external TMS) τ 8.04 (s, 1, CH_3), 8.32–9.50 (complex m, 3, *n*-butyl), 9.84 (s, 3, Me_3Si), 9.81 (s, 3, Me_3Si).

(C) (15%), showed ir and nmr spectra identical with those of **8**.

(D) (8%) ir (neat) ν (cm^{-1}) 2960 s, 2940 msh, 2900 msh, 2880 wsh, 2120 m, 1900 vw, 1890 vw, 1610 vw, 1460 vw, 1410 vw, 1260 vw, 1155 w, 1070 w, 840 vs, 760 m, 690 w, 660 vw; nmr (CCl_4, external TMS) τ 8.14 (s, 1, CH_3), 8.32–9.40 (complex m, 3, *n*-butyl), 9.86 (s, 3, Me_3Si), 9.94 (s, 3, Me_3Si).

The C≡C triple bond stretching absorption at 2120 cm^{-1} in A, B, and D is characteristic for $R_3Si—C≡C—$.

A, B, and D are probably isomers of $Me_3SiC≡CC(Me_3Si)=C(C_4H_9)CH_3$; they were not further characterized.

Organometallic Reaction Mechanisms. X. Concerning the Effect of Magnesium Metal Purity and the Method of Preparation of Grignard Reagents on Reaction with Ketones and Nitriles

E. C. Ashby,* H. M. Neumann, F. W. Walker, J. Laemmle, and Li-Chung Chao

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received July 6, 1972*

Abstract: Reaction rates and product analysis for the addition of methylmagnesium bromide to benzophenone, 2,4-dimethyl-4′-methylmercaptobenzophenone, 2-methylbenzophenone, and benzonitrile have been evaluated. The reaction conditions were such that a large excess of one reagent was employed. In addition, dilute solutions (<0.1 *M*) of Grignard reagent were used to ensure that complications due to associated organomagnesium species would not arise. The Grignard reagents were prepared from several grades of magnesium employing both an excess of magnesium and an excess of methyl bromide. The reaction of methylmagnesium bromide with benzophenone under pseudo-first-order conditions (in excess methylmagnesium bromide) gives rate constants which are dependent on the initial ketone concentration and also gives significant amounts of nonaddition products. These effects are significantly reduced when the purity of the magnesium used to prepare the Grignard reagent is increased. When ultrapure magnesium was used for the preparation of methylmagnesium bromide, the complications described were essentially eliminated and the rate data were found to be consistent with a specific mechanism in which both $(CH_3)_2Mg$ and CH_3MgBr react with ketone in a first-order fashion. Similar results were observed in the reaction of Grignard reagents with benzonitrile. In those cases in which large excesses of 2-methylbenzophenone and benzonitrile were employed, no by-products were detected and the rate constants were found to be independent of the manner in which the Grignard reagent was prepared or of the purity of the magnesium employed.

Mechanisms describing the addition of Grignard reagents to ketone have received much attention in recent years.[1] The experimental technique most often used in these investigations has been kinetics. The kinetic methods employed have been the following: allowing the Grignard reagent and ketone to react in nearly equal ratios,[2a,b] employing a large excess of Grignard reagent,[2c–i] and, more recently, employing a large excess of ketone.[2j,k] The advantage of the latter two methods is that the concentration of the reagent used in excess remains essentially constant throughout the course of the reaction. Thus, the kinetic dependence of the reagent used in excess is eliminated and a direct determination of the order of the reagent used in limited amount is possible. The order of the reagent used in large excess can be determined indirectly from the functional dependence of k_{obsd} on its concentration.

Smith and coworkers[2c–e] have investigated the reaction of methylmagnesium bromide with 2,4-dimethyl-4′-methylmercaptobenzophenone,[2c,d] 4-methylmercaptoacetophenone,[2e] and benzophenone.[2e] The Grignard reagent was prepared from singly sublimed magnesium employing an excess of magnesium turnings. The kinetic method employed involved the use of large excesses of the Grignard reagent. Interpretation of the resultant data was not straightforward. At low concentrations, *ca.* 10^{-5} *M*, of 2,4-dimethyl-4′-methylmercaptobenzophenone and 4-methylmercaptoacetophenone, the pseudo-first-order rate constants showed a dependence on the initial ketone concentration at constant Grignard reagent concentration. At lower ketone concentrations, *i.e.*, higher Grignard reagent to ketone ratios, larger rate constants were observed. The problem could be reduced by adding a small concentration of acetone to the Grignard reagent prior to the kinetic experiment, or by recrystallization of the Grignard reagent. Analysis of the products from the reaction of both 2,4-dimethyl-4′-methylmercaptobenzophenone and 4-methylmercaptoacetophenone with methylmagnesium bromide showed that only addition had occurred. Rate constants obtained from the reaction of methylmagnesium bromide with benzophenone displayed the largest dependence on initial ketone concentration of the three ketones investigated.[2e]

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[1] E. C. Ashby, *Quart. Rev., Chem. Soc.*, **2**, 259 (1967).

[2] (a) M. Anteunis, *J. Org. Chem.*, **26**, 4214 (1961); (b) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1962); (c) S. G. Smith and G. Su, *J. Amer. Chem. Soc.*, **86**, 2750 (1964); (d) S. G. Smith and G. Su, *ibid.*, **88**, 3995 (1966); (e) J. Billet and S. G. Smith, *ibid.*, **90**, 4108 (1968); (f) E. C. Ashby, R. Duke, and H. M. Neumann, *ibid.*, **89**, 1964 (1967); (g) E. C. Ashby, F. W. Walker, and H. M. Neumann, *J. Chem. Soc. D*, 330 (1970); (h) J. Koppel, L. Margua, and A. Tuulmets, *Reakts. Sposobnost. Org. Soedin*, **5**, 1041 (1968); (i) A. Tuulmets, *ibid.*, **6**, 854 (1969); (j) E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **93**, 4601 (1971); (k) E. C. Ashby, J. Laemmle, and H. M. Neumann, *ibid.*, **94**, 5424 (1972).

Methods which reduced this problem with the other ketones were less successful with benzophenone. In addition, analysis of the products from the reaction of benzophenone with methylmagnesium bromide showed significant amounts of nonaddition by-products, benzopinacol[2e] (14% at Grignard:ketone ratio = 200) and benzhydryol[3] (54.5% at Grignard:ketone ratio = 419). The following conclusions were drawn from these studies. (1) The variation in rate constants with ketone concentration is due to small impurities in methylmagnesium bromide prepared from singly sublimed magnesium. The effect of these impurities can be reduced significantly by the addition of small concentrations of acetone or by recrystallization of the Grignard reagent. (2) In the case of 2,4-dimethyl-4′-mercaptomethylbenzophenone and 4-methylmercaptoacetophenone, acceptable rate data for quantitative analysis could be obtained. (3) In the case of benzophenone, acceptable rate data necessary to establish a mechanism could not be obtained.[2e]

By-products indicative of radical type side reactions were first observed many years ago by Russian workers in the reaction of cyclohexylmagnesium iodide with benzophenone.[4] More recently, Blomberg and Mosher obtained a 20% yield of benzopinacol from the reaction of neopentylmagnesium chloride with benzophenone.[5] The occurrence of benzophenone–magnesium ketyl during Grignard addition to benzophenone has been verified by means of electron spin resonance spectroscopy.[2e,6] Holm and Crossland have shown that benzophenone and substituted benzophenones react with *tert*-butylmagnesium chloride to yield 1,2-, 1,4-, and 1,6-addition products in addition to benzopinacols.[7] They present evidence which shows an initial rate-limiting step, common to all four reactions, involving a one-electron transfer from Grignard reagent to benzophenone. With methylmagnesium bromide, however, an ionic mechanism was suggested.[7] An emerging picture of Grignard reagent addition to ketones expressed in terms of an ionic or single electron transfer mechanism indicates that single electron transfer participation increases in the order CH_3 < i-C_3H_7 < t-C_4H_9[7] with respect to the alkylmagnesium halide and is also dependent on the reduction potential of the ketone, acetone < benzophenone < fluorenone, and the solvent, HMPA > THF > ether.[8]

Reports to date concerning the addition of Grignard reagents to ketones have not provided satisfactory explanations for the following points: (1) the relationship between by-product formation and the behavior of the pseudo-first-order rate constants, (2) the relationship between by-product formation and normal addition, (3) the role played by the impurities in the magnesium used in Grignard reagent preparation with respect to by-product formation and erratic rate behavior, and (4) the role played by the manner in which the Grignard reagent is prepared, *i.e.*, employing excess magnesium or excess alkyl halide, with respect to by-product formation and erratic rate behavior. With respect to the latter two points, we reported in a recent communication[2g] that methylmagnesium bromide prepared from triply sublimed magnesium employing an excess of methyl bromide drastically reduces the per cent of by-product formation (20 to 6%) in benzophenone alkylation compared to methylmagnesium bromide prepared using excess triply sublimed magnesium. In addition methylmagnesium bromide prepared from ultrapure magnesium employing an excess of methyl bromide essentially eliminates by-product formation and ketone concentration dependence of the pseudo-first-order rate constants in benzophenone alkylation. Thus, under conditions described above, data obtained with benzophenone can be analyzed quantitatively. The present study differs from previous reports[2c–e] in several respects. The reaction of benzophenone with large excesses of methylmagnesium bromide was investigated. The Grignard reagents were prepared from several sources of magnesium employing both excess magnesium and excess methyl bromide. Pseudo-first-order rate constants were recorded for several ketone concentrations at constant methylmagnesium bromide concentration of each Grignard reagent. In addition, samples from the actual kinetic runs were quenched at infinite time and the extent of by-product formation was determined. This allowed us to relate the variation of pseudo-first-order rate constants to the extent of by-product formation. In previous studies,[2e] product analysis was performed on a limited number of samples and none on samples from which rate constants were obtained. Maximum methylmagnesium bromide concentration was held below 0.03 *M* since the reagent in this concentration range is known to contain only monomeric species defined by the Schlenk equilibrium.[9a,b] Other workers[2c–e] report results in concentration ranges in which the Grignard reagent is known to exist in a variety of associated forms.[9a,b] In addition to benzophenone, the behavior of methylmagnesium bromide with excess 2-methylbenzophenone and with benzonitrile is also reported. The behavior of benzophenone with methylmagnesium bromide prepared from an ultrapure source of magnesium is presented in detail.

Experimental Section

Materials. Doubly and triply sublimed magnesium were obtained from the Dow Chemical Co.[10] The magnesium was milled prior to use. Single crystal magnesium from Ventron Corp. (reported purity, 99.9995%) was milled with a carbide tool taking special precautions to maintain the purity of the magnesium. In addition, an unmilled chunk was used in one preparation of methylmagnesium bromide in order to determine the effect of magnesium particle size on the purity of Grignard formed. Methylmagnesium bromide was also prepared from a small amount (~2 g) of "ultrapure magnesium"[11] chunks. Prior to milling, or in the case where magnesium chunks were used prior to Grignard reagent preparation, all magnesium was etched with dilute HCl to remove

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[3] S. E. Rudolph and S. G. Smith, *J. Chem. Soc. D*, 1428 (1970).

[4] A. E. Arbuzov and I. A. J. Arubzov, *J. Gen. Chem. USSR*, **2**, 338 (1932).

[5] (a) C. Blomberg and H. S. Mosher, *J. Organometal. Chem.*, **13**, 519 (1968); (b) C. Blomberg, R. M. Salinger, and H. S. Mosher, *J. Org. Chem.*, **34**, 2385 (1969).

[6] K. Maruyama, *Bull. Chem. Soc. Jap.*, **37**, 897 (1964).

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

[8] J. F. Fauvarque and E. Rouget, *C. R. Acad. Sci., Ser. C*, 1355 (1971).

[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).

[10] We are indebted to the Dow Chemical Co. for a generous gift of both doubly and triply sublimed magnesium. For typical analysis of Dow sublimed magnesium see: R. M. Salinger and H. S. Mosher, *ibid.*, **86**, 1782 (1964).

[11] We are indebted to Professor Royal W. Stark, University of Chicago, for the sample of ultrapure magnesium. The residual resistance ratios of *ca.* 5 × 10^{-6} compared with the best Dow triply sublimed value of 10^3. No impurities could be detected using an AEI, MS-7 spark source mass spectrometer. All evidence indicates <10^{-8} impurity.

surface contamination, quenched with distilled water, and then dried by rinsing with 95% ethanol followed by anhydrous ether.

Benzophenone (Eastman's Reagent) was distilled (88.0°, 0.05 mm) twice *in vacuo* in a nitrogen system through an 18-in. vacuum-jacketed column packed with glass helices. A glpc analysis of the distilled product dissolved in diethyl ether established the purity at 99.54%.

Eastman highest purity 2-methylbenzophenone was distilled *in vacuo* from Linde 4A molecular sieve. Glpc analysis of the distilled material showed it to be better than 99.9% pure.

2,4-Dimethyl-4′-mercaptomethylbenzophenone was prepared by methods previously described.[2c] The crude material was purified by repeated crystallization from hexane and ethanol–water. The purified material was dried overnight on a vacuum line and stored under nitrogen. Mass spectral analysis of the purified ketone showed a parent peak at mass 256 and gave the expected fragmentation pattern. Nmr analysis was identical with that previously reported.[2c]

Eastman Spectrograde benzonitrile was dried and purified by distillation over solid, ether-free, methylmagnesium bromide. Glpc analysis indicated a purity of better than 99.99%.

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.

Diethyl ether (Fisher Anhydrous) was distilled under nitrogen from $LiAlH_4$ through a 60-cm, glass-helix-packed distilling column.

Preparations. The preparation of methylmagnesium bromide employing an excess of methyl bromide and the subsequent preparation of dilute solutions for kinetic studies have been previously described.[2k] In those preparations employing an excess of magnesium, the addition of methyl bromide was continued until about half the magnesium had been consumed and the reaction mixture was allowed to stir overnight. Elemental analysis of all Grignard solutions revealed a high purity product with no detectable coupling. Typical analyses of several solutions for C–Mg:Mg:Br are as follows: 1.00:0.99:0.99, 1.00:1.03:0.99, and 1.00:1.04:0.98.

Kinetic Studies. The kinetic techniques employed to study the reaction of excess 2-methylbenzophenone with methylmagnesium bromide and the reaction of benzonitrile with methylmagnesium bromide have been described in detail elsewhere.[2k,12]

The following kinetic techniques were employed in the investigation of the reaction of benzophenone with excess methylmagnesium bromide. Dilute methylmagnesium bromide solutions were maintained at 25.00 ± 0.02° in a water bath. Benzophenone solution was added *via* syringe under a heavy nitrogen flow through the three-way Teflon stopcock at the top of the kinetic flask. Samples were withdrawn, again under a heavy nitrogen flow, at appropriate intervals using syringes that were flamed, dried, and purged with nitrogen just prior to use. The reaction samples were quenched by injection into an ether-saturated 10% H_2SO_4 solution in test tubes with ground glass stoppers. The absorbance values of standard benzophenone solutions were unchanged when quenched in this solution. The absorbance values for unreacted benzophenone were determined at 251 mμ (ε 1.8 × 10^4) by filling either 1.00-cm or 1.01-mm quartz cells *via* syringe with the ether layers of the quenched solutions. Hydrolyzed methylmagnesium bromide, of the same concentration as the reaction solution, was used in the reference cells. The absorbance values at 251 mμ were corrected for the product 1,1-diphenylethanol (ε 349 at 251 mμ).

A procedure identical with that used in the benzophenone case was employed in those experiments in which 2,4-dimethyl-4′-mercaptomethylbenzophenone was the ketone studied. The wavelength of maximum absorption for this ketone is 314 mμ.[2c]

Product Studies. Methods for the analysis of products arising from the reaction of methylmagnesium bromide with excess 2-methylbenzophenone and with benzonitrile have been previously described.[2k, 12]

Smith and coworkers reported the direct analysis for benzopinacol by glpc at 200° employing a 6-ft column of 10% Ucon fluid on Chromosorb W.[2e] The reported column temperature is 14° above the reported thermal decomposition temperature of benzopinacol into benzophenone and benzhydrol.[13]

Since our reaction solutions were so dilute, *ca.* 10^{-5} *M*, that isolation of the products was impossible, a direct analysis for benzopinacol by glpc analysis was desirable. However, all attempts to analyze benzopinacol by glpc analysis failed. At injection port and oven temperatures above 185°, benzopinacol decomposed in every case. At injection port and column temperatures below 185°, benzopinacol and its decomposition products failed to emerge from the columns. The analysis was attempted with the following 6 ft × 1/8 in. stainless steel columns: 10% Ucon Polar 50HB5100 on Chromosorb W; 2% and 6% Ucon Polar 50 HB5100 on Gaschrom Q; 2% and 10% Carbowax 20M on Chromosorb W; 10% SE-30 on Chromosorb S; Polypak 1; and 10% Polyphenol on Gaschrom Q. An attempt was made to analyze directly for benzopinacol using 0.25 in. glass columns, a glass lined injection port, and 1% Ucon Polar 50HB5100 on glass beads. Even under these mild conditions benzopinacol failed to emerge or decomposed depending on the temperature.

In the case of the reaction of benzophenone with excess methylmagnesium bromide, the product distribution was determined on the solutions obtained from the kinetic studies. The reaction solutions were so dilute, *ca.* 10^{-5} *M*, that isolation of the products was impossible. The quenched samples were concentrated under a stream of nitrogen and analyzed without further treatment. The analyses were carried out with an F&M Model 700 flame ionization gas chromatograph equipped with dual 6-ft × $^1/_8$ in. stainless steel 10% Carbowax 20M columns (flow rate 60 ml/min, oven temp 190°). The analyses were carried out in the following manner. The solution from each kinetic run was allowed to stand for several hours to ensure complete reaction and an infinite time sample was quenched. The sample was then subjected to ultraviolet analysis and in no case was unreacted ketone detected. The samples were then subjected to glpc analysis and in each case (except when the Grignard was prepared from ultrapure magnesium) five peaks were recorded: 1,1-diphenylethylene (the dehydration product of 1,1-diphenylethanol), an unidentified peak, benzophenone, 1,1-diphenylethanol, and benzhydrol. The per cent addition reaction was taken to be the area representing 1,1-diphenylethylene and 1,1-diphenylethanol divided by the total area of all peaks. It must be noted that this method does not allow the direct determination of the percentage of benzopinacol, since some benzhydrol may be formed directly.[3]

Owing to the number and variety of products in solution, a satisfactory internal standard could not be found. Therefore, in order to check the reaction yield, samples were withdrawn early in the reaction, the absorbance of benzophenone was determined, and the solutions were analyzed by glpc. Since it had been determined that all of the compounds have the same response ratio on a molar basis, the molarity of the solutions with respect to each compound could be calculated by comparing the relative areas directly with the area from the known amount of benzophenone. A number of determinations indicated an overall yield of 100 ± 5%. The uncertainty is probably due to accumulated inaccuracies in computing the areas of the number of peaks and the regeneration of benzophenone in the later fractions by decomposition of benzopinacol in the gas chromatograph as discussed above. Nevertheless, it seems fairly certain that the sum of the areas closely represents the total reaction product and it was on this basis that the per cent yields shown in Table III were calculated.

Results and Discussion

Benzophenone reacts with excess methylmagnesium bromide to produce on hydrolysis the expected alcohol, 1,1-diphenylethanol, as well as several nonaddition products. Two of the nonaddition products have been identified as benzopinacol[2e,g] and benzhydrol.[3] In kinetic experiments employing a large excess of methylmagnesium bromide, reaction rates have been found to be dependent on the initial concentration of ketone.[2c–e,g] The severity of the erratic rate behavior and the extent of by-product formation were reported in a previous communication[2g] to be a function of the purity of magnesium used to prepare the Grignard reagent as well as a function of how the Grignard reagent was formed, *i.e.*, employing excess magnesium or excess methyl bromide. It was also reported that by-product formation was essentially eliminated and rate constants behaved

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[12] E. C. Ashby, L.-C. Chao, and H. M. Neumann, *J. Amer. Chem. Soc.*, in press.

[13] (a) "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1965, p 368; (b) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 861; (c) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, 49, 236 (1929).

normally when the Grignard reagent was prepared from ultrapure magnesium employing excess methyl bromide.[2g]

Results with Triply Sublimed Magnesium. Several experiments were carried out with methylmagnesium bromide prepared from triply sublimed magnesium employing an excess of magnesium. Both benzophenone and 2,4-dimethyl-4′-mercaptomethylbenzophenone were examined.

Two principle features of the rate data with both ketones were noticed. First, the reaction of methylmagnesium bromide and ketone under pseudo-first-order conditions (using excess methylmagnesium bromide) is not clearly first order in ketone. The initial portion of the reaction shows curvature on a first-order plot. The latter portion comprising the bulk of the reaction gives a reasonably good first-order fit (Figure 1).

Secondly, when the initial concentration of methylmagnesium bromide is held constant and several different ketone concentrations are used, the rate constant changes (Table I). The constancy of the Grignard concentrations was assured by filling four reaction flasks from the same Grignard preparation and storing the sealed flask in the glove box away from light. The reactions were run in a staggered fashion to demonstrate that any difference in the rate constants was not simply a reflection of Grignard deactivation by moisture or oxygen during storage. Clearly, the ketone is not disappearing in a purely first-order fashion since the rate constant should be independent of the initial ketone concentration.

Table I. Rate Constants for the Reaction of Methylmagnesium Bromide with Benzophenone (a) and 2,4-Dimethyl-4′-mercaptomethylbenzophenone (b) in Diethyl Ether at 25°

Ketone	$10^3[G]_0$	$10^5[K]_0$	10^4k_{obsd}, sec^{-1}
a	6.45	2.90	95.0
a	6.45	4.70	85.6
a	6.45	5.95	86.6
a	6.45	12.00	82.5
b	7.50	1.80	6.32
b	7.50	3.39	4.61
b	7.50	9.33	3.74

In an effort to determine if the behavior of the pseudo-first-order rate constants was related to by-product formation, a series of experiments was carried out in which pseudo-first-order rate constants were obtained and product analyses on the actual kinetic solutions were carried out. The results are shown in Table II.

Table II. Product Analysis and Pseudo-First-Order Rate Constants from the Reaction of 0.00838 *M* Methylmagnesium Bromide with Benzophenone in Diethyl Ether at 25°

$10^5[K]_0$	10^3k_{obsd}, sec^{-1}	% addition
2.40	14.1	72
3.72	12.4	75
6.28	11.5	78
11.8	9.9	87

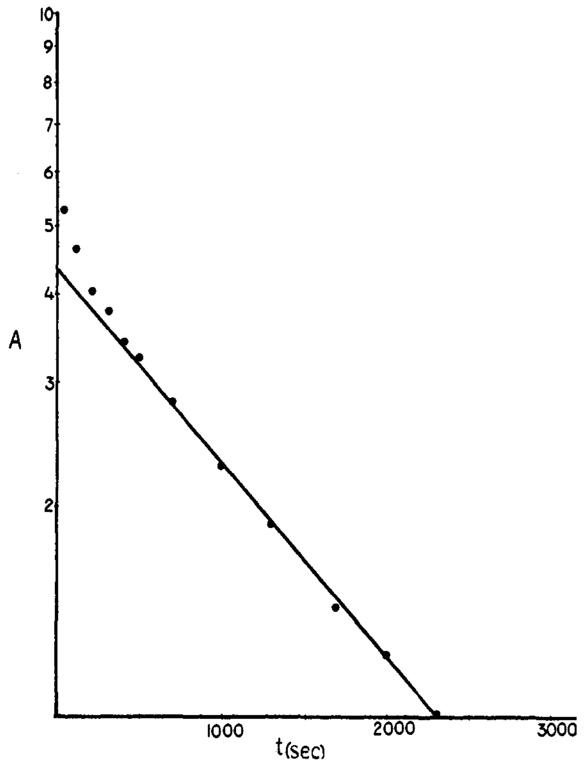

Figure 1. Reaction of methylmagnesium bromide prepared from triply sublimed magnesium with 2,4-dimethyl-4′-mercaptomethylbenzophenone demonstrating initial curvature and the extraction of the pseudo-first-order rate constant (data from Table I, low ketone concentration run).

The data clearly illustrate that those reactions in which the Grignard to ketone ratio is larger have larger pseudo-first-order rate constants and a larger percentage of by-products.

The fact that the rate-constant variation parallels the extent of by-product formation suggests that the addition reaction may be related to the reaction producing by-product, perhaps through a common intermediate. In order to gather more information concerning this point, an experiment was carried out in which several samples were quenched. Each sample was then analyzed by ultraviolet spectroscopy and by glpc. The results are shown in Table III. The ratio of 1,1-diphenylethanol to benzyhydrol appears to be constant within experimental error throughout the course of the reaction indicating that the addition reaction and the side reaction are related in some manner.

Table III. Product Formation with Time from the Reaction of 0.00645 *M* Methylmagnesium Bromide with 1.2 × 10^{-4} *M* Benzophenone in Diethyl Ether at 25°

Time, sec	Benzophenone, %	Benzhydrol, %	1,1-Diphenylethanol, %	1,1-Diphenylethanol/ benzydrol
28	76.8	3.0	20.2	6.7
50	64.2	3.8	32.0	8.4
75	53.1	4.2	42.7	10.2
99	43.2	5.6	51.2	9.2
123	36.4	6.1	57.5	9.4
148	31.7	7.2	61.1	8.5
175	30.8	7.2	62.0	8.6
225	24.2	7.8	68.0	8.7
248	23.2	7.6	69.2	9.1

Table IV. Product Analysis and Pseudo-First-Order Constants from the Reaction of Methylmagnesium Bromide with Benzophenone in Diethyl Ether at 25°

Source of magnesium	Grignard prepared with excess	$[G]_0$	$10^5[K]_0$	$[G]_0/[K]_0$	k_{obsd}, sec^{-1}	$k_{obsd}/[G]_0$	% addition
Doubly sublimed	Mg	0.00958	2.04	470	0.0218	2.28	72.7
	Mg	0.00958	8.52	112	0.0134	1.40	84.6
	Mg	0.00958	16.7	57	0.0117	1.23	91.9
	CH_3Br	0.00995	2.04	487	0.0128	1.29	92.2
	CH_3Br	0.00995	8.52	117	0.0106	1.07	96.9
	CH_3Br	0.00995	16.7	60	0.00994	1.00	98.1
Single crystal	Mg	0.00953	2.04	467	0.0155	1.63	88.1
	Mg	0.00953	8.52	112	0.0126	1.33	94.6
	Mg	0.00953	16.7	57	0.0119	1.25	96.3
	CH_3Br	0.00978	2.04	479	0.0135	1.38	95.0
	CH_3Br	0.00978	8.52	115	0.0135	1.23	97.9
	CH_3Br	0.00978	16.7	58	0.0114	1.17	98.1
Unmilled single crystal	CH_3Br	0.00970	2.04	475	0.0131	1.35	94.7
	CH_3Br	0.00970	8.52	114	0.0127	1.31	96.5
	CH_3Br	0.00970	16.7	58	0.0114	1.18	98.3

The results described thus far were all obtained with methylmagnesium bromide prepared from triply sublimed magnesium employing an excess of magnesium turnings. The results clearly demonstrate the difficulties encountered by ourselves[2b,g] and other workers[2c–e] in the use of pseudo-first-order kinetics in excess of Grignard reagent for determining reaction mechanisms. The above results clearly show that pseudo-first-order rate constants and by-product formation are dependent on the Grignard reagent to ketone ratio at constant Grignard reagent concentration. They also indicate that the magnitude of the rate constant is related to the extent of by-product formation and that the addition reaction and the side reaction are related in some manner.

Results with Doubly Sublimed and Single Crystal Magnesium. There appear to be two basic factors that could lead to radical type side reactions in the reaction of methylmagnesium bromide with benzophenone. The first factor is the existence of small amounts (ppm) of transition metal impurities known to exist in sublimed magnesium. The second factor is the possible formation of small amounts of magnesium(I) bromide ($Mg + MgBr_2 \rightarrow 2BrMg$) in the Grignard solution. Magnesium(I) bromide is reported to reduce benzophenone to benzopinacol. The first factor should be diminished by preparing the Grignard reagent from a purer source of magnesium. The second factor should be diminished by using an excess of methyl bromide in the preparation of methylmagnesium bromide, thereby consuming all the magnesium metal and eliminating the reaction leading to magnesium(I) bromide.

In order to determine the relative effect of the factors mentioned above, four solutions of methylmagnesium bromide were prepared. Two solutions were prepared from doubly sublimed magnesium, one employing an excess of magnesium and the other employing an excess of methyl bromide. Two like solutions were also prepared from single crystal magnesium. In addition, a Grignard solution was prepared employing an excess of methyl bromide from a cleaned chunk of single crystal magnesium in order to determine the effect of milling magnesium. The solutions were allowed to settle but were not filtered. Grignard solution was carefully drawn from the clear top portion in order to prepare kinetic solutions. Four sets of kinetic runs were carried out with solutions prepared from each of the four standard Grignard reagent solutions and three runs were carried out from that Grignard prepared from a magnesium chunk. The experiments were designed such that the concentration of Grignard reagent in each experiment was essentially the same. In each set of experiments a large excess of methylmagnesium bromide was employed and three different initial concentrations of benzophenone were used. The same concentrations of benzophenone were used in each set of experiments. First-order plots were linear, and did not show curvature like that in Figure 1. Pseudo-first-order rate constants and product analysis at infinite time were obtained from each run. The results are shown in Table IV. The results are quite clear. Grignard reagents prepared from milled and unmilled magnesium give identical results. Grignard reagents prepared from the same grade of magnesium give much better results if all the magnesium is consumed by employing an excess of methyl bromide. For example, in the case of doubly sublimed magnesium, the percentage of addition can be increased by 20% in the run employing the lowest ketone concentration by preparing the Grignard reagent with excess methyl bromide. The effect is general for all ketone concentrations and for both grades of magnesium. Also, the purity of magnesium has a significant effect. Methylmagnesium bromide prepared from doubly sublimed magnesium employing an excess of magnesium gave only 72.7% addition at the lowest ketone concentration, while the comparable run with single crystal magnesium gave 88.1% addition. In the latter case the percentage of addition increased to 95% when excess methyl bromide was used. The rate-constant behavior follows the same trend. The greatest variations are found with methylmagnesium bromide prepared from doubly sublimed magnesium while the least variation is found with methylmagnesium bromide prepared from single crystal magnesium. Both factors, *i.e.*, the mode of methylmagnesium bromide preparation and the purity of magnesium, are important in considering the rate data.

A general trend in all the reactions of methylmagnesium bromide with ketones is that at higher ketone concentrations (lower Grignard reagent to ketone ratios), the magnitude of the rate constants decreases as the per cent of addition increases.[2] Because of this trend, it was important to determine if the purity of magnesium used and the mode of preparation employed in the preparation of methylmagnesium bromide had any effect on the reaction of methylmagnesium bromide with excess ketone. A set of experiments similar to those described for excess methylmagnesium bromide with benzophenone was carried out employing an excess of 2-methylbenzophenone with methylmagnesium bromide. The results are given in Table V. The initial rate constants were all identical regardless of the method of preparation of the Grignard reagent or the purity of the magnesium used. In addition, product analysis of selected runs gave 100% yield of addition within the limits of the experiments.

Table V. Product Analysis and Initial Pseudo-First-Order Rate Constants from the Reaction of Methylmagnesium Bromide with 0.46 *M* 2-Methylbenzophenone in Diethyl Ether at 20°

Source of magnesium	Grignard prepared with excess	$[G]_0$	Initial k_{obsd}, sec^{-1}	% addition
Doubly sublimed	Mg	0.00382	0.0110	100
	Mg	0.0126	0.0106	
	Mg	0.0231	0.0109	
	CH_3Br	0.00382	0.0117	100
	CH_3Br	0.0126	0.0112	
	CH_3Br	0.0231	0.0105	
Single crystal	Mg	0.00382	0.00981	100
	Mg	0.0126	0.0105	
	Mg	0.0231	0.0105	
	CH_3Br	0.00382	0.0109	100
	CH_3Br	0.0126	0.0106	
	CH_3Br	0.0231	0.0101	

Table VI. Product Analysis and Pseudo-First-Order Rate Constants from the Reaction of Methylmagnesium Bromide with Benzonitrile in Diethyl Ether at 25°

Source of magnesium	Grignard prepared with excess	$[G]_0$	$10^2[N]_0$	$[G]_0/[N]_0$	10^4k_{obsd}, min^{-1}	$10^3k_{\text{obsd}}/[G]_0$	% addition
Doubly sublimed	Mg	0.0860	0.462	186	2.98	3.46	88.3
	Mg	0.0860	1.38	62	2.61	3.03	95.8
	Mg	0.0860	2.31	37	2.23	2.60	98.6
	CH_3Br	0.0842	0.470	179	4.46	5.30	100
	CH_3Br	0.0842	1.41	60	2.82	3.35	100
	CH_3Br	0.0842	2.35	36	2.16	2.56	100
Single crystal	Mg	0.0837	0.462	181	2.44	2.91	98.0
	Mg	0.0837	1.38	61	2.04	2.44	99.5
	Mg	0.0837	2.31	36	2.07	2.47	99.6
	CH_3Br	0.0835	0.462	181	2.39	2.86	100
	CH_3Br	0.0835	1.38	61	2.26	2.71	100
	CH_3Br	0.0835	2.31	36	2.18	2.61	100
Unmilled single crystal	CH_3Br	0.0858	0.462	186	2.51	2.92	100
	CH_3Br	0.0858	1.38	62	2.39	2.78	100
	CH_3Br	0.0858	2.31	37	2.22	2.59	100

The mechanism of the addition of Grignard reagents to nitriles also has been the subject of considerable interest in recent years.[14] Although no previous pseudo-order kinetic study employing either a large excess of Grignard reagent or nitrile has been described, we have recently completed such a study involving the reaction of methylmagnesium bromide with benzonitrile.[12] It was found during the course of this study that when the Grignard reagent was prepared from triply sublimed magnesium employing an excess of magnesium, pseudo-first-order rate constants (using excess methylmagnesium bromide) were dependent on the initial benzonitrile concentration. In addition, an unidentified by-product was formed in yields up to 13%. Since this behavior is similar to that found in the reaction of excess methylmagnesium bromide with benzophenone, an evaluation study similar to that previously described for the reaction of methylmagnesium bromide with benzophenone was undertaken concerning the reaction of excess methylmagnesium bromide with benzonitrile. The results are given in Table VI.

The results obtained from the reaction of excess methylmagnesium bromide with benzonitrile parallel those found for the reaction with benzophenone. Perhaps the most striking feature of the results obtained with benzonitrile is the fact that when the Grignard reagent is prepared employing an excess of magnesium, both single crystal magnesium and doubly sublimed magnesium give some side reaction with benzonitrile. On the other hand, Grignard reagents prepared from either doubly sublimed magnesium or single crystal magnesium employing an excess of methyl bromide give 100% addition in the reaction with benzonitrile. As in the benzophenone case, the best results in the reaction of methylmagnesium bromide with benzonitrile (considering both the % addition as well as the constancy of the rate constant) were obtained when the Grignard reagent was prepared from single crystal magnesium employing an excess of methyl bromide. In this case no by-product was detected and the pseudo-first-order rate constants were essentially independent of the initial benzonitrile concentration.

A set of experiments similar to those described for excess methylmagnesium bromide with benzonitrile was carried out employing an excess of benzonitrile with methylmagnesium bromide. The results are given in Table VII. The data indicate that the purity of magnesium employed in the preparation of the Grignard reagent and the method of preparation of the Grignard reagent have no effect on the rate data ob-

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Table VII. Pseudo-First-Order Rate Constants from the Reaction of Methylmagnesium Bromide with Excess Benzonitrile in Diethyl Ether at 25°

Source of magnesium	Grignard prepared with excess	$[N]_0$	$[G]_0$	10^4k_{obsd}, min^{-1}	$10^3k_{obsd}/[N]_0$
Doubly	Mg	0.113	0.00436	2.70	2.40
sublimed	CH_3Br	0.113	0.00467	2.81	2.49
Single	Mg	0.108	0.00444	2.61	2.42
crystal	CH_3Br	0.108	0.00463	2.54	2.35

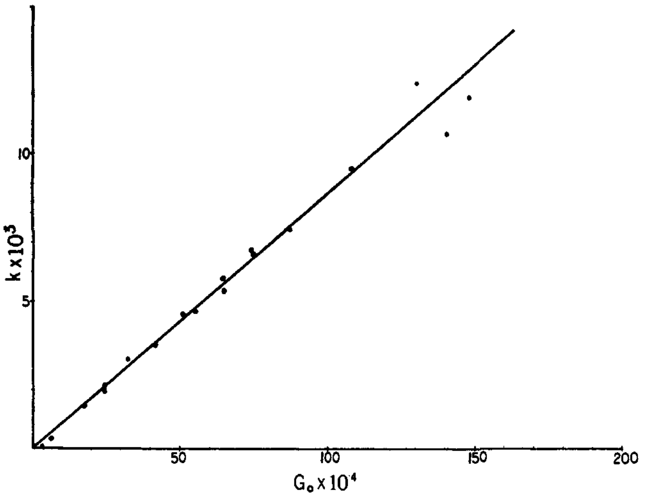


Figure 2. Graphical test for the proposed mechanism in the reaction of methylmagnesium bromide prepared from ultrapure magnesium with benzophenone.

Table VIII. Pseudo-First-Order Rate Constants for the Reaction of 0.00243 *M* Methylmagnesium Bromide Prepared from Ultrapure Magnesium with Benzophenone in Diethyl Ether at 25°

$10^5[K]_0$	10^3k_{obsd}, sec^{-1}
3.42	2.08
6.25	1.95
9.35	2.07
13.0	2.16

tained with excess benzonitrile. These results are consistent with rate data gathered employing an excess of ketone. The overall data indicate that the problems encountered in reactions employing a large excess of methylmagnesium bromide are due to minor impurities in the Grignard reagent which play a significant role under these conditions. When limited amounts of the Grignard reagent are employed, the role of the minor impurities on the course of the reaction is insignificant.

Results with Ultrapure Magnesium. Two standard solutions of methylmagnesium bromide were prepared from two small chunks (~1 g each) of ultrapure magnesium[11] employing an excess of methyl bromide. Reaction solutions from each of the standard methylmagnesium bromide solutions gave identical results.

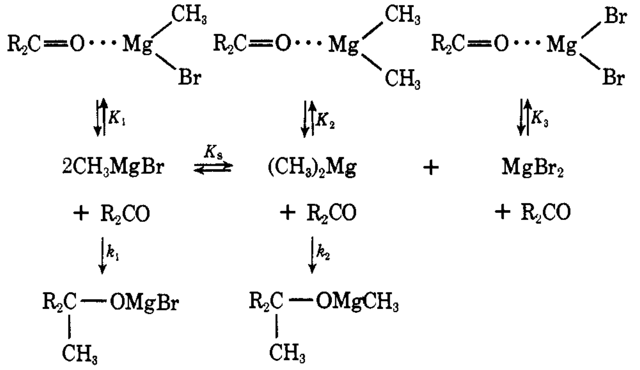
Two features of the reaction of methylmagnesium bromide with benzophenone under pseudo-first-order conditions (using excess methylmagnesium bromide) are different when the Grignard reagent is prepared from ultrapure magnesium. First, side reactions found in other cases are essentially eliminated and the normal addition product is formed in 98.5–100% yield. Secondly, the pseudo-first-order rate constants are independent of the initial ketone concentration at constant Grignard reagent concentration (Table VIII).

The large percentage of addition and the well-behaved pseudo-first-order rate constants observed in the reaction of benzophenone with methylmagnesium bromide prepared from ultrapure magnesium allow the data from this reaction to be analyzed in terms of a specific mechanism. Several experiments were carried out in which the initial concentration of methylmagnesium bromide was varied between 0.000324 and 0.0148 *M*.

The data are consistent with the mechanism established earlier.[2i,k] Equation 1 relates the observed rate

$$k_{obsd} = \frac{(k_2K_s^{1/2} + k_1)[G]}{1 + 2K_s^{1/2} + K_1[G] + K_3K_s^{1/2}[G]} \qquad (1)$$

constant to the concentration of Grignard reagent in the kinetic experiments. All available evidence indicates that K_1 and K_3 are small, *ca.* 1–4.[2c–3,i,k] Thus, in



our experiments $[G]_0 < 0.014$ *M*, $K_1[G]$ and $K_3[G]$ are much smaller than one, and eq 1 reduces to eq 2, which

$$k_{obsd} = \frac{(k_2K_s^{1/2} + k_1)[G]}{1 + 2K_s^{1/2}} = k[G] \qquad (2)$$

predicts that a plot of k_{obsd} *vs.* [G] should give a straight line which intersects the origin. Figure 2 shows indeed that a plot of k_{obsd} *vs.* [G] does give such a straight line. Equation 2 also predicts that $k_{obsd}/[G]_0$ for all experiments should give a constant, k, the apparent second-order rate constant for the reaction of methylmagnesium bromide Grignard with benzophenone. The best value for k is 0.87 l. mol^{-1} sec^{-1}. This value is somewhat lower than values obtained with other grades of magnesium, *ca.* 1.2 l. mol^{-1} sec^{-1} (Table IV). The result is not surprising in view of the fact that in all cases studied, kinetic runs which had the lowest per cent of side reaction also had the smallest pseudo-first-order rate constants (Tables II and IV). Thus, methylmagnesium bromide prepared from ultrapure magnesium which gives 100% addition with benzophenone also gives the smallest pseudo-first-order rate constants at comparable Grignard reagent concentrations.

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

Chromium Atoms in Organometallic Synthesis

P. S. Skell,* D. L. Williams-Smith, and M. J. McGlinchey

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received September 1, 1972

Abstract: Cocondensation of atomic chromium vapor with organic substrates at −196° at pressures below 10^{-4} Torr yields organochromium complexes. It is possible to synthesize not only bis(cyclopentadienyl)chromium, but also bis(arene)chromium compounds in which the arenes contain highly electronegative substituents. Chromium atoms trimerize acetylenes to benzenes, isomerize 1-butene to a mixture of 2-butenes, and also form complexes with 1,3-butadiene and with propene. The mode of complexation in the latter two cases has been investigated by deuterolysis studies.

The use of high-temperature species as synthetic reagents has been developed over the past decade,[1] and some areas within this field have been reviewed.[2,3] The use of transition metal atoms is of much more recent vintage and has allowed the direct synthesis of a number of organometallic complexes, previous routes to which were cumbersome.[4,5] Furthermore, it has proved possible to isolate at low temperatures several interesting and unstable compounds whose existence had only been inferred through mechanistic studies.[6,7]

Chromium vapor, generated from a resistively heated crucible in an evacuated apparatus similar to that used for the reactions of carbon vapor,[1] is predominantly monoatomic. The chromium atoms thus produced, when cocondensed with a variety of unsaturated hydrocarbons at −196°, react to yield isolable organochromium complexes.

Sandwich Compounds. Cocondensation of chromium atoms with an excess of cyclopentadiene monomer yields, after removal of the excess substrate, volatile red crystals of chromocene, which was identified by its mass spectrum and melting point.

Arenes react with chromium atoms to give good yields of bis(arene)chromium complexes. Bis(benzene)chromium had previously been synthesized directly in this manner,[4] but the scope of the reaction has now been extended to include not only bis(alkylbenzene)chromium but also bis(halobenzene)chromium compounds. Conventional methods of making bis(arene)chromium complexes fail when the arene possesses a strongly electron-withdrawing substituent, presumably attributable to the low π-electron density of the aromatic ring.[8] Nevertheless, using the cocondensation procedure chlorobenzene, fluorobenzene, and even *p*-difluorobenzene successfully formed bis(arene)chromium compounds. Tetrafluorobenzene failed to yield a compound thermally stable at room temperature.

The bis(alkylbenzene)chromium compounds are sufficiently volatile to be pumped out of the reaction flask over a several-hour period and collected directly for spectroscopic analysis. The bis(halobenzene)chromium complexes are also volatile but possess sufficient air stability to allow their extraction using benzene or toluene. Yields quoted are of pure isolated complex and vary from 12 to 60% depending on the substituents.

The ^{1}H nmr spectra of these complexes are rationalizable in terms of increased shielding since the ring current is drastically reduced on complexation to a transition metal; thus the peaks are shifted upfield with respect to those exhibited by the free ligand (see Table I). The mass spectra of these compounds exhibit moderate to strong parent ions, and the major fragmentation pattern appears to involve stepwise loss of the intact aromatic rings as shown in Table II.

Preliminary experiments with cycloheptatriene indicate the formation of the extremely air- and temperature-sensitive chromium sandwich compound, but the identification is based solely on mass spectral data and must remain tentative until a more definitive nmr spectrum is available. Treatment of the low temperature reaction matrix with PF_3 failed to produce the expected $(C_7H_8)Cr(PF_3)_3$ analogous to the known $(C_7H_8)Cr(CO)_3$.[9]

Acetylenes. The trimerization of acetylenes by metal atoms has previously been reported for nickel,[6] and it has now been demonstrated using chromium atoms. 2-Butyne is trimerized to hexamethylbenzene, and terminal acetylenes such as 1-butyne (or 1-pentyne) yield isomeric mixtures of 1,2,4- and 1,3,5-triethyl- (or tripropyl-) benzenes. The yields, however, are not catalytic, and dark green involatile residues remain in the reaction flask after sublimation or solvent extraction of the benzenes. Nmr investigations of these residues

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