Organometallic Reaction Mechanisms. XI. Mechanism of Dimethylmagnesium Addition to Benzonitrile[1]

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Abstract: The reaction of dimethylmagnesium with benzonitrile in diethyl ether at 25° was examined in detail. Kinetic studies carried out under pseudo-first-order conditions using either excess dimethylmagnesium or excess nitrile were successful in determining the integral order behavior of both the dimethylmagnesium and the benzonitrile. The reaction was found to be first order in benzonitrile and first order in dimethylmagnesium. A mechanistic description for this reaction can be found in eq 7–9.

Little is known concerning the mechanism of reaction of dialkylmagnesium compounds with nitriles. Becker[2] reported that diethylmagnesium in THF reacts with benzonitrile; however, only 50% of the ethyl groups participated in the reaction and the remaining groups failed to give a positive Gilman test. In addition, Becker reported two distinct rates of reaction for the alkyl groups that did react. Since dialkylmagnesium compounds make a contribution to the total description of the Grignard reagent and contribute to the total rate of the reaction of Grignard reagents with organic substrates such as nitriles, it is important to have an understanding of the kinetics of the reaction of a typical dialkylmagnesium compound with a representative nitrile. For this reason, a kinetic study of the reaction of dimethylmagnesium with benzonitrile in diethyl ether, parallel to that conducted with the Grignard reagent,[3] was carried out.

Benzonitrile and dimethylmagnesium were chosen as reactants in order to eliminate certain side reactions known to occur with other nitriles and other organomagnesium compounds. Since no α hydrogen exists on benzonitrile, enolization cannot occur as a side reaction and since no β hydrogen exists on dimethylmagnesium, reduction cannot occur as a side reaction. The expected reaction product is $C_6H_5C(CH_3)NMgCH_3$ before hydrolysis and acetophenone after hydrolysis. Because diethyl ether is the most common solvent for Grignard compounds and because dimethylmagnesium is associated in this solvent at concentrations $>0.1\ m$, the kinetic studies were carried out in diethyl ether at $(CH_3)_2Mg$ concentrations $<0.1\ m$.

Experimental Section

Chemicals. Eastman Spectrograde benzonitrile was distilled under vacuum over solid methylmagnesium bromide. *n*-Tetradecane (Chemical Samples, 99.9% purity), used as an internal standard, was dried and distilled at 55° and 0.02 mm pressure from Linde 4A Molecular Sieves. Acetophenone (Eastman) was distilled from a spinning band distillation column under vacuum. It was used as a standard to identify the reaction product. Dimethylmercury (Strem Chemicals) was used without further purification. Diethyl ether (Fisher Anhydrous) was distilled under nitrogen from $LiAlH_4$ through a 60-cm distilling column packed with glass rings.

Preparation of Dimethylmagnesium. An excess of magnesium (single crystal, Ventron Corp.) turnings (2.7 g, 0.11 g-atom) was stirred overnight with dimethylmercury (5.9 ml, 0.075 mol) in the drybox. The resulting dimethylmagnesium was extracted with diethyl ether and stored in a glass flask equipped with a three-way Teflon stopcock. Diethyl ether solutions of $(CH_3)_2Mg$ are clear and colorless. Analysis of dimethylmagnesium was carried out by both Gilman and EDTA titrations and gave a C–Mg/Mg ratio of 2.006:1.000. The thioacetamide test for ionic mercury on hydrolyzed samples of $(CH_3)_2Mg$ was negative.

Instrumentation and Apparatus. An inert atmosphere box equipped with a recirculating system[4] to remove moisture and oxygen was used during the manipulations of air-sensitive reagents. As an added precaution, a special line of prepurified nitrogen was available in the glove box in order that all materials could be transferred in Schlenk tubes under a blanket of prepurified nitrogen.[5]

All visible and ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. A Zeiss PMQ II single beam spectrophotometer was employed for making absorbance measurements for the kinetic studies. Matched quartz cells (Beckman, 10.0 mm) equipped with a 1 mm bore two-way Kimax micro Teflon stopcock and Zeiss, 1.00-mm cells were used for all ultraviolet measurements. A Sargent constant-temperature water bath was used (±0.02°) for the kinetic solutions. The kinetic flasks were fabricated by sealing a three-way Teflon stopcock to the top of a 100-ml heavy-walled glass bulb. The syringes used for transfer of the samples were calibrated with stainless steel needles. Deliveries could be reproduced to ±0.5%. Variable-temperature nmr spectra were obtained using a Jeol 100-MHz nmr spectrometer. The nmr tubes were loaded in the drybox, TMS was added, and then the tubes were capped for sealing outside of the drybox.

Analyses. All solutions were analyzed for magnesium by titration with EDTA. The concentration of basic magnesium bonded to carbon was determined by adding a known excess amount of acid and back-titration with standard base using phenolphthalein as an indicator (Gilman titration). Glpc analyses were performed using 6-ft matched stainless steel columns of 10% FFAP on 80–100 mesh Diatoport S. Synthetic mixtures containing known amounts of *n*-tetradecane, benzonitrile, and acetophenone were prepared in diethyl ether and subjected to gas chromatography to give the relationship, (mol of nitrile)/(mol of *n*-tetradecane) = 1.95(area nitrile)/(area *n*-tetradecane) and (mol of nitrile)/(mol of ketone) = 1.048(area nitrile)/(area ketone). The retention times for *n*-tetradecane (internal standard), benzonitrile, and acetophenone are 6, 18, and 23 min at a column temperature of 105°, injection port and detector temperature of 230°, and a flow rate of 40 ml/min.

Product Yield Study. Since previous workers[2] reported that only 50% of the alkyl groups react when diethylmagnesium was allowed to react with benzonitrile in THF, benzonitrile and $(CH_3)_2Mg$ were allowed to react in diethyl ether in 1:1 and 2:1 ratios. A 1:1 mole ratio mixture of benzonitrile and dimethylmagnesium was prepared by mixing 50 ml of an ether solution of benzonitrile (8.5629 g, 8.304×10^{-2} mol) with 158 ml of a 0.525 *M* solution of $(CH_3)_2Mg$. Reaction proceeded rapidly to produce the alkylation

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[1] (a) We are indebted to the National Science Foundation (Grant No. Sp-14795) for partial support of this work. (b) This work was abstracted, in part, from the Ph.D. Thesis of L.-C. Chao, Georgia Institute of Technology, 1972.

[2] S. J. Storfer and E. I. Becker, *J. Org. Chem.*, 27, 1868 (1962).

[3] E. C. Ashby, L.-C. Chao, and H. M. Neumann, *J. Amer. Chem. Soc.*, 95, 4896 (1973).

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

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

product in 100% yield within 7 hr. A 2:1 mole ratio mixture was prepared by adding 1 ml of benzonitrile (2.882 *M*) to 2 ml of $(CH_3)_2Mg$ (0.6798 *M*) in 70 ml of diethyl ether. This solution stood at room temperature for 17 days. Analysis of the mixture, after hydrolysis, using an internal standard, showed 90.3% acetophenone and 7.1% benzonitrile.

Kinetic studies were carried out both in excess dimethylmagnesium and excess benzonitrile. The procedures for the studies in excess dimethylmagnesium were similar to those used in excess Grignard reagent.[3]

Kinetic studies in excess benzonitrile were performed in the following fashion. Quartz 10-mm uv cells, glass sealed with a 1 mm bore two-way Kimex Teflon stopcock, were dried by heating, and then transferred to the drybox. Syringes with stainless steel needles, 25-ml volumetric flasks sealed with a three-way Teflon stopcock, and other glassware were transferred to the drybox by routine procedures. The 25-ml flasks and uv cells were purged with prepurified nitrogen *via* a needle before loading the samples. The desired amounts of standard benzonitrile solution and *n*-tetradecane were added under nitrogen flow to the 25-ml volumetric flask which was subsequently diluted to the mark with diethyl ether. A definite amount of standard dimethylmagnesium solution was then added to the 25-ml volumetric flask. The flask was rapidly shaken to ensure mixing. A 4-ml portion of the reaction solution was immediately transferred from the volumetric flask to the uv cell *via* a calibrated syringe. The uv cell and volumetric flask were removed from the drybox as quickly as possible. The uv cell was placed in the constant-temperature compartment of the Zeiss spectrophotometer. The volumetric flask was placed in a constant-temperature water bath. At various time intervals, samples (generally 8–10 in number) were withdrawn from the volumetric flask and quenched in saturated ammonium chloride solution. The quenched reaction mixtures were analyzed for acetophenone by gas chromatography. Simultaneously, 10 sets of time–uv absorbance values were taken for each kinetic experiment.

Fractional Crystallization of the Reaction Product of Dimethylmagnesium Addition to Benzonitrile in Diethyl Ether. To dimethylmagnesium (196 ml, 0.615 *M* solution in diethyl ether), prepared from methylmagnesium bromide by the dioxane precipitation method, was added 400 ml of a dilute solution of benzonitrile (12.42 g, 0.121 mol) in diethyl ether. The resulting reaction mixture was allowed to reflux for 24 hr during which time the color changed from light yellow to dark brown. The resulting solution was allowed to cool to room temperature and fractionally crystallized into two fractions (Table I).

Table I. Fractional Crystallization of the Product from the Reaction of Dimethylmagnesium with Benzonitrile in Diethyl Ether

Fractions	Sample wt, g	Mg, %	Mol wt
1	1.58	11.2	208
2	2.28	11.6	214
Calcd for $C_6H_5C(CH_3)NMgCH_3 \cdot Et_2O$		10.4	231

Ebullioscopic Determination of Molecular Association of $C_6H_5C(CH_3)NMgCH_3$ in Diethyl Ether. Apparent molecular weights were determined ebullioscopically in Et_2O at 740 mm using a modified Cottrell boiling point elevation apparatus. Solvent and samples were introduced through a septum on the apparatus by means of carefully weighed and sealed syringes. Details of the operation of this apparatus with organometallic systems have been presented elsewhere.[6] Calculations were made using eq 1 which was derived

$$i = \frac{W_2M_1}{W_1M_2}\left(\frac{1}{e^{-\Delta T_B M_1/1000K_B} - 1}\right) \qquad (1)$$

in the usual manner by assuming an ideal, but not necessarily dilute, solution. The additional terms include M_2, the formula weight of the solute; M_1, the molecular weight of the solvent (74.12 g for diethyl ether); and K_B, the molal boiling point elevation constant (2.01 for diethyl ether at an internal nitrogen pressure of 740.0 mm). The association data are presented in Figure 1.

Extinction Coefficient of $C_6H_5C(CH_3)NMgCH_3$. A solution (25 ml, 0.111 *M* in diethyl ether) of $C_6H_5C(CH_3)NMgCH_3$ was prepared by the reaction of $(CH_3)_2Mg$ with C_6H_5CN in 2:1 ratio.

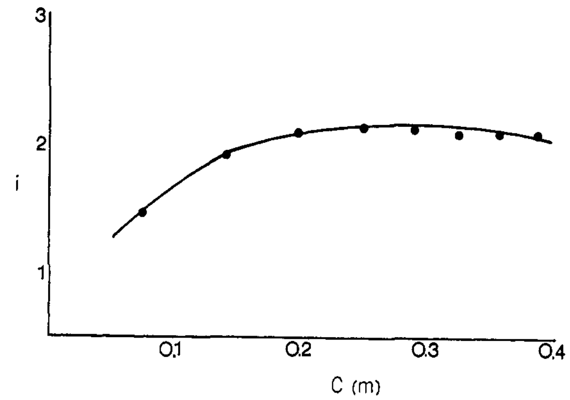

Figure 1. Association of $C_6H_5C(CH_3)NMgCH_3$ in diethyl ether.

The molar extinction coefficient of $C_6H_5C(CH_3)NMgCH_3$ was determined at several concentrations in diethyl ether at 338 mμ. A 4-ml portion of freshly distilled Et_2O was transferred to an uv cell which was sealed with a two-way Teflon stopcock. A measured amount of $C_6H_5C(CH_3)NMgCH_3$ was then added to the uv cell *via* a microliter syringe, and the absorbance measured at 338 mμ. Another measured amount of compound was added to the uv cell, and the absorbance was measured again. The difference between the first absorbance and second absorbance is attributed to the second amount added. This subtraction method avoids hydrolysis errors. The average value of the molar extinction coefficient of $C_6H_5C(CH_3)NMgCH_3$, calculated using Beer's law, is 127 ± 0.4.

Results and Discussion

Structure of the Product. The reaction product of $(CH_3)_2Mg$ with benzonitrile has been investigated by fractional crystallization, molecular association, and nmr. From fractional crystallization, the compound $C_6H_5C(CH_3)NMgCH_3$ in the solid state was found to be associated with one molecule of diethyl ether.

The results of the molecular associaution stdy are shown in Figure 1, where the association constant (*i*) (observed molecular weight/calculated molecular weight) is plotted *vs.* solute concentration (molality). The data show that the compound $C_6H_5C(CH_3)NMgCH_3$ is predominantly monomeric at low concentration, and exists exclusively as dimeric species when the concentration is >0.15 *m*.

The association of organomagnesium compounds in diethyl ether has been reported recently for alkylmagnesium alkoxides as well as thio- and aminomagnesium alkyls. The association is explained on the basis of available empty orbitals on magnesium overlapping with those orbitals of oxygen,[7,8] sulfur,[9] and nitrogen[10] containing nonbonded electron pairs. Previous workers have also pointed out that nitrogen is a better bridging group than halogen or alkyl groups. The structure of the dimer of $C_6H_5C(CH_3)NMgCH_3$, which exists in ether solution, can be represented by A, B, or C. Although structure A is probably the most stable structure, no direct evidence exists to substantiate such a choice.

Recently, Wade and coworkers have also reported that azomethine derivatives of organometallic compounds (M = Li, Be, Al, and B) associate in diethyl

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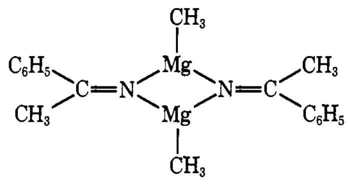
[6] F. Walker and E. C. Ashby, *J. Chem. Educ.*, 45, 654 (1968).

[7] G. E. Coates, J. A. Heslop, M. E. Redwood, and D. Ridley, *J. Chem. Soc. A*, 1118 (1968).

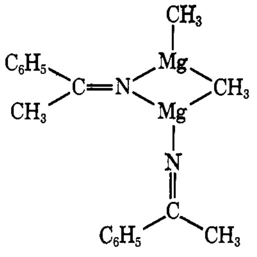
[8] A. G. Pinkus, J. G. Lindberg, and A. Wu, *Chem. Commun.*, 1350 (1969).

[9] G. E. Coates and J. A. Heslop, *J. Chem. Soc. A*, 631 (1968).

[10] G. E. Coates and D. Ridley, *J. Chem. Soc. A*, 56 (1967).



A



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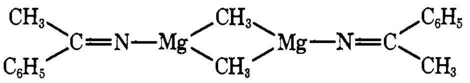
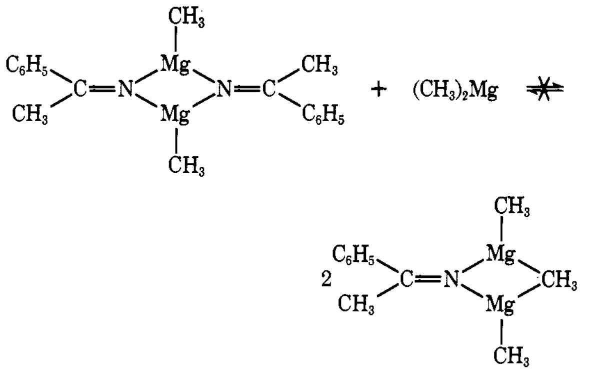


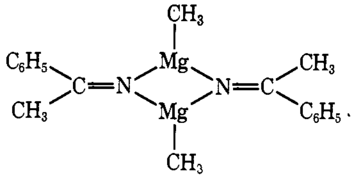
C

ether through a nitrogen bridge.[11] For example, benzonitrile reacts with $(CH_3)_3Al$, $(C_2H_5)_3Al$, $(C_6H_5)_3Al$, and $(CH_3)_2AlCl$ to form 1:1 adducts which rearrange at 130–200° to form $[C_6H_5(CH_3)C{=}N{-}Al(CH_3)_2]_2$, $[C_6H_5CH{=}N{-}Al(C_2H_5)_2]_2$, $[(C_6H_5)_2C{=}N{-}Al(C_6H_5)_2]_2$, and $[C_6H_5(CH_3)C{=}N{-}Al(CH_3)\,Cl]_2$, respectively. The nmr spectra of these compounds support a nitrogen-bridged structure for the dimers.[12]

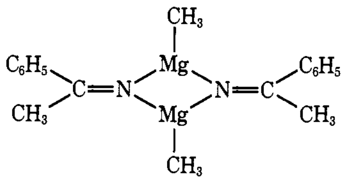
The success of structure determination by nmr spectroscopy of a nitrogen-bridged dimer in the reaction of organoaluminum compounds with nitriles encouraged similar study with organomagnesium compounds. Low-temperature 100-MHz nuclear magnetic resonance spectroscopy was employed in a study of the structure of $C_6H_5C(CH_3)NMgCH_3$. At $-100°$, the nmr spectrum of a 0.4 M solution of $C_6H_5C(CH_3)NMgCH_3$ in ether shows three peaks (τ 11.33, 11.46, and 11.72) attributed to $Mg-CH_3$ groups. The intensity of the peak at τ 11.46 is eightfold larger than those at τ 11.33 and 11.72; the two smaller peaks having approximately equal intensity. Nmr spectra of mixtures of $C_6H_5C(CH_3)NMgCH_3$ and $(CH_3)_2Mg$ have also been observed in the stoichiometry ratio of $C_6H_5C(CH_3)NMgCH_3$ to $(CH_3)_2Mg$ of 1:1, 1:2, and 1:3. In these spectra the chemical shifts of the peaks changed only slightly. The relative ratios of the peaks are nearly constant; only the peak attributed to $(CH_3)_2Mg$ increases as the ratio of $(CH_3)_2Mg$ to $C_6H_5C(CH_3)NMgCH_3$ increases. The spectra reveal that addition of $(CH_3)_2Mg$ does not change the structure of the dimeric species of $C_6H_5C(CH_3)NMgCH_3$ in diethyl ether. Thus, it seems reasonable to assume that the equilibrium represented by eq 2 does not exist.



(2)



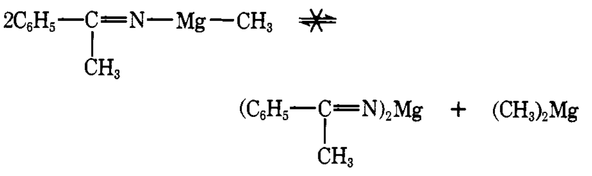
AI(trans)



AII(cis)

The available information suggests that $C_6H_5C(CH_3)NMgCH_3$ is dimeric in diethyl ether at concentrations greater than 0.1 M and possesses structures such as AI and AII. The nmr peak at τ 11.46 which has a relatively large intensity is due to the two equivalent $Mg-CH_3$ groups in a trans structure (AI) and the two smaller peaks at τ 11.33 and 11.72 which have approximately equal intensities are due to the two nonequivalent sets of $Mg-CH_3$ groups in a cis structure (AII).

Kinetics. The kinetic studies in excess $(CH_3)_2Mg$, using gas chromatographic analysis of products, show that benzonitrile and dimethylmagnesium react to form the expected alkylation product $C_6H_5C(CH_3)NMgCH_3$ in quantitative yield without the side reactions of enolization or reduction. The product yield studies show that the same is true when C_6H_5CN and $(CH_3)_2Mg$ react in a 1:1 or 2:1 mole ratio. These studies demonstrate that both groups on $(CH_3)_2Mg$ are reactive, although the second group reacts much more slowly with C_6H_5CN. The ketimine group, by virtue of its steric requirement and its ability to increase the electrophilic character of the magnesium atom, should reduce the tendency of $C_6H_5C(CH_3)NMgCH_3$ to react with nitriles. It also appears unlikely that equilibrium 3 leads to a



$$2C_6H_5-\underset{CH_3}{\underset{|}{C}}=N-Mg-CH_3 \;\not\rightleftharpoons\; (C_6H_5-\underset{CH_3}{\underset{|}{C}}=N)_2Mg + (CH_3)_2Mg \qquad (3)$$

detectable concentration of $(CH_3)_2Mg$. Earlier studies[2] that reported only 50% of the alkyl groups in $(C_2H_5)_2Mg$ react with benzonitrile could be due to the fact that these studies were carried out in tetrahydrofuran, a solvent in which Grignard reactions are known to be slower compared with diethyl ether.

In excess benzonitrile, significant changes occur in the visible and ultraviolet spectra during the course of the reaction. Separate solutions of $(CH_3)_2Mg$ in ether and concentrated solutions of C_6H_5CN show no absorbance at wavelengths longer than 290 mμ. After mixing solutions of $(CH_3)_2Mg$ and C_6H_5CN, a broad band slowly appears in the region of 300–450 mμ and increases with time. The absorbances of reaction mixtures were measured at four different wavelengths (325, 338, 414, and 430 mμ) over a period of 30 days. At 325 and 338 mμ the absorbances increased with time, each finally reaching an almost constant value. At

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[11] (a) R. Snaith, K. Wade, and B. K. Wyatt, *J. Chem. Soc. A*, 380 (1970); (b) C. Summerford and K. Wade, *ibid.*, 2010 (1970); (c) C. Summerford, K. Wade, and B. K. Wyatt, *ibid.*, 2016 (1970); (d) B. Samuel, R. Snaith, C. Summerford, and K. Wade, *ibid.*, 2019 (1970); (e) R. Snaith, C. Summerford, K. Wade, and K. Wyatt, *ibid.*, 2635 (1970).

[12] J. E. Lloyd and K. Wade, *J. Chem. Soc.*, 2662 (1965).

414 and 430 mμ the absorbances increased with time, reached a maximum point, and then decreased steadily (Figure 2). The shapes of these curves suggest a greater complexity to the reaction than expected; at least three reactions must be occurring over the time period shown.

Before meaningful kinetic data could be obtained by uv measurements, it was necessary to determine how these reactions were related to the addition reaction of interest. Accordingly, measurements of both product yield and absorbancy were made on a sample undergoing reaction during the period of time that the absorbancy was rising to its maximum. Small portions of the sample in the uv cell were withdrawn at appropriate time intervals, quenched, and hydrolyzed in saturated NH_4Cl solution, and analyzed for acetophenone by glc. The yield of product and measured absorbancies are reported in Table II.

Table II. Correlation between Absorbance and Percentage of Product in the Reaction of Benzonitrile (0.0900 *M*) with Dimethylmagnesium (2.47×10^{-3} *M*)

Reaction time, min	Absorbance 338 mμ	Absorbance 430 mμ	Product, % Found	Calcd[a]
687	0.346	0.136	37	49
1011	0.680	0.465	43	50
1284	1.034	1.027	38	47
1487	1.632	1.621	36	43
1698	2.20	2.30	<10	39

[a] Product % was computed according to eq 5.

The fact that the absorbancies increase during a period of time when the percentage of product decreases reveals that the strong absorbance in the latter stage of the reaction is not due to the main product but to condensation products[13] which have high molar extinction coefficients.

Since the initial reaction is the one of greatest interest, the rate during the first 30% of the reaction was measured. Two methods were used. The first was a spectrophotometric method, utilizing measurements at 338 mμ. The molar extinction coefficient, ϵ, of the initial product, $C_6H_5C(CH_3)NMgCH_3$, was determined independently. If reaction proceeded solely to this product the final absorbancy, A_f, would be $A_f = \epsilon C$, where C is the initial concentration of dimethylmagnesium. Plots of log $(A_f - A)$ *vs.* t were linear, as expected, during the early stages of the reaction, and from the slopes of these lines the pseudo-first-order rate constant,[14] k_N, were determined.

The second method was carried out simultaneously with the first. Individual samples of the reaction mixture were withdrawn at appropriate time intervals and quenched in saturated ammonium chloride; the amount of acetophenone was measured by glc. Table III reports pseudo-first-order rate constants that demonstrate the reaction is first order in $(CH_3)_2Mg$. The constancy of $k_N/[N]_0$ demonstrates that the reaction is also first order in nitrile. The agreement in the values obtained by the two methods is satisfactory.

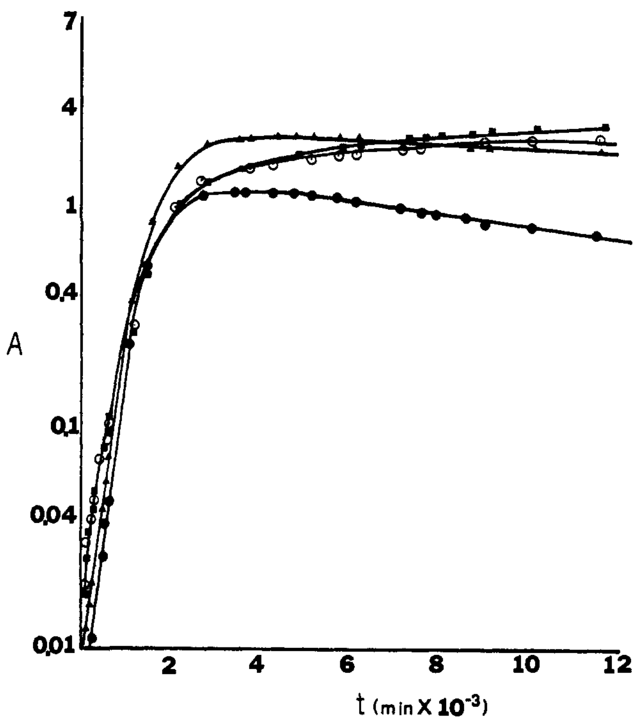

Figure 2. The absorbance of the reaction mixtures of dimethylmagnesium with excess benzonitrile at different wavelengths: (○) at 325 mμ; (■) at 338 mμ; (▲) at 414 mμ; (●) at 430 mμ.

Table III. Rate Constants for Reaction of $(CH_3)_2Mg$ with Excess Benzonitrile at 25°

Run	$[(CH_3)_2Mg]_0$	$[C_6H_5CN]_0$	$k_N/[N]_0 \times 10^2$ l. mol^{-1} min^{-1} by glc	$k_N/[N]_0 \times 10^2$ l. mol^{-1} min^{-1} by uv at 338 mμ
1	0.00158	0.0334	1.95	1.81
2	0.00267	0.0660	1.87	1.79
3	0.00267	0.100	1.76	1.74
4	0.00267	0.125	1.74	1.76
5	0.00267	0.168	1.99	1.82
6	0.00267	0.188	1.86	1.78
7	0.00267	0.213	2.08	1.72
			Av 1.89 ± 0.10	1.77 ± 0.03

Although the later stage of the reaction was not the major interest in this work, the uv absorbancy data were analyzed at 430 mμ. The absorbancy first increased with time to a maximum value, and then decreased steadily. In the very late stage of the reaction, plots of log Abs *vs.* time were linear for each run. An observed first-order rate constant, k_3, could then be extracted from this portion of each reaction. The line defining k_3 was extrapolated to zero reaction time and from its value at appropriate times was subtracted the measured absorbancy. Plots of log (extrapolated line − Abs) *vs.* time resolved into another first-order straight line with curvature at the initial stage. The line defining k_2 was extrapolated to zero reaction time and from its value was subtracted the values on the curve k_2. Plots of log [extrapolated line k_2 − (extrapolated line k_3 − Abs)] *vs.* time resolved into a third first-order component, k_1. The resolution of k_1, k_2, and k_3 for a specific experiment is demonstrated in

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[13] A. A. Scala, M. M. Bikales, and E. I. Becker, *J. Org. Chem.*, **30**, 303 (1965).

[14] For reaction in excess nitrile, the pseudo-first-order rate constant is designated k_N; for reaction in excess dimethylmagnesium, the pseudo-first-order rate constant is designated k_D.

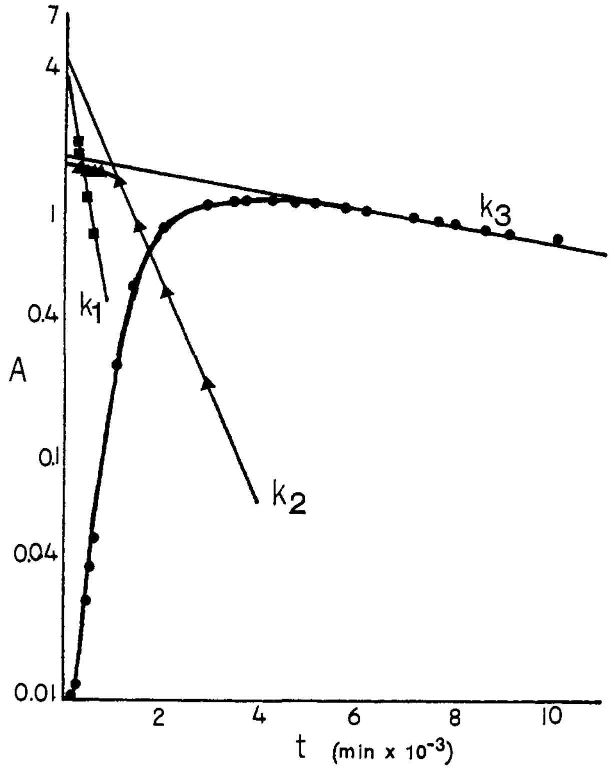

Figure 3. Demonstration of reaction rates in the reaction of dimethylmagnesium with excess benzonitrile at 430 mμ.

Figure 3. The results obtained from this mode of analysis are summarized in Table IV.

Table IV. Observed Rate Constants for the Organometallic Species Involved in the Reaction of 8.22 × 10^{-4} *M* $(CH_3)_2Mg$ with Varying Excess of Nitrile at 430 mμ

Run	$[C_6H_5CN]_0$	$k_1/[N]_0 \times 10^2$ l. mol^{-1} min^{-1}	$k_2/[N]_0 \times 10^3$ l. mol^{-1} min^{-1}	$k_3/[N]_0 \times 10^4$ l. mol^{-1} min^{-1}
8	0.0346	1.79	8.96	6.91
9	0.0461	1.64	9.10	7.07
10	0.0900	1.76	8.80	6.60
11	0.113	1.92	8.07	5.67
12	0.140	1.66	7.87	6.25
13	0.205	1.83	8.35	
14	0.298	1.83	9.06	
15	0.460	1.79	8.15	6.33
		Av 1.78	8.55	6.47

If this analysis is correct, it suggests a series of pseudo-first-order reactions involving three products. Support for this view is provided by the consistency of the

$$(CH_3)_2Mg \xrightarrow[k_1]{C_6H_5CN} P_1 \xrightarrow[k_2]{C_6H_5CN} P_2 \xrightarrow[k_3]{C_6H_5CN} P_3 \qquad (4)$$

results in Table IV as the C_6H_5CN concentration is varied from 0.0346 to 0.460 *M*, and by the excellent agreement of the value of $k_1/[N]_0$ with the values of $k_N/[N]_0$ shown in Table III.

Each step of the reaction is first order in the appropriate organometallic species, *i.e.*, $(CH_3)_2Mg$, P_1, or P_2, and first order in C_6H_5CN. The product P_1 was shown to be $C_6H_5C(CH_3)NMgCH_3$ by gas chromatography. The product P_2 must be a condensation product that does not give acetophenone on hydrolysis, in order to account for the product yield shown in Table II. Using this assumption, and the rate constants k_1 and k_2 from Table IV, the expected yield of acetophenone was calculated from the eq 5. The values are

$$\frac{[P_1]}{[D]_0} = \frac{k_1}{k_1 - k_2}(e^{-k_2 t} - e^{-k_1 t}) \qquad (5)$$

shown in the last column of Table II. The structures of P_2 and P_3 are unknown.

A detailed study of the reaction of C_6H_5CN with excess $(CH_3)_2Mg$ was undertaken. The kinetic data were obtained by quenching individual samples of the reaction mixture in saturated NH_4Cl solution at appropriate intervals of time and measuring the amount of nitrile in each sample by gas chromatographic analysis. Samples were taken over the range 5–80% reaction. In each kinetic experiment the amount of nitrile decreased in a first-order fashion. The pseudo-first-order rate constant, k_D, was computed according to eq 6, where $[C]_0$ and $[C]$ are the initial concentration and

$$k_D = \frac{1}{t}\ln\frac{[C]_0}{[C]} = \frac{1}{t}\ln\frac{100}{x} \qquad (6)$$

the concentration at time, *t*, respectively, and *x* is the per cent of unreacted nitrile.

In the first set of experiments the rate constant was determined at a constant concentration of $(CH_3)_2Mg$ while the initial C_6H_5CN concentration was varied over better than a fourfold range. Surprisingly, the rate constant was found to depend on the initial concentration of C_6H_5CN (Table V). This result can be rationalized by assuming that the reaction rate with C_6H_5CN concentration below 10^{-3} *M* is affected by impurities in the magnesium.[15] Transition metal impurities in the magnesium used are iron, cobalt, and nickel each of which is present in less than 2 ppm. In 0.0445 *M* $(CH_3)_2Mg$, the concentration of each impurity could then be about 10^{-7} *M*. In the remaining kinetic studies, the concentration of C_6H_5CN employed was higher than 10^{-3} *M*, since under these conditions the rate constant seems to be independent of the concentration of C_6H_5CN.

Table V. Rate Constants for the Reaction of $(CH_3)_2Mg$ at Constant Concentration (0.0445 *M*) with a Variable Concentration of Benzonitrile

Run	$[C_6H_5CN]_0 \times 10^4$, *M*	$k_D \times 10^4$, min^{-1}
16	5.1	10.59
17	10.2	6.09
18	15.4	4.56
19	19.8	4.57
20	22.0	4.44

In Table VI the results of experiments are summarized in which the concentration of $(CH_3)_2Mg$ (in excess) is varied. Comparison of the values of $k_D/[(CH_3)_2Mg]_0$ with the bimolecular rate constant, 1.77 × 10^{-2} l. mol^{-1} min^{-1}, obtained from the studies in excess benzonitrile, indicates that $(CH_3)_2Mg$ is not solely present as monomer. This conclusion agrees with association studies of dimethylmagnesium in diethyl ether solution re-

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(15) E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **94**, 5421 (1972); E. C. Ashby, H. M. Neumann, F. W. Walker, J. Laemmle, and L. Chao, *J. Amer. Chem. Soc.*, **95**, 2597 (1973).

Table VI. Rate Constants for the Reaction of Benzonitrile with Excess Dimethylmagnesium

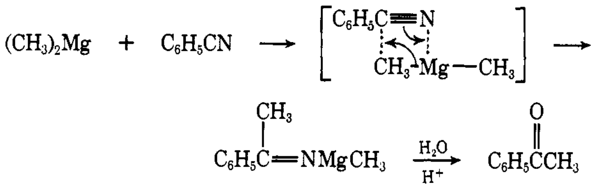
Run	$[(CH_3)_2Mg]_0$	$[C_6H_5CN]_0 \times 10^3$	$k_D \times 10^4$ min^{-1}	$k_D \times 10^2/[(CH_3)_2Mg]_0$, l. mol^{-1} min^{-1}	$[M]_0 \times 10^2$	i
21	0.101	1.34	9.26	0.915	5.23	1.33
22	0.0882	1.39	7.94	0.900	4.49	1.32
23	0.0737	1.40	7.02	0.952	3.96	1.30
24[a]	0.0562	1.46	6.04	1.08	3.42	1.24
b	0.0444		4.28	0.964	2.42	1.29
26	0.0351	1.51	3.66	1.05	2.07	1.25

[a] Contained $PhC(CH_3)NMgCH_3$ of which concentration was 1.50×10^{-3} *M*. [b] The average of runs 18 and 25.

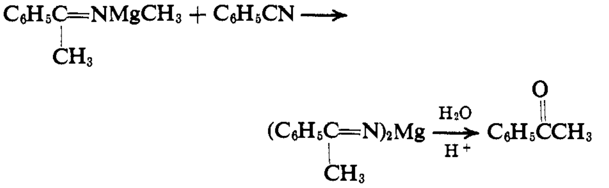
ported earlier.[16] At 0.1 *M*, the association constant, i, for $(CH_3)_2Mg$ in ether solution is 1.33. This means that at this concentration the $(CH_3)_2Mg$ solution contains monomer and some associated species. Due to the small value of i, it seems reasonable to assume that the equilibrium is between monomer and dimer, with the higher associated species in negligible amount. If we assume that reaction occurs only through the monomeric species, and that the bimolecular rate constant is 1.77×10^{-2} l. mol^{-1} min^{-1}, the concentration of monomer, $[M]_0$, can be calculated from the value of k_D. Values of $[D]_0$ and i can be calculated from this model. The results of these calculations are shown in Table VI. The i values are in good agreement with values obtained from the association study;[16] $i = 1.11$ at 0.0168 *M* $(CH_3)_2Mg$, and $i = 1.39$ at 0.0609 *M*. These results indicate that, at most, only a small amount of reaction proceeds through dimer.

An interesting practical observation has emerged from this work. In the product yield studies using a 2:1 ratio of benzonitrile to $(CH_3)_2Mg$, more than 50% of addition product was ultimately obtained, while in the kinetic study of Table II the maximum yield of addition product never reached 50%. The difference cannot arise merely because the benzonitrile is in large excess in the latter case, since the two competing reactions forming condensation product I and $(C_6H_5C(CH_3){=}N)_2Mg$ are each first order in C_6H_5CN. The important difference in the two kinds of experiments is the concentration, and hence the form, of the initial product $C_6H_5C(CH_3){=}NMgCH_3$. In the kinetic experiment the product would be present as monomer, in which form it reacts quite readily to give condensation product I. In the product yield studies, the initial product is present principally as dimer, which apparently does not react as rapidly to give condensation products as the monomer and hence produces more $(C_6H_5C(CH_3){=}N)_2Mg$ which on hydrolysis produces the addition product acetophenone. These conclusions suggest that, from a preparative point of view, the yield of addition products relative to condensation products is improved by increasing the concentration of the dialkylmagnesium reagent, even at low ratios of reactants.

According to all the information presented, the detailed mechanism describing the reaction of dimethylmagnesium with benzonitrile in diethyl ether is shown in eq 7. When the C_6H_5CN to $(CH_3)_2Mg$ ratio is 2:1,

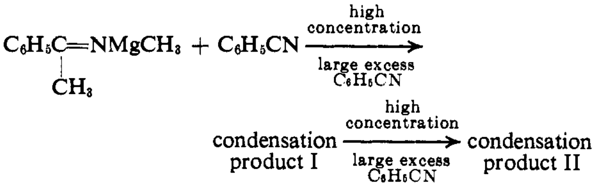

(7)

the intermediate $C_6H_5C(CH_3){=}NMgCH_3$ reacts further with C_6H_5CN although at a slower rate than the reaction of $(CH_3)_2Mg$ with C_6H_5CN (eq 8). In the



$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NMgCH_3 + C_6H_5CN \longrightarrow (C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}{=}N)_2Mg \xrightarrow[H^+]{H_2O} C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}CH_3 \quad (8)$$

presence of a large excess of C_6H_5CN and at higher concentrations than that used in (8), substantial amounts of condensation products are produced in addition to the products produced in the sequence of reactions shown above (eq 7 and 8).



$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NMgCH_3 + C_6H_5CN \xrightarrow[\text{large excess } C_6H_5CN]{\text{high concentration}} \begin{matrix}\text{condensation}\\ \text{product I}\end{matrix} \xrightarrow[\text{large excess } C_6H_5CN]{\text{high concentration}} \begin{matrix}\text{condensation}\\ \text{product II}\end{matrix} \quad (9)$$

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[16] F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969).