $ROMgCH_3$ with excess 2-methylbenzophenone in the presence of $MgBr_2$ (equal molar to that of the added $ROMgCH_3$) occurs at a much faster rate than does the reaction of $ROMgCH_3$ with no added $MgBr_2$. In fact, the rate is identical within the limits of the experiments with the rate of the reaction of methylmagnesium bromide + ROMgBr with the same concentration of ketone. In addition, the initial absorbance characteristic of $ROMgCH_3$ in ketone solution is much higher than the initial absorbance of $ROMgCH_3$ + $MgBr_2$ in the presence of excess ketone, the latter absorbance being about the same as the initial absorbance of methylmagnesium bromide + ROMgBr in the presence of the same concentration of ketone.

Typical results illustrated in Figure 4 indicate that $MgBr_2$ rapidly exchanges with $ROMgCH_3$ to produce an equilibrium (eq 19) which lies very far, if not completely, to the right. The rate of exchange of $MgBr_2$ with $ROMgCH_3$ is immediate on the time scale of reac-

$$ROMgCH_3 + MgBr_2 \rightleftarrows ROMgBr + CH_3MgBr \qquad (19)$$

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[24] E. C. Ashby and J. Nackashi, unpublished data.

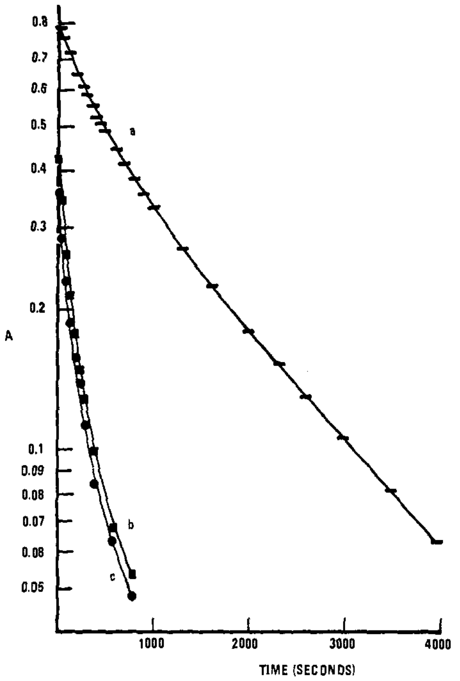


Figure 4. Reaction of 0.460 *M* 2-methylbenzophenone with (a) 0.0124 *M* $ROMgCH_3$, (b) 0.0124 *M* $ROMgCH_3$ and 0.0124 *M* $MgBr_2$, and (c) 0.0101 *M* methylmagnesium bromide and 0.0102 *M* ROMgBr.

tion of active methyl groups with ketone. Nmr experiments confirm that the reaction of $ROMgCH_3$ and $MgBr_2$ is rapid and that the equilibrium 19 lies completely to the right.[24] Mixtures of $MgBr_2$ and $ROMgCH_3$ and mixtures of ROMgBr and methylmagnesium bromide gave identical nmr spectra both at room and low temperature (−80°). The spectra are much different than those of $ROMgCH_3$ and methylmagnesium bromide.[24]

In order to confirm that the reaction of $ROMgCH_3$ with $MgBr_2$ does indeed take place and that the reaction of $ROMgCH_3$ with ketone was not somehow catalyzed by the presence of $MgBr_2$, two experiments were carried out in which $ROMgCH_3 + 0.5\ MgBr_2$ was allowed to react with excess 2-methylbenzophenone. In these experiments, the absorbancy at 410 mμ rapidly disappeared until about one-half the initial absorbancy had been reached, and thereafter declined very slowly. The conclusion is that the $MgBr_2$ exchanged completely with half of the $ROMgCH_3$, producing Grignard reagent which then rapidly added to ketone, leaving the remaining $ROMgCH_3$ to react very slowly with ketone. Magnesium bromide, then, does not catalyze a rapid addition of $ROMgCH_3$ to ketone but produces Grignard reagent by eq 19.

As noted before, ROMgBr and $ROMgCH_3$ are initially formed in almost equal amounts. It was possible that these species might react to form a mixed dimer, $ROMgCH_3 \cdot ROMgBr$. If this species did not exchange with $MgBr_2$, the deviation from pseudo-first-order kinetics would occur as $ROMgCH_3 \cdot ROMgBr$ and $MgBr_2$ build up in the reacting solution, for reasons previously stated. The species $ROMgCH_3 \cdot ROMgBr$ was prepared by the addition of $ROMgCH_3$ to ROMgBr in a 1:1 ratio and solutions were injected into solutions of excess 2-methylbenzophenone in diethyl ether. The behavior of this species was different from that of $ROMgCH_3$ itself, indicating the formation of $ROMgCH_3 \cdot ROMgBr$ had occurred. Its reaction with ketone was, like $ROMgCH_3$, very slow. Solutions of mixed dimer were injected into solutions of 2-methylbenzophenone and $MgBr_2$ in diethyl ether. The reaction with ketone occurred rapidly with a rate characteristic of the reaction of ketone with Grignard reagent in the presence of ROMgBr, showing that $ROMgCH_3 \cdot ROMgBr$ rapidly and completely redistributes with $MgBr_2$. Therefore, $ROMgCH_3 \cdot ROMgBr$ has no significant existence in reacting solutions of the Grignard reagent with the ketone.

Since exchange studies involving magnesium bromide with all possible products arising from the reaction of ketone with $(CH_3)_2Mg$, *i.e.*, $ROMgCH_3$ and $ROMgCH_3 \cdot ROMgBr$, show that these species have but fleeting existence in the Grignard reaction, the complicated features of the latter portion of the reaction must be caused by the interaction of the final product, ROMgBr, with the species CH_3MgBr, $(CH_3)_2Mg$ and $MgBr_2$, and their respective ketone complexes.

In order to facilitate presentation of the features of the latter portion of the reaction, two assumptions will be made. The first assumption is that the ratio $CH_3MgBr:(CH_3)_2Mg:MgBr_2$ remains constant throughout the reaction. Thus, the fractions of the reaction proceeding through $(CH_3)_2Mg$ and CH_3MgBr remain the same. This assumption is reasonable since exchange experiments involving $MgBr_2$ with all possible products arising from $(CH_3)_2Mg$ show rapid redistribution to ROMgBr and CH_3MgBr. Thus, no buildup of $MgBr_2$ or depletion of $(CH_3)_2Mg$ occurs, and the Schlenk equilibrium is not affected by reaction of Grignard reagent with ketone. The second assumption is that the interaction of ROMgBr with Grignard reagent can be considered to be predominantly the interaction of ROMgBr with CH_3MgBr. No evidence was found that indicates that ROMgBr interacts preferentially with any single species, *i.e.*, CH_3MgBr, $(CH_3)_2Mg$, and $MgBr_2$. Since CH_3MgBr comprises better than 92% of the species present in a solution of methylmagnesium bromide, this assumption is quite reasonable.

The complicated features of the later stages of reaction are due to the fact that ROMgBr ties up reactive methyl groups in a less reactive form. Association studies of the product arising from the reaction of methylmagnesium bromide with 2-methylbenzophenone (ROMgBr) show this species to be dimeric.[24] The effect of added initial ROMgBr on the reaction of methylmagnesium bromide with 2-methylbenzophenone was investigated in several experiments. Solutions of methylmagnesium bromide were rapidly injected into diethyl ether solutions of ketone containing added ROMgBr. The reactions were followed by noting the change in absorbance at 410 mμ with time. The rate of the reaction of methylmagnesium bromide with ketone is drastically reduced by the addition of product. As larger amounts of initial product are added, the reaction rate continues to decrease. The magnitude of the decrease in rate with added product becomes small when the initial ratio of product to Grignard reagent is 3:1 or greater (Figure 5). Plots of log *A* *vs.* *t* continue to show curvature regardless of how large

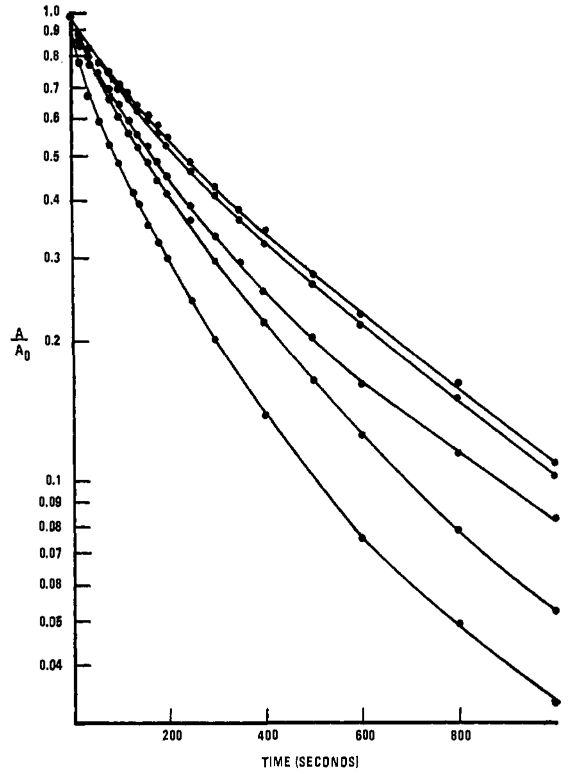


Figure 5. Reaction of 0.460 *M* 2-methylbenzophenone with 0.0101 *M* methylmagnesium bromide in the presence of added reaction product. Normalized curves from top to bottom are for initial concentrations of product equal to 0.183, 0.0465, 0.0204, 0.0102 *M*, and no added product.

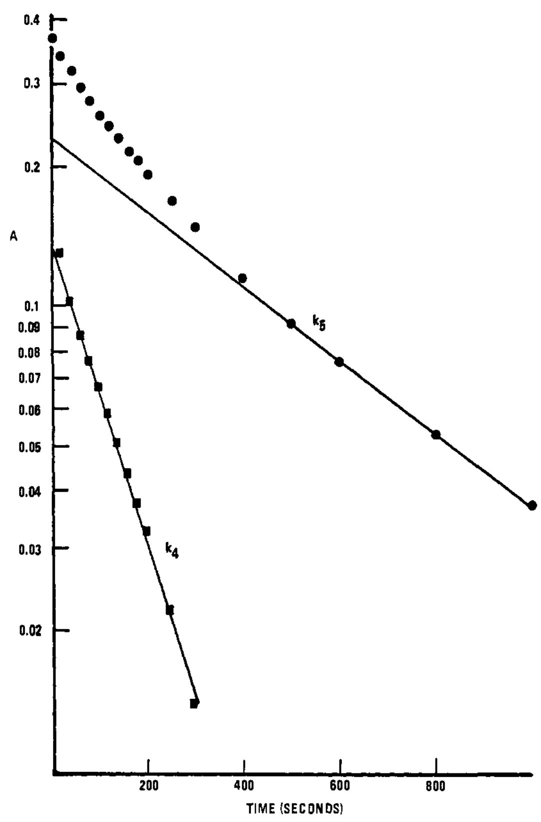


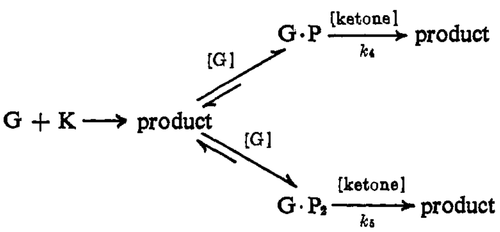
Figure 6. Reaction of 0.460 *M* 2-methylbenzophenone with 0.0101 *M* methylmagnesium bromide in the presence of initial 0.0306 *M* ROMgBr, demonstrating the resolution of k_4 and k_5.

Table V. Reaction of 0.0101 *M* Methylmagnesium Bromide with 0.46 *M* 2-Methylbenzophenone in the Presence of Added ROMgBr

[ROMgBr], *M*	k_4, sec^{-1}	Intercept-4	k_5, sec^{-1}	Intercept-5
0.0			0.00202[a]	
0.0102			0.00206[a]	
0.0204			0.00169[a]	
0.0306	0.00766	0.140	0.00183[b]	0.231
0.0465	0.00686	0.120	0.00181[b]	0.230
0.100	0.00786	0.115	0.00188[b]	0.298
0.183	0.00772	0.090	0.00192[b]	0.304

[a] Taken from final two points. [b] Linear for greater than a half-life.

the amount of added product is. All plots have a common feature; however, the final slope is the same regardless of whether no ROMgBr is added or a large initial amount of ROMgBr is added (Figure 5). This suggests that the final reactive species is the same in all cases. In addition, at ROMgBr to Grignard reagent ratios greater than or equal to 3:1, a significant portion of the latter part of the reaction is linear, suggesting independent concurrent pseudo-first-order reactions



(20)

where G = Grignard, G·P = $CH_3MgBr\cdot ROMgBr$, and $G\cdot P_2$ = $CH_3MgBr\cdot 2ROMgBr$. An observed first-order rate constant, k_5, could be extracted from the late portion of each reaction. In those cases where the ratio of ROMgBr to methylmagnesium bromide was 3:1 or greater, the line defining k_5 lies on experimental points near the end of the reaction for greater than a half-life and could be extrapolated to zero time with confidence. The value of this line at the appropriate times was substracted from those absorbances which fell above the line defined by k_5. Plots of log (A − extrapolated line) *vs.* t resolved into a second first-order component, k_4 (Figure 6). The results of these experiments are given in Table V. In those cases in which the ratio of initial ROMgBr to methylmagnesium bromide was less than 3:1, plots of log A *vs.* t gave no final linear portions; however, a line was drawn through the last two points, and a value of k_5 computed from its slope. These values are also listed in Table V. The following observations are consistent with the data. The product, ROMgBr, ties up Grignard reagent very strongly but not completely except where the amount of ROMgBr is in large excess over the Grignard reagent. This condition occurs in those reactions with no added product near the final portion when a large amount of ROMgBr has formed. This condition is also present to an even greater extent in those experiments in which the initial ratio of ROMgBr to methylmagnesium bromide is 3:1 or greater. The reaction slows down drastically with the initial additions of product due to the fact that free Grignard reagent is being removed from the system. As product accumulates in the sys-

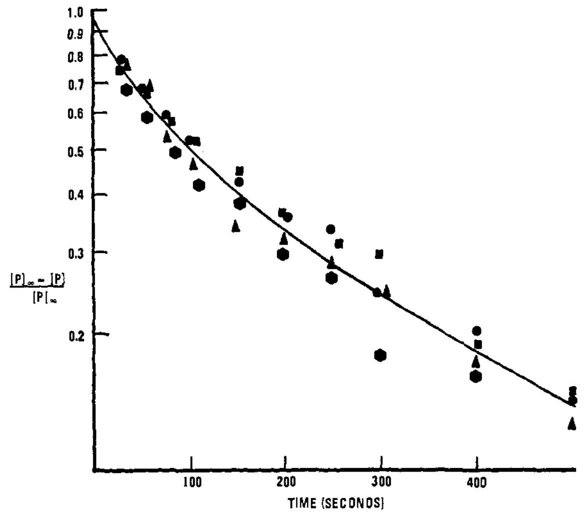
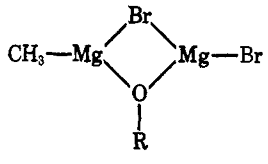
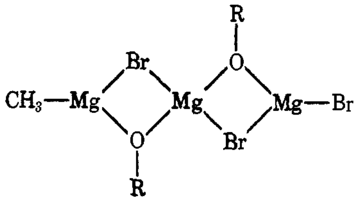


Figure 7. Disappearance of active methyl groups from quenching experiments using 0.45 *M* 2-methylbenzophenone with methylmagnesium bromide. Normalized curve represents Grignard concentrations of (circles) 0.0263 *M*, (squares) 0.0127 *M*, (triangles) 0.00572 *M*, and (hexagons) 0.00212 *M*.

tem either through initial additions or by reactions, two species are formed, G·P, whose rate of reaction is defined by rate constant k_4, and G·P_2, whose rate of reaction is defined by rate constant k_5. When the condition is reached in which no free Grignard reagent remains, G·P and G·P_2 are not interconvertible with one another and react independently with ketone (Figure 6). Reasonable structures for G·P and G·P_2 are given below. The structure suggested for G·P is similar to structures already known in organoaluminum systems.[25] The structure suggested for G·P_2 arises from the interaction of Grignard reagent with a molecule of ROMgBr dimer. It has two strong oxygen bridge bonds and would be expected to have significant stability. It should be noted that G·P_2 uses all possible oxygen bridges and no further alkoxy bridging is available for further interaction with Grignard reagent. As was mentioned earlier the interaction of product with Grignard reagent to form a new species (possibly G·P and G·P_2) was demonstrated by low-temperature nmr analysis.


(G·P)


(G·P_2)

The fact that the reaction continues to slow up upon continued addition of ROMgBr beyond the point where all free methylmagnesium bromide is removed is due to the relative amounts of G·P and G·P_2. As larger and larger amounts of initial ROMgBr are added to the reaction, the relative concentration of the slower reacting species, G·P_2, is greater as would be expected. The intercepts for G·P and G·P_2 (Table V) are directly proportional to their concentrations in solution. The final reactive form of methylmagnesium bromide, regardless of whether or not initial ROMgBr was added, is G·P_2.

It should be noted that the reaction scheme outlined implies that G·P and G·P_2 form complexes with ketone with equilibrium constants and extinction coefficients the same as those for free Grignard reagent. Two facts indicate that this is true. First, in those experiments in which large amounts of ROMgBr were added, the initial absorbance remained the same for all concentrations of ROMgBr and was the same as the experiment with no added ROMgBr. Thus, although the reactive species changed, the initial absorbance did not. Secondly, the close correspondence between the decrease in absorbance and the decrease in active methyl groups (Figure 1) suggests that the absorbance is very nearly directly related to the concentration of active methyl groups throughout the course of the reaction.

Several experiments were carried out in which the concentration of 2-methylbenzophenone was held constant and the concentration of initial Grignard reagent was varied. A set of reactions was carried out over a threefold range of concentration of Grignard reagent and the disappearance of complex was observed (Table I). In addition, a set of reactions was carried out over a tenfold range of concentration of Grignard reagent at constant ketone concentration and the disappearance of active methyl groups was recorded by glpc analysis. The data from both sets of experiments were normalized by adjusting the initial value from each experiments to 1. The total reaction rates for all experiments were compared by constructing plots of log A/A_0 *vs.* *t* or plots of log $\{([P]_\infty - [P])/[P]_\infty\}$ *vs.* *t* for all runs on a single graph. It was found that the normalized curves of both sets of experiments were identical, showing that the reaction rate, expressed in terms of fraction reacted, is independent of the initial concentration of Grignard reagent. The normalized data for the set of experiments where the disappearance of active methyl groups was followed by glpc analysis are illustrated in Figure 7.

The fact that the reaction rate in excess ketone is independent of the initial methylmagnesium bromide concentration is consistent with the reaction scheme outlined. The product, ROMgBr, complexes methylmagnesium bromide very tightly. If the equilibria $2G + P_2 \rightleftarrows 2G\cdot P$ and $G + P_2 \rightleftarrows G\cdot P_2$ did not lie very far to the right, a significant rate enhancement would have been seen in the normalized curves of Figure 7 at the lower Grignard concentrations, due to the fact that the percentage of free methylmagnesium bromide would be significantly larger. Consistent with this conclusion is an association study of an equimolar mixture of ROMgBr and methylmagnesium bromide. The following values were obtained calculating the species ROMgBr·CH_3MgBr as monomer: C = 0.040 m, i = 0.696; C = 0.0711 m, i = 0.746; C = 0.0951 m, i = 0.763; C = 0.119 m, i = 0.766. It should be noted that the i values are less than one indicating some dissociation of the product–Grignard reagent complex in the 1:1 ratio. The i values do not change with concentration within experimental error, showing that the equilibrium involving methylmagnesium bromide and ROMgBr lies very far to the right.

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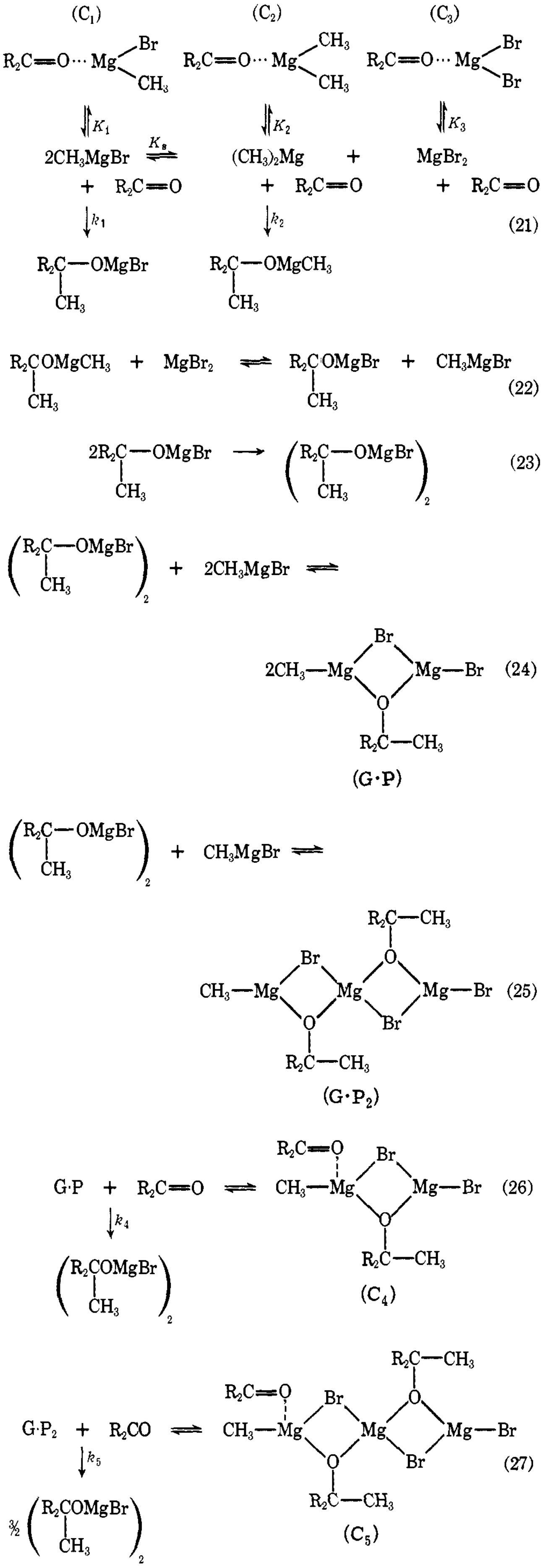
(25) (a) E. C. Ashby, J. Laemmle, and G. E. Parris, *J. Organometal. Chem.*, **19**, P24 (1969); (b) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, 23, 715 (1970).

Scheme II



Thus, the shapes of the rate curves found when ROMgBr is added to the reaction mixtures, the fact that the fractional reaction rate is independent of the initial concentration of Grignard reagent, and the association data are all consistent with the view that ROMgBr complexes methylmagnesium bromide and that the equilibria involved lie very far toward the complex for low ROMgBr to Grignard reagent ratios and completely toward the complex at high ROMgBr to methylmagnesium bromide ratios.

Plots of the reaction of methylmagnesium bromide with 2-methylbenzophenone in the presence of added $MgBr_2$ were found to be linear for a large excess of $MgBr_2$ (Figure 3). The linearity was attributed to the fact that the Schlenk equilibrium had been driven completely to CH_3MgBr. A second feature is important in causing linearity. It has been pointed out that $MgBr_2$ formed an insoluble compound with ROMgBr. When the concentration of added $MgBr_2$ is equal to 200% of the initial Grignard reagent concentration, the ROMgBr formed is completely removed by $MgBr_2$ and is no longer available to tie up CH_3MgBr. Thus, the removal of ROMgBr prevents the complication normally seen in the Grignard reagent.

The equations in Scheme II show in detail the mechanism by which methylmagnesium bromide is thought to react with 2-methylbenzophenone. The reactions are depicted as occurring through bimolecular collision rather than through rearrangement of complexes although the two possibilities are kinetically indistinguishable.

There is no intention here to propose that this mechanism is the only reaction path for all Grignard reagent additions to all ketones in all possible polar solvents. Indeed, recent reports by Fauvarque[26] indicate that in HMPA considerable free ketyl is observed in the reaction of dibenzylmagnesium with fluorenone whereas in diethyl ether only a trace of ketyl is observed. In addition, Holm[27] has recently reported that the reaction of *tert*-butylmagnesium chloride with substituted benzophenones produces considerable amount of 1,2-, 1,4- and 1,6-addition product in addition to benzopinacols, indicating a ketyl intermediate. Thus, an emerging pattern at this time seems to be that free ketyl formation increases with an increase in polarity of the solvent, a decrease in the reduction potential of the ketone and an increase in the stability of the free radical produced in the single electron transfer. Although a free ketyl is not involved to a noticeable extent in the reaction of methylmagnesium bromide with 2-methylbenzophenone, there is no way of knowing from our data or the data of others the exact nature of the alkyl transfer. Indeed, a single electron transfer *via* a solvent caged intermediate or carbanion transfer *via* a polar intermediate are both possible. More work will be required to determine the exact nature of the alkyl transfer.

General Conclusions

The total mechanism written above satisfies the major observations, namely: all absorbancy data, the detailed treatment of the initial rates, those experiments with added $MgBr_2$, the exchange experiments involving products arising from $(CH_3)_2Mg$ and ketone with

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[26] J. F. Fauvarque and E. Rouget, *C. R. Acad. Sci., Ser. C*, 267, 1355 (1968).

[27] T. Holm and I. Crossland, *Acta Chem. Scand.*, 25, 59 (1971).

$MgBr_2$, the experiments involving a large excess of product, ROMgBr, with the resolution of k_4 and k_5, the independence of the total rate behavior on initial Grignard reagent concentration at constant excess ketone concentration, and the association data. Nowhere are additional parameters, *e.g.*, salt effects, required to fit the data to a particular mechanism. All conclusions are drawn from fundamental values, *i.e.*, measured equilibrium constants and measured rates.

It should be emphasized that all of the steps represented by eq 21–27 are important in describing the reaction of methylmagnesium bromide with excess 2-methylbenzophenone. The same mechanistic steps hold for the reaction in excess Grignard reagent except that the steps after eq 21 become relatively unimportant. This is due to the fact that the concentrations and reactivity of $ROMgCH_3$, G·P, and $G \cdot P_2$ are relatively low compared to $(CH_3)_2Mg$ and CH_3MgBr and, therefore, the reaction proceeds mainly by the sequence described by eq 21. When the Grignard to ketone ratio is the same or nearly the same, it is clear that the steps described by eq 22–27 once again become important.

Chemistry of Atomic Silicon. III. Reactions of Electron Bombardment Produced Silicon Vapor with Silanes

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Abstract: Silicon atoms were found to react with trimethylsilane, dimethylsilane, methylsilane, and disilane exclusively by insertion into silicon–hydrogen bonds. The resulting silenes inserted into a silicon–hydrogen bond of another substrate molecule, or polymerized to form linear and cyclic polysilanes. The electron bombardment of solid-phase silanes at 77°K gave products derived from silene intermediates.

The fact that compounds containing silicon–hydrogen bonds are notably good trapping agents for carbenes,[1] carbon atoms,[2] and silenes[3] made this class of substrates a logical choice for a study of silicon atom reactions. The cocondensation of thermally produced silicon vapor with trimethylsilane has previously been reported.[4] Reactions of recoil silicon atoms produced by the nuclear transformation $^{31}P(n,p)^{31}Si$ with silane[5,6] and by the transformation $^{30}Si(n,\gamma)^{31}Si$ with silane[7] and with silane, disilane, and trisilane[8] have also been reported.

Experimental Section

The apparatus and procedure used was basically the same as that described for the study of carbon atom reactions.[9] Reactions were carried out by simultaneously depositing silicon vapor and a large excess of substrate on the liquid nitrogen cooled walls of an evacuated ($<1 \times 10^{-4}$ Torr) reaction flask. Silicon vapor was produced by electron bombardment heating of a silicon electrode to its melting point using a Varian 4000-V electron gun. Gaseous substrates were introduced into the system by means of a perforated glass inlet bulb, designed to produce an even layer of coverage in the zone of silicon deposition. Reactions occurred in the condensed phase at the walls of the system, either at ~77°K, or upon warm-up.

In a typical reaction, 20–30 mg of silicon and ~10 g of substrat were continuously deposited over a period of about 1 hr. The reaction flask was then warmed to room temperature and the volatile contents were transferred to a standard vacuum line for work-up. Noncondensible gases produced both during the codeposition and during warm-up were collected *via* a Toeppler pump and analyzed by vpc. Products were separated by trap to trap fractionations and vapor-phase chromatography, and identified by comparison of their infrared, nmr, and mass spectra with authentic samples or with literature spectra. The identification of products for which no spectra could be found in the literature are presented below.

Blank reactions were run by depositing the substrates on the flask walls with the electron gun turned on, but with no silicon source material present. The reaction and work-up conditions of the corresponding reactions were duplicated as closely as possible in the blanks.

Yields of silicon atom products reported were based on millimoles of product divided by millimoles of silicon vapor reaching the walls of the system.

Trimethylsilane was purchased from Peninsular Chemical Research and used without further purification. Dimethylsilane and methylsilane were synthesized by the reduction of dimethyldichlorosilane and methyldichlorosilane, respectively, with lithium aluminum hydride. Disilane was synthesized by the lithium aluminum hydride reduction of hexachlorodisilane.

Identification of Products. 1,1,3,3-Tetramethyltrisilane was identified by its 70-eV mass spectrum (parent ion at *m/e* 148 (6.7%), base peak at *m/e* 88), vapor infrared spectrum (10-mm cell; C–H (3000 cm^{-1}), SiH (~2120 cm^{-1}), Si–CH_3 (~1255 cm^{-1}), no absorptions in the Si–O or $SiCH_2Si$ regions (1200–950 cm^{-1})), and nmr spectrum in benzene (Table I).

Table I. The 60-Mc Nmr Spectrum of 1,1,3,3-Tetramethylsilane

Resonance	Chemical shift,[a] τ	Rel area	*J*, cps
$-CH_3$ (doublet)	9.73	6.17	~4
$-Me_2Si-H$ (multiplet)	5.87	1.03	
$-SiH_2-$ (triplet)	6.02	1.00	~4

[a] Referred to the benzene solvent absorption at τ 2.72.

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