dehydration. Alternatively, some of these enzymes may catalyze the dehydration of their aldehyde substrates.

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Kinetics of the Addition of Grignard Reagents to Ketones. The Addition of Methylmagnesium Bromide to 2,4-Dimethyl-4′-methylmercaptobenzophenone[1]

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Abstract: The rate of addition of methylmagnesium bromide to 2,4-dimethyl-4′-methylmercaptobenzophenone in diethyl ether at 25.0° has been measured for Grignard concentrations from 0.04 to 1.5 *M*. The ultraviolet spectrum of reacting solutions has been interpreted in terms of a complex in equilibrium with the Grignard reagent and ketone which gives rise to the formation of addition products.

Because of wide applicability in synthesis, the reactions of Grignard reagents have received extensive study.[3] An understanding of the mechanism of, *e.g.*, the addition of Grignard reagents to ketones depends in part on knowledge of the nature of the Grignard reagent as well as the composition of the transition state and potential intermediates.[4,5]

Recent magnesium exchange data,[6,7] X-ray studies,[8] and molecular weight determinations[9] on various Grignard reagents in ether have been interpreted in terms of a monomeric reagent, RMgX, at low concentrations[9] (<0.1 *M*). Attributing all deviations of observed molecular weights[9] in ether from theoretical values to association suggests[9d-f] that dimerization becomes important at concentrations above *ca.* 0.1 *M*,[9d-f] the extent of association being a function of the specific reagent. Measurements of Smith and Becker[10] of the heat of reaction (3.6 kcal/mole) of diethylmagnesium with magnesium bromide were interpreted[10] as indicating that, for this reagent in ether, equilibrium strongly favors the formation of the Grignard, EtMgBr, at 0.1 *M*.

Most of the various species conceivably present in an ether solution of a Grignard reagent have been implicated in many of the diverse[3,9d,11-13] proposals which have been made for the mechanism of the addition reaction with ketones. For example, Becker[12] has recently formulated the reaction as proceeding by way of a low concentration of a 1:1 complex between ketone and dimeric methylmagnesium bromide, based on an initial rate which is first order in benzophenone and first order in methylmagnesium bromide in tetrahydrofuran. It was suggested[12] that the complex rearranged to form product in a rate-determining step. Similar mechanisms have been suggested by Mosher[13] and others[3] in ether solvent.

To explain the reported observation that the reaction of methylmagnesium iodide with acetone is zero order in ketone,[14] the high reactivity of dialkylmagnesium compounds, as well as the tendency of magnesium halides to decrease reaction rates,[12] House[15] has suggested that the addition reaction occurs by way of a 1:1 complex between the ketone and the dialkylmagnesium in equilibrium with the Grignard reagent in ether.

In a modification of Swain's[16] early suggestion, Ashby[9c] has suggested that the monomeric reagent, RMgX, is involved. His proposed mechanism employs a rate-determining attack of ketone on monomeric Grignard displacing an ether of solvation followed by rapid reaction with a second monomeric Grignard forming a complex which rearranges to product. Reaction by way of dissociated Grignard species has also been suggested by Ashby.[9d]

In a previous communication[5] we reported spectroscopic[4] and kinetic studies in support of the addition mechanism (eq 1) involving rapid complex formation

$$\text{ketone} + \text{Grignard} \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k} \text{product} \qquad (1)$$

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(1) Research supported by a grant from the National Science Foundation.

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(9) (a) W. Slough and A. R. Ubbelohde, *J. Chem. Soc.*, 108 (1955); (b) A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963); (c) E. C. Ashby and W. E. Becerk, *J. Am. Chem. Soc.*, **85**, 118 (1963); (d) E. C. Ashby and M. B. Smith, *ibid.*, **86**, 4363 (1964); (e) E. C. Ashby, *ibid.*, **87**, 2509 (1965); (f) H. Hashimoto, T. Nakano, and H. Okada, *J. Org. Chem.*, **30**, 1234 (1965).

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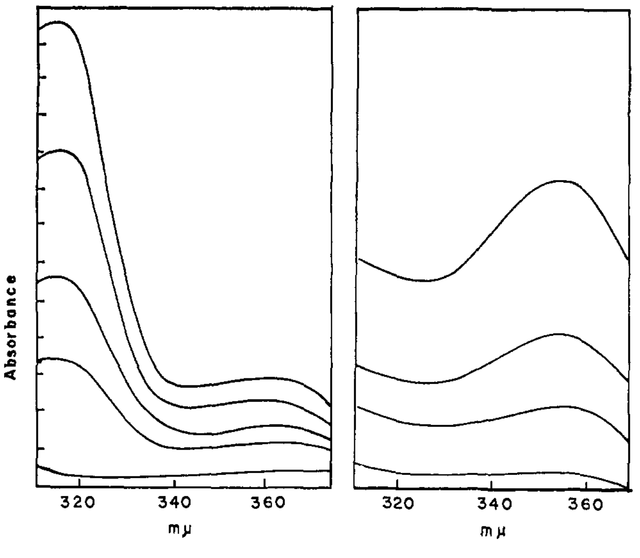
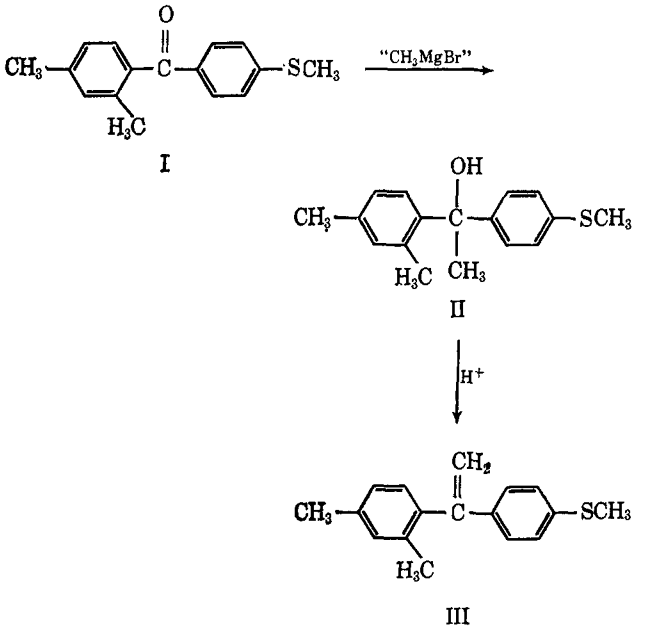


Figure 1. Absorbance of *ca.* 10^{-4} *M* ketone I in ether solutions of methylmagnesium bromide. Curve A was obtained with 0.055 *M* Grignard; curve B was measured in a solution 1.5 *M* in Grignard. The additional scans of each solution were made a few minutes apart.

followed by a relatively slow first-order step to yield the product. For the addition reaction of 2,4-dimethyl-4′-methylmercaptobenzophenone (I) with methylmagnesium bromide in ether at 25.0°, it was shown that this scheme is consistent with kinetic data at methylmagnesium bromide concentrations up to 0.34 *M* with an equilibrium constant, *K*, of 6.2 l./mole and a rate constant, *k*, of 1.1 × 10^{-2} sec^{-1}. This paper provides additional observations on this system and extends the concentration range to 1.5 *M* methylmagnesium bromide.



Results

The Grignard Reagent. The Grignard solutions used in these studies were prepared on a vacuum line. All apparatus was dried at reduced pressure and then filled with dry argon. The magnesium was Dow[17] single sublimed. Ordinary "Grignard Grade" magnesium and single sublimed magnesium which was resublimed gave results indistinguishable from those obtained with single sublimed metal except that solutions made from "Grignard Grade" turnings were not absolutely colorless. The ether used to prepare the reagents was distilled on the sealed line from a degassed preparation of methylmagnesium bromide.

The Grignard reagent used in kinetic and spectral studies was prepared by slowly distilling a weighed quantity of methyl bromide into a cooled and stirred mixture of a *ca.* twofold excess of magnesium in ether. After the reaction was completed ether was distilled into the reagent to make the desired final concentration. After two filtrations through fritted glass filters, aliquots were transferred to tared, sealed ampoules, ultraviolet cells, and calibrated pycnometers.

Ampoules were analyzed for Grignard content by three methods. To some samples a known amount of a standard solution of iodine in benzene was injected. The tube was then opened and the excess iodine titrated by standard procedures. Other aliquots were hydrolyzed and titrated for total base and halide content. Results for typical solutions are given in Table I. The densities required were calculated from measured weights, volumes, and titers. Samples retained constancy of titer to within 2% over 3 days at 25.0°. In general, the bromide titer tended to be larger than the total base or iodine titer by *ca.* 3%, indicating some coupling.

Table I. Typical Analyses for Methylmagnesium Bromide Preparations in Diethyl Ether

I_2 titration, *M*	Total base, *M*	Total bromide, *M*
0.062	0.073	0.074
0.118	0.130	0.150
0.192	0.207	0.222
0.223	0.222	0.246
0.255	0.248	0.273
0.323	0.328	0.331
0.50	0.51	0.51
0.60	0.62	0.62
0.91	0.95	0.96
0.98	1.04	1.10
1.02	1.20	1.20
1.15	1.18	1.23
1.22	1.27	1.26

Products. The products were investigated by adding a small amount of the ketone I to a 1 *M* solution of methylmagnesium bromide. Work-up with sulfuric acid followed by dehydration in benzene with *p*-toluenesulfonic acid gave the corresponding olefin III, mp 56–57°, in 98% yield.

Spectroscopy. 2,4-Dimethyl-4′-methylmercaptobenzophenone (I) displays a strong absorbance with λ_{max} 315 mμ (ϵ 2.5 × 10^4) in diethyl ether at 25.0°. When methylmagnesium bromide is added to the ether an additional band, λ_{max} 355 mμ, is produced with concurrent decrease in absorbance at 315 mμ (Figure 1). The Grignard reagent is essentially transparent in this region under the conditions employed. At methyl-

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(17) We are indebted to the Dow Chemical Co. for supplying the magnesium used in these experiments.

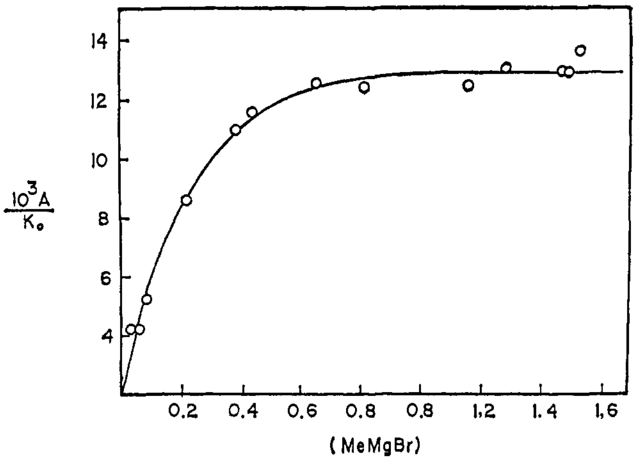

Figure 2. Plot of absorbance at 355 mμ divided by initial ketone concentration *vs.* concentration of methylmagnesium bromide in diethyl ether at 25.0°.

magnesium bromide concentrations of 1 to 1.5 *M*, the spectrum of *ca.* 6 × 10^{-5} *M* ketone I consists of a broad flat absorbance in the region of the ketone maximum with the new maximum at 355 mμ (Figure 1). The appearance of a new absorbance at a higher wavelength was previously[4] observed for 2,4,6-triisopropyl-4′-methoxybenzophenone and ascribed to a 1:1 complex between the ketone and Grignard reagent.

Since ketone I reacts with methylmagnesium bromide, the spectrum rapidly decays to the solvent base line. Several scans are illustrated in Figure 1. Analysis is facilitated by reconstructing the spectrum to correspond to zero reaction. This was accomplished by rapidly adding the ketone in ether solution to the Grignard reagent with a calibrated syringe at a specified time, t_0, placing the cell in the spectrometer, and scanning the desired region at a known rate several times. The time at the start of each scan was recorded, making it possible to construct a first-order rate plot for any desired wavelength. Extrapolation of the data back to t_0 gives the absorbance at various wavelengths at zero reaction. Typical data are summarized in Table II. A plot of absorbance of the complex divided by the initial ketone concentration for a 1-cm path length cell (the apparent ε of the complex) *vs.* concentration of the Grignard reagent is given in Figure 2. These data indicate that at 355 mμ the complex has an extinction coefficient of *ca.* 1.3 × 10^4.

Table II. Initial Absorbance at 355 mμ of Ketone I for Various Concentrations of Methylmagnesium Bromide in Ether at 25.0°

Initial ketone, $10^5 M$	MeMgBr,[a] *M*	Initial *A* (355 mμ)
5.86	0.040	0.251
6.17	0.055	0.270
6.16	0.092	0.331
6.36	0.215	0.540
5.95	0.396	0.650
6.89	0.447	0.794
6.58	0.69	0.810
6.57	0.82	0.804
6.10	1.12	0.768
5.90	1.25	0.770
6.26	1.47	0.813
6.69	1.48	0.852
6.44	1.51	0.852

[a] Base titrations.

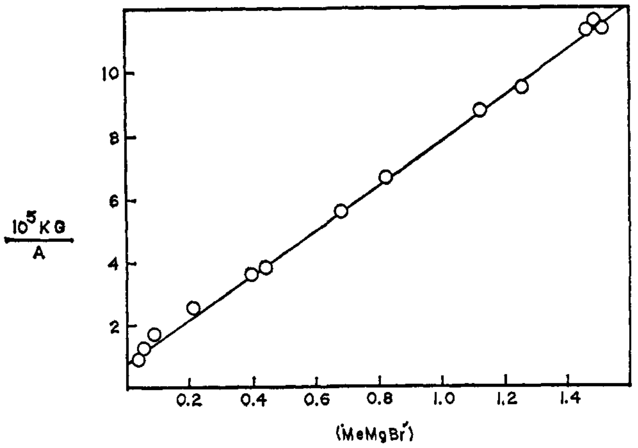

Figure 3. Scott plot, eq 2, for the absorbance of ketone I at 355 mμ in ether solutions of methylmagnesium bromide at 25.0°.

$$\frac{(\text{ketone})(\text{Grignard})l}{A} = \frac{1}{K\epsilon} + \frac{1}{\epsilon}(\text{Grignard}) \qquad (2)$$

An approximate value for an apparent equilibrium constant may be estimated from these data by application of the Scott[18] procedures (eq 2), where (ketone) and (Grignard) are initial concentrations, *l* is the path length, *A* is the observed absorbance of the complex at 355 mμ, ε is the extinction coefficient of the complex, and *K* is the equilibrium constant for complex formation. For an *l* of 1 cm, plotting the left side of eq 2 *vs.* the concentration of the Grignard reagent gives a slope of 1/ε and an intercept of 1/*K*ε. Such a plot is illustrated in Figure 3. The least-squares intercept and slope correspond to an equilibrium constant, *K*, of 8.4 l./mole and an ε for the complex of 1.4 × 10^4. It should be emphasized that since the slope and intercept of the Scott plot are very sensitive to errors in measurement,[19] such as are encountered in our procedures because of the reactivity of the system, derived values of *K* and ε may be subject[19] to rather large errors. These calculations further assume that the state of aggregation of the Grignard reagent is constant over the concentration region investigated. Knowledge of the nature of methylmagnesium bromide in ether would make it possible to refine these calculations. However, the fact that it is possible to construct a linear Scott plot may not be taken as proof that only monomeric Grignard species are involved. Considerable dimerization of the Grignard reagent coupled with complex formation with the ketone is difficult to distinguish from the involvement of only monomeric species using the present data.

Kinetics. The rate of disappearance of either the ketone or complex was followed by adding an ether solution of the ketone (10–30 μl) to a thermostated sample of the Grignard (3 ml) in an ultraviolet cell mounted in a thermostated brass block in the sample compartment of a Perkin-Elmer 202 spectrometer. The final concentration of the ketone I was usually in

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(18) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

(19) (a) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, **86**, 1025 (1964); (b) W. B. Person, *ibid.*, **87**, 167 (1965); (c) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

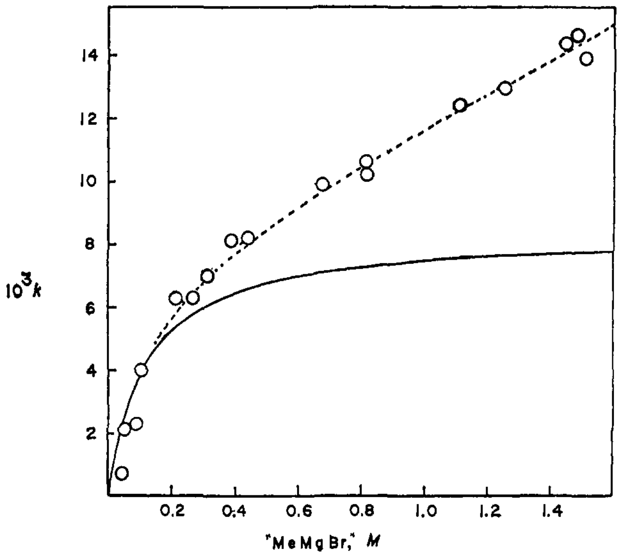

Figure 4. Plot of k_{obsd} *vs.* concentration of methylmagnesium bromide for ketone I in ether at 25.0°. The solid line was calculated for eq 1 with an equilibrium constant of 8.4 l./mole and a rate constant of 8.5×10^{-3} sec^{-1}. The dotted line, eq 2, includes a linear medium effect correction.

the range of 10^{-3} to 10^{-4} M while the Grignard concentration varied from 0.04 to 1.5 M giving pseudo-first-order kinetics. Increasing the ketone concentration by a factor of 4 did not change the results. The temperature, measured by a thermocouple in the cell compartment, was maintained at 25.00 ± 0.05°. A continuous plot of absorbance at a selected wavelength *vs.* time was obtained on an auxiliary strip-chart recorder. First-order rate constants were calculated from 10 to 20 sets of absorbance and time points using an IBM 7094 program which gives the best least squares fit to the first-order rate law with the points weighted in proportion to the absolute magnitude of the absorbance. Table III summarizes first-order rate constants for various concentrations of methylmagnesium bromide and Table IV gives a sample kinetic run.

Table III. Reaction of Methylmagnesium Bromide with 2,4-Dimethyl-4′-methylmercaptobenzophenone in Diethyl Ether at 25.0°

"MeMgBr," M	10^3k_{obsd}, sec^{-1}
0.040	0.78
0.055	2.18
0.092	2.24
0.106	4.00
0.215	6.28
0.275	6.28
0.315	6.99
0.396	8.15
0.447	8.18
0.69	9.9
0.82	10.6
1.12	12.4
1.25	13.1
1.47	14.6
1.48	14.8
1.51	13.8

Table IV. Reaction of 5×10^{-4} M Ketone I with 0.82 M Methylmagnesium Bromide in Diethyl Ether at 25.0°

Time, sec	Rel A (360 mμ)	10^3k, sec^{-1} (integrated)
0	8.09	
15	6.99	9.7
30	5.97	10.1
45	5.17	10.0
60	4.43	10.0
75	3.79	10.1
90	3.04	10.9
120	2.22	10.8
150	1.55	11.0
180	1.15	10.8
	Weighted least squares	10.9

Discussion

The spectral data summarized in the Results section indicate that ketone I complexes with methylmagnesium bromide in diethyl ether solvent to form a new species with λ_{max} 355 mμ. As described, the change in the absorbance of the complex with concentration of the Grignard reagent gives an apparent equilibrium constant of 8.4 l./mole and an extinction coefficient, ϵ, of 1.4×10^4. Previously we reported[5] a kinetic analysis which yielded a value of 6.2 l./mole for this equilibrium constant. Considering[19] the difficulties in making the measurements, it is likely that these two values agree within experimental error. It is apparent that the calculation of equilibrium constant is critically dependent upon a knowledge of the state of aggregation of the methylmagnesium bromide and the tendency of various possible species to form complexes with the ketone. Although a rigorous treatment of the data requires more information about the nature of methylmagnesium bromide than is currently available, it is clear that ketone I is fairly completely complexed at methylmagnesium bromide concentrations above *ca.* 0.5 M.

Formulating the mechanism of the addition reaction as given in eq 1 gives a satisfactory fit to the kinetic data[5] up to *ca.* 0.3 M using the spectroscopically determined equilibrium constant. This fit is illustrated in Figure 4 where the line is calculated for the scheme in eq 1 with a K of 8.4 l./mole and a rate constant[20] for conversion of complex to product of *ca.* 8.5×10^{-3} sec^{-1}. At higher concentrations of the Grignard reagent the reaction proceeds at a faster rate than predicted on this basis.

The kinetic and spectral data actually allow a fairly wide range of reaction schemes to accommodate the data at higher concentrations, and it is instructive to consider two possibilities. For example, the rate of reaction of a Grignard reagent with a ketone would be expected to depend upon the nature of the reaction medium. The reaction of, *e.g.*, benzonitrile with ethylmagnesium bromide has been found[21] to be faster in diethyl ether than in tetrahydrofuran by a factor of

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(20) (a) The numerical value of the rate constant which gives the best fit to these data depends, of course, on the choice of the equilibrium constant K. When the smaller value of 6.2 l./mole is used[5] for K, increasing the rate constant to 1.1×10^{-2} sec^{-1} improves the fit. Both the spectroscopic and kinetic estimates of K assume monomeric Grignard reagent. (b) The data, of course, do not require that the complex is on the reaction path leading to product. However, since the complex contains both the ketone and the Grignard reagent, the likely composition of the transition state, for simplicity it seems reasonable to formulate the reaction as proceeding by way of the complex.

(21) A. A. Scala and E. I. Becker, *J. Org. Chem.*, 30, 3491 (1965).

6. The concentrations employed in the present studies are such that changes in the concentration of the Grignard reagent may make substantial changes in the nature of the medium which will necessitate changes in the values of equilibrium constants and rate constants. Invoking a medium or salt effect which is linear[22] in the concentration of titratable Grignard reagent, G, on the rate constant, k, of eq 1, results in the expression for the observed rate constant given in eq 3, where b is a measure of the sensitivity[22] of k to changes in the concentration of the Grignard.

$$k_{\text{obsd}} = \frac{KGk(1 + bG)}{KG + 1} \qquad (3)$$

As illustrated in Figure 4, the introduction of this additional adjustable parameter in the form of a relatively small medium effect with a b of 0.6 is adequate to describe the experimental data.

It should be noted that the term "Grignard" in the expressions used to describe the reaction can involve contributions from more than one organometallic species. For example, the fraction of dimethylmagnesium in equilibrium with MeMgBr may be relatively constant over this concentration range with reaction proceeding through both species.[15]

In addition to general medium effects, changes in the gross nature of the Grignard reagent with concentration should be considered in any interpretation of the kinetic data. Considering, for example, the possible conversion of monomeric Grignard, G_1, into dimeric Grignard, G_2, with increasing concentration gives the reaction scheme outlined in eq 4 to 6 in which both G_1 and G_2 are considered to complex with the ketone followed by conversion to the product. To the extent that this scheme represents the actual chemical situation, the complex observed spectroscopically would be a mixture of complexes, C_1 and C_2, involving monomeric and dimeric Grignard, respectively.

$$\mathrm{I} + \mathrm{G_1} \overset{K_1}{\rightleftharpoons} \mathrm{C_1} \xrightarrow{k_1} \mathrm{P} \qquad (4)$$

$$2\mathrm{G_1} \overset{K_2}{\rightleftharpoons} \mathrm{G_2} \qquad (5)$$

$$\mathrm{I} + \mathrm{G_2} \overset{K_3}{\rightleftharpoons} \mathrm{C_2} \xrightarrow{k_2} \mathrm{P} \qquad (6)$$

Because of the large number of parameters in this scheme it is inevitable that a number of sets of values of the various equilibrium constants and rate constants can be found to describe the experimental data. Detailed knowledge of the state of aggregation of methylmagnesium bromide in ether solution at these concentrations would facilitate the description of the reaction mechanism. The data of Ashby and Smith[9d] for ethyl- and phenylmagnesium bromide suggest that K_2 has a value of about 10 l./mole. Using this as an approximation to K_2 it is possible to fit the kinetic data as illustrated in Figure 5 in which the line was calculated[23] for values of the equilibrium constants K_1 and K_3 of 10 and 5 l./mole, with the rate constants k_1 and k_2 having values of 2.5×10^{-3} and 28×10^{-3} sec^{-1}, respectively. In principle the Scott plot for an apparent simple equilibrium constant from this scheme involving two complexes and the above values for the equilibrium constants should be a curve; however, such curvature is difficult to either detect or exclude with the present data.

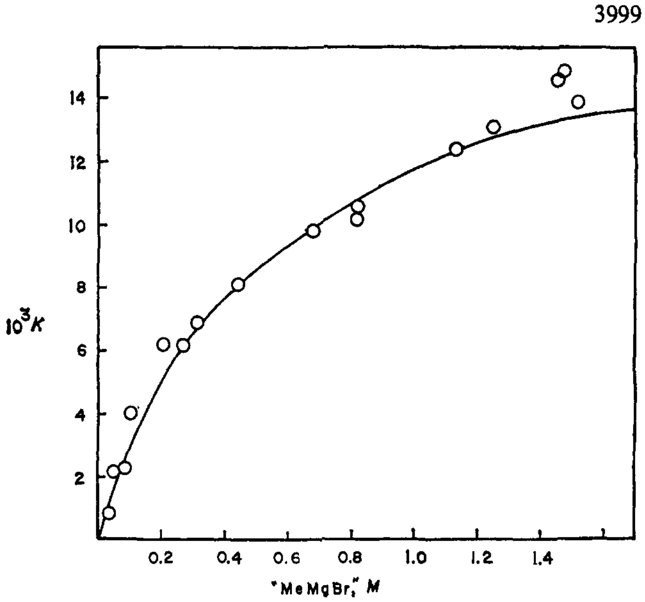

Figure 5. Plot of k_{obsd} vs. concentration of methylmagnesium bromide. The line is calculated for the equilibrium constants K_1, K_2, and K_3 equal to 10, 10, and 5 l./mole, respectively (eq 4, 5, and 6) and a rate constant k_1 of 2.5×10^{-3}. A value of 28×10^{-3} sec^{-1} was used for k_2.

In the scheme outlined in eq 4–6 additional compensation in the values of all equilibrium and rate constants for medium effects may be required.

Many other reaction mechanisms can be written which, with suitable choice of numerical parameters, are consistent with the available experimental data. Although there is considerable merit in employing the simple scheme outlined in eq 1 with a small medium effect on the rate constant to describe this reaction, it is apparent that refinement of the description of the mechanism requires additional experimental data. Such experiments are in progress.

Experimental Section

Methylmagnesium Bromide. Magnesium turnings cut from Dow Chemical Corp.[17] single sublimed magnesium with carbide tools were washed with ether and dried under vacuum before use. To obtain suitable solvents Mallinckrodt anhydrous diethyl ether was used in the preparation of a *ca.* 0.5 *M* solution of methylmagnesium bromide.[6] The reagent was degassed by bubbling purified argon through it for at least 1 hr followed by refluxing for at least 0.5 hr. Ether was then distilled from this solution through a 10-in Vigreux column directly into the reaction flask used in preparation of the reagent for kinetic work. The system was all glass, vacuum tight, and contained no ground joints or stopcock grease.

Matheson methyl bromide was dried by passing through a flushed tower containing Linde, Type 4A, molecular sieves before condensing in a cooled, tared, evacuated flask. Before use, the condensed methyl bromide was degassed by repeated evacuations at *ca.* −70° followed by refilling with argon. The methyl bromide was then distilled directly into the reaction flask.

The Linde high-purity argon, used as the inert atmosphere, was purified by passing through a column of activated BTS catalysts to remove traces of oxygen and then through a tower of Linde molecular sieves to remove water.

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[22] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 78, 2763 (1956).

[23] The calculations were performed by programming the equilibrium constant and differential equations representing eq 4 to 6 for an EAI TR 20 analog computer. The computer produced plots of concentration of complex or product *vs.* time for selected values of the parameters and Grignard concentration. Various values for the equilibrium and rate constants were tried until a set was found which gave plots of concentration *vs.* time from which observed rate constants could be calculated, by standard procedures, which approximated the experimental data. Other sets of values can, of course, be found which fit the data. We are indebted to Mr. Peter Halbert of Electronics Associates, Inc., for helpful discussions on these calculations.

In a typical preparation of methylmagnesium bromide, 11 g of magnesium was placed in the 300-ml reaction flask. The system was closed and flushed with argon. It was then evacuated (0.1 mm), heated with an infrared lamp, and refilled with argon several times. After enough ether had been distilled into the reaction flask to cover the magnesium, 32 g of methyl bromide was slowly distilled into the mixture. During the reaction the temperature was maintained at 25 ± 5° by external cooling. A magnetic stirrer provided the necessary agitation. After two filtrations through sintered-glass filter sticks, samples were delivered under positive argon pressure into ampoules and ultraviolet cells capped with silicone rubber seals. Dilutions of the reagent were accomplished by distillation of purified solvent directly into the cells.

Analysis of Grignard Preparations. The concentrations of Grignard preparations were determined by iodine,[24] total base, and total halide titrations. For iodine titrations, an aliquot of a solution of iodine in benzene was injected, with a syringe, into silicone-rubber-sealed samples of the Grignard reagent. The tube was opened and the contents washed into an aqueous solution of potassium iodide. The excess iodine was titrated by standard procedures.[25] The total base titrations were done in the usual manner[26] except that ethanol was used instead of water to increase the solubility of the basic magnesium salts. Total halide titrations on hydrolyzed samples were done by standard Volhard titrations. Typical results are summarized in Table I. The reproducibility of duplicate determinations was better than ±2%.

2,4-Dimethyl-4′-methylmercaptobenzophenone. 2,4-Dimethylbenzoyl chloride was obtained by reaction of the commercially available 2,4-dimethylbenzoic acid with thionyl chloride as described by Davies and Perkin.[27] Friedel–Crafts acylation of thioanisole with this acid chloride under conditions described by Kenyon[28] gave the desired ketone in 49% yield. Recrystallization to constant melting point from aqueous ethanol and then Skelly B gave material with mp 52–53°. The nmr spectrum displayed absorbances at τ 7.72, 7.64, and 7.50 and complex aromatic absorbance centered at τ 2.6 with relative areas 3.1, 3.1, 3.0, and 7.0, respectively.

Anal. Calcd for $C_{16}H_{16}OS$: C, 74.95; H, 6.29. Found: C, 74.99; H, 6.37.

Products. To 30 ml of a 1.1 *M* solution of methylmagnesium bromide was added, with rapid stirring, 1.0600 g (0.004 *M*) of ketone I dissolved in 5 ml of diethyl ether. An initial brown color which disappeared after 10 min was observed when the ketone was added. The reaction was allowed to proceed for 40 min. The reaction mixture was hydrolyzed with just enough 0.4 *M* aqueous sulfuric acid to dissolve all the magnesium salts. After separation of the two layers, the ether portion was washed with 10 ml of saturated aqueous potassium carbonate solution, followed by another washing with 10 ml of aqueous sodium chloride solution. The ether was then carefully driven off by heating in an oil bath. To the residue was added 20 ml of benzene and 50 mg of *p*-toluenesulfonic acid. This benzene solution was heated until about half the benzene was azeotroped off. After the solution was cooled, 20 ml of ether was added, and the mixture was washed successively with aqueous potassium carbonate and sodium chloride solutions. This product mixture was dried with 2 g of magnesium sulfate, and the solvents were carefully removed by mild heating on an oil bath followed by blowing a stream of dry nitrogen over it. A solid was obtained. The final traces of ether and benzene were removed by pumping on the solid product at a pressure of 0.5 mm for 2 hr. The product was then melted at atmospheric pressure and again evacuated to the same pressure for 2 hr. This process was done for a total of three times. A yield of 98.2% (1.0330 g) of product, mp 56–57°, was obtained. The product was characterized as the expected olefin, 1-(2,4-dimethylphenyl)-1-(4′-methylmercaptophenyl)ethylene (III); nmr spectrum of the product showed singlet peaks at τ 8.00 (3.0), 7.70 (3.0), 7.62 (3.0); doublets at τ 4.93 (0.93), 4.35 (0.93); and a multiplet for the aromatic protons centered at τ 3.0 (7.0). The infrared spectrum did not show hydroxyl or carbonyl absorbances. Vapor phase chromatography using a 30% Apiezon L on a Chromosorb W column with 4-methylbenzophenone as the internal standard indicated the product to be 100.7 ± 1% olefin as calculated from the relationship (weight of olefin)/(weight of standard) = 1.095·(area of olefin)/(area of standard). This relationship was obtained from the calibration plot of (weight of olefin)/(weight of standard) *vs.* (area of olefin)/(area of standard) using an authentic sample of the olefin and the same internal standard.

Kinetics. To a silicone-rubber-capped 1-cm quartz ultraviolet cell containing *ca.* 3 ml of a thermostated sample of Grignard reagent 10–30 μl of a 6×10^{-3} *M* thermostated solution of ketone I in dry degassed ether was added with a microsyringe. The mixture was rapidly mixed and placed in a close-fitting brass block mounted in the cell compartment of a Perkin-Elmer 202 spectrometer. The temperature of the block was maintained by a flow of thermostated water through internal holes and measured by means of a thermocouple in the block. The temperature was maintained at 25.00 ± 0.05° as determined by comparison with an NBS certified thermometer. The concentration[29] of ketone I was generally between 10^{-4} and 10^{-3} *M* while Grignard concentrations ranged from 0.04 to 1.5 *M*. A plot of absorbance *vs.* time at a selected wavelength was obtained on an auxiliary strip-chart recorder. The infinity absorbance was usually within 0.02 absorbance unit of the base line. First-order rate constants were calculated from 10 to 20 sets of time and absorbance values plus the infinity readings. The reported constants are least-squares fits to the first-order rate law with the points weighted in proportion to the absolute magnitude of the absorbance.

Ultraviolet Measurements. Samples of ketone I were introduced into ultraviolet cells containing Grignard reagent as described for kinetic measurements. The time of injection of the ketone was recorded and taken as t_0. Scans of absorbance *vs.* wavelength were made as rapidly as possible, noting the time at the start of each scan and the scanning rate of the instrument. To construct an initial reaction condition spectrum, plots of log $(A_t - A_\infty)$ *vs.* time were made for several wavelengths and extrapolated to t_0.

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[29] At 10^{-5} *M* ketone I the rate constants tended to lack reproducibility. The use of 10^{-3} to 10^{-4} *M* ketone I or a mixture of 10^{-5} *M* ketone I and 10^{-3} *M* acetone give reproducible rate constants.