Organometallic Reaction Mechanisms. XII. Mechanism of Methylmagnesium Bromide Addition to Benzonitrile[1]

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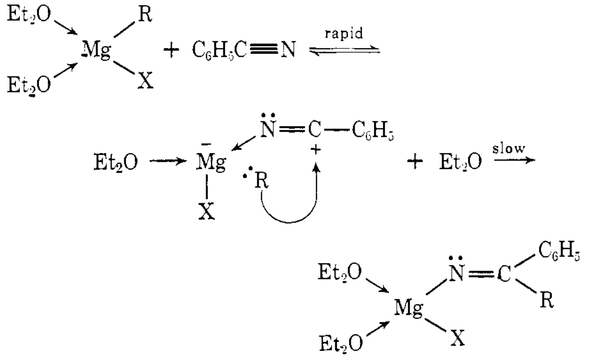
Abstract: The kinetics of the reaction of methylmagnesium bromide with benzonitrile in diethyl ether at 25° was examined in detail in both excess Grignard reagent and excess nitrile. The reaction was found to produce, on hydrolysis, the alkylation product acetophenone in quantitative yield when the Grignard reagent was prepared from single crystal magnesium. The kinetic data of the reaction show a second-order reaction, first order in Grignard reagent and first order in nitrile. The results of rate studies in the presence of added $MgBr_2$ show that the reaction of the Grignard reagent with benzonitrile occurs through both the $(CH_3)_2Mg$ and CH_3MgBr species. All of the accumulated information is consistent with a mechanism which follows two reaction paths. One path involves reaction of benzonitrile with CH_3MgBr species, whereas the other path involves reaction of benzonitrile with $(CH_3)_2Mg$ to form $C_6H_5C(CH_3)NMgCH_3$ which subsequently and rapidly redistributes with $MgBr_2$ to form the final product $C_6H_5C(CH_3)NMgBr$ and methylmagnesium bromide. The detailed mechanism of this reaction is given in Scheme I in the main body of this paper.

The mechanism of Grignard reagent addition to nitriles has been the subject of considerable study for 3 decades. In spite of efforts on the part of several groups, there appears to be no general agreement concerning the exact mechanism of this reaction. The history of the controversy surrounding this area has been intertwined with the controversy concerning the composition of Grignard reagents in ether solvents,[2] since it is necessary to know the nature of the reactive species in solution before an exact mechanism can be described.

Several mechanisms have been proposed to describe Grignard compound addition to nitriles. The first kinetic study was reported by Swain, who investigated the reaction of *n*-butylmagnesium bromide with benzonitrile.[3] Swain found the reaction to be second order overall and suggested that the mechanism which best fits the data involved rapid complexation of monomeric $n\text{-}C_4H_9MgBr$ with benzonitrile followed by a slower rearrangement to form the intermediate product (eq 1).



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Although the mechanism suggested by Swain is compatible with the reported data, there are a number of weaknesses to the study which continue to leave the mechanism in doubt. The following criticisms appear valid: (1) only four kinetic runs were reported and the concentrations of each reactant and their relative ratios were not widely varied; (2) the kinetic solutions were not homogeneous; (3) the concentration of the Grignard reagent was such that a large percentage of the species present in solution would be associated,[2] although the species present were assumed to be monomeric; (4) the reactions were followed by analyzing for unreacted Grignard reagent and no attempt was made to verify the nature of the product formed. Although Swain was the first worker to propose the formation of an intermediate complex prior to the alkylation step, no direct evidence was given to support its existence. Also, it was not possible for Swain to designate from his data the nature of the reactive species (RMgX, R_2Mg, $R_2Mg\cdot MgX_2$) or the exact nature of alkyl transfer.

Later, Vekemans and Bruylants[4] in 1958 repeated Swain's work by following the reaction spectrophotometrically. Bruylants claimed his method of analysis to be more precise than the gasometric method used by Swain and obtained a rate constant 3.5×10^{-4} l. mol^{-1} sec^{-1} for the reaction of benzonitrile with *n*-butylmagnesium bromide at 25°. The spectrophotometric method of analysis was also applied to a kinetic study of the reaction of pivalonitrile with a tenfold excess of ethylmagnesium bromide. The reaction was described as homogeneous and second order with a rate constant of 3.1×10^{-5} l. mol^{-1} sec^{-1} at 25°. Bruylants essentially supported the mechanism proposed by Swain.

The next major development in this area was a direct result of a report in 1957 describing the composition of Grignard reagents in terms of the unsymmetrical dimeric species ($R_2Mg\cdot MgX_2$).[5] Sometime later, Storfer and Becker[6] adopted the unsymmetrical dimeric structure ($R_2Mg\cdot MgX_2$) for the Grignard reagent to describe Grignard compound addition to nitriles and rejected the Swain mechanism which had proposed monomeric RMgX as the reactive species. Storfer and

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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 Li-Chung Chao, Georgia Institute of Technology, 1972.

[2] E. C. Ashby, *Quart. Rev., Chem. Soc.*, **21**, 259 (1967).

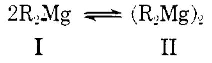
[3] C. G. Swain, *J. Amer. Chem. Soc.*, **69**, 2306 (1947).

[4] J. Vekemans and A. Bruylants, *Bull. Soc. Chim. Belg.*, **68**, 541 (1959).

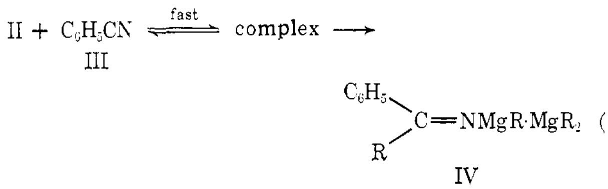
[5] R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Amer. Chem. Soc.*, **79**, 3476 (1957).

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

Becker investigated the kinetics of the reaction of both ethylmagnesium bromide and diethylmagnesium with benzonitrile in tetrahydrofuran. Only 50% of the ethyl groups in diethylmagnesium or in ethylmagnesium bromide were reported to react with benzonitrile. During the reaction two distinct reaction rates were observed, an initial fast rate for the first 30% of the reaction followed by a considerably slower rate for the remainder of the reaction. No simple rate equation could be derived to fit the entire reaction; however, the first part of the reaction was said to fit a second-order rate expression. The results were best interpreted by postulating that diethylmagnesium reacts as $[(C_2H_5)_2Mg]_2$, and that ethylmagnesium bromide reacts as $(C_2H_5)_2Mg \cdot MgBr_2$ and $[(C_2H_5)_2Mg]_2$. The following mechanism was proposed for the reaction of diethylmagnesium with benzonitrile (eq 2–4). More recently, however, it has been shown that ethylmagnesium bromide is monomeric in tetrahydrofuran over a wide concentration range and is best described by the Schlenk equilibrium which contains essentially an equal amount of RMgX and R_2Mg species ($K = \sim 4$).[7] Thus, Becker's proposal that the reactions of benzonitrile with ethylmagnesium bromide and diethylmagnesium proceed by reaction of $[(C_2H_5)_2Mg]_2$ or $(C_2H_5)_2Mg \cdot MgBr_2$ is not probable.



$$\underset{\text{I}}{2R_2Mg} \rightleftharpoons \underset{\text{II}}{(R_2Mg)_2} \qquad (2)$$



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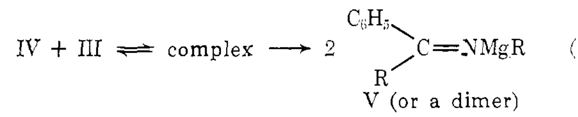
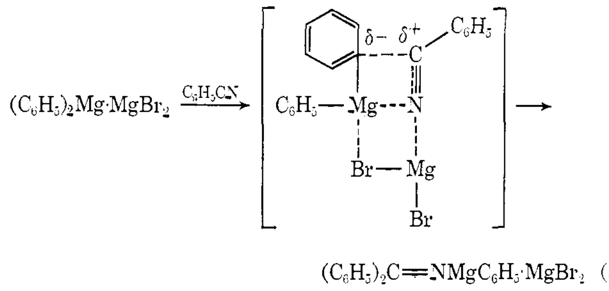


(4)

In 1965–1966 two reports appeared concerning the mechanism of Grignard compound addition to nitriles. The first report[8] described the reaction of ethylmagnesium bromide with benzonitrile in THF and other solvents as proceeding through the mechanism originally proposed by Swain (eq 1). The second report[9] described the reaction of phenylmagnesium bromide with benzonitrile in THF (eq 5) as proceeding through a transition state involving attack of $(C_6H_5)_2Mg \cdot MgBr_2$ in the rate-determining step.



$$(C_6H_5)_2C{=}NMgC_6H_5 \cdot MgBr_2 \qquad (5)$$

Because the mechanism of this reaction is so fundamental and because there seems still many unanswered questions about the exact description of the reaction, we set out to make a detailed kinetic study of the reaction of a Grignard compound with a nitrile in order to resolve the essential features of the mechanism. The main points of the problem basically involve the kinetic order of the reaction in both nitrile and organomagnesium reagent, the nature of the reactive species in those cases where several species exist in equilibrium, and the exact nature of the alkyl transfer whether it be *via* complex formation or as a result of direct bimolecular collision.

In an attempt to determine the mechanism of this reaction it is important to consider the composition of the Grignard reagent under the conditions the reaction is being studied. We found earlier that Grignard compounds are monomeric in THF even at high concentrations whereas in diethyl ether bromo and iodo Grignard compounds are monomeric only below 0.1 *M*. Thus, by operating at Grignard concentrations in diethyl ether below 0.1 *M*[10] under pseudo-first-order conditions in excess Grignard reagent and in excess nitrile it should be possible to determine directly the reaction order of each reactant, avoiding the complication of the presence of associated Grignard species. Furthermore, the rate of reaction of only R_2Mg species with nitrile can be determined by independent kinetic experiments, and the determination of the rate of reaction of only the RMgX species with nitrile should be possible by reaction of nitrile with Grignard reagent to which has been added a sufficient excess of $MgBr_2$ such that the Schlenk equilibrium is shifted in favor of the RMgX species. Such rate information should make it possible to determine the role of both R_2Mg and RMgX species in the reaction with nitriles.

Finally, we know from our previous work involving the reaction of Grignard reagents with ketones that the purity of the magnesium metal used to prepare the Grignard reagent is crucial.[11] Grignard reagent prepared from triply sublimed magnesium produced byproducts in the reaction of benzophenone with excess methylmagnesium bromide, whereas the same Grignard reagent prepared from single crystal magnesium eliminated this problem.

The system chosen for study was the reaction of benzonitrile with methylmagnesium bromide in diether at 25°. In this reaction no reduction or enolization is possible and by the use of Grignard reagent prepared from single crystal magnesium, by-product formation should be minimized. Preliminary studies showed that only addition product is formed and in essentially quantitative yield.

Experimental Section

Chemicals. Single crystal magnesium (Ventron Electronics Corp., Bradford, Pa.) was milled with a carbide tool. The turnings were washed several times with anhydrous diethyl ether, then dried, and stored under nitrogen. The purity of single crystal mag-

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[7] (a) E. C. Ashby and W. E. Becker, *J. Amer. Chem. Soc.*, **85**, 118 (1963); (b) R. M. Salinger and H. S. Mosher, *ibid.*, **86**, 1782 (1964); (c) M. B. Smith and W. E. Becker, *Tetrahedron*, **23**, 4215 (1967).

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

[9] H. Edelstein and E. I. Becker, *J. Org. Chem.*, **31**, 3375 (1966).

[10] (a) A. D. Vreugdenhill and C. Blomberg, *Recl. Trav. Chim. Pays-Bas*, **82**, 453 (1963); (b) E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, **86**, 4363 (1964).

[11] E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **94**, 5421 (1972).

nesium is 99.9995%, with less than 2 ppm of Ni, Co, and Fe as impurities.[12]

Eastman Spectrograde benzonitrile was dried and purified by distillation over solid, ether-free, methylmagnesium bromide. The nitrile was distilled at 30° and 0.5 mm. The middle fraction of the distillation was collected for the kinetic studies. Since glpc analysis (flame ionization detector) of the distilled material showed no extraneous peaks, the nitrile is believed to be at least 99.99% pure. The distilled material was stored in a reaction flask equipped with a three-way Teflon stopcock, shielded from light and stored in an inert atmosphere box.

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 Sieves. *n*-Tetradecane (Chemical Samples, 99.9% purity) was dried and distilled at 55° and 0.02 mm pressure from Linde 4A Molecular Sieves. It was used as an internal standard in the kinetic study. Acetophenone (Eastman) was purified by distillation under vacuum using a spinning band column. Mercury bromide (Baker Analyzed reagent) was used without further purification. Diethyl ether (Fisher Anhydrous) was distilled under nitrogen from $LiAlH_4$ through a 60-cm, glass helix packed column.

Magnesium bromide was prepared by a method described earlier involving the reaction of mercury bromide with magnesium in diethyl ether.[13] Elemental analysis of the product showed the ratio of Mg:Br to be 1.00:1.94.

Instrumentation and Apparatus. An inert atmosphere box equipped with a recirculating system[14] to remove moisture and oxygen was used during the manipulation of air-sensitive reagents. As an added precaution, a special line for prepurified nitrogen was added to the glove box and all materials were transferred in Schlenk tubes under a blanket of prepurified nitrogen.[15]

An F & M Model 700 flame ionization gas chromatograph was used to analyze the products.

Infrared spectra were obtained using a Perkin-Elmer 621 high resolution grating spectrophotometer and sodium chloride absorption cell.

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 in order to determine extinction coefficients and obtain Beer's law plots at a single wavelength. Either matched quartz cells (Beckman, 10.0 mm) sealed with a 1-mm bore two-way Kimax micro Teflon stopcock or Zeiss 1.00-mm cells were used for the ultraviolet measurements.

A Sargent constant-temperature water bath was used for controlling the temperature (±0.02°) of the kinetic solutions; temperatures were monitored with a calibrated thermometer reading to 0.1° with estimates to 0.02°.

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 equipped with stainless steel needles employed for transfer of the samples were calibrated prior to use. Deliveries could be reproduced to better than ±0.5%.

Analytical Methods. Solutions were analyzed for magnesium by titration with EDTA. Solutions of the Grignard compounds and magnesium halides were analyzed for halogen by the Volhard method. The concentration of basic magnesium bonded to carbon was determined by Gilman titration.

Glpc analyses of reaction mixtures were performed using 6-ft, $^1/_8$ in. matched stainless steel columns of 10% FFAP on 80–100 mesh Diatoport S. Absolute yields were determined by use of *n*-tetradecane as an internal standard. The components of the reaction mixture could be satisfactorily separated using the conditions: column temperature, 105°; flow rate, 40 ml/min; injection and detection temperature, 230°. The retention times for *n*-tetradecane, benzonitrile, and acetophenone are 6, 18, and 23 min under these conditions. Three different ratios of standard mixtures 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 of nitrile)/(area of *n*-tetradecane) and (mol of nitrile)/(mol of ketone) = 1.048(area of nitrile)/(area of ketone).

Preparation of Methylmagnesium Bromide.. Since the Grignard reagent is used in such low concentration, a precise method of preparing the reagent is crucial. The ether still was connected to a Dry Ice–acetone condenser and a 250-ml, round-bottom, one-neck flask containing 3.0 g of single crystal magnesium, and a stirring bar was attached below the condenser. After appropriate heating followed by N_2 flushing, approximately 100 ml of diethyl ether was distilled into the reaction flask. The ether was then removed under vacuum. This procedure rinsed the internal part of the still and condenser that could not be dried by external heating. Then the entire apparatus was dried under vacuum (0.01 mm) by flash flaming the apparatus followed by N_2 flushing. The above procedure was repeated twice. The condenser was charged with Dry Ice and after distillation of approximately 50 ml of ether into the reaction flask, methyl bromide (appropriately purified) was introduced through a side arm near the base of the condenser. After the reaction had begun, as evidenced by bubbling and heat release, stirring was begun. Diethyl ether was distilled into the reaction flask and methyl bromide added at a rate required to maintain gentle reflux without external heating. Addition of methyl bromide was continued until all of the magnesium was consumed. The distillation of the ether was continued until the flask contained approximately 200 ml of solution. Stirring was continued until the reaction had ceased and the flask had cooled to room temperature. Since an excess of methyl bromide was used in the preparation, complete solvent removal was effected under vacuum followed by redistillation of ether into the flask. The diethyl ether solution of methylmagnesium bromide prepared by this procedure was clear and colorless. The composition of the Grignard was determined by Gilman titration for C–Mg, EDTA for total magnesium, and Volhard for halogen. The results gave a C–Mg:Mg:Br ratio of 0.99:1.000:0.99. Clearly, there is no significant amount of coupling product. The Grignard reagent was transferred *via* syringe into a reaction flask equipped with a three-way Teflon stopcock, and stored in the drybox.

Product Studies. Benzonitrile (4.82×10^{-2} mol) and methylmagnesium bromide (4.82×10^{-2} mol) in 100 ml of diethyl ether were allowed to react with stirring at room temperature for 5 days. The mixture was hydrolyzed with 5% hydrochloric acid solution. Acetophenone, identified by comparison of the glpc retention time with that of an authentic sample, was found in 94.5% conversion with 5.5% unreacted benzonitrile recovered.

To a solution of methylmagnesium bromide (8.12×10^{-2} mol in 200 ml of diethyl ether) in a 500-ml, one-neck, round-bottom flask containing a stirring bar and equipped with a three-way Teflon stopcock, was added *via* syringe under prepurified nitrogen flow 100 ml of an ether solution of benzonitrile (3.98×10^{-2} mol). The reaction mixture was stirred for 6 days during which time a large amount of precipitate was formed. Glpc analysis indicated that the reaction was complete. The resulting mixture was fractionally crystallized into three fractions, which were dried under vacuum for 24 hr. The results of elemental analysis of the fractions are shown in Table I.

Table I. Fractional Crystallization of the Reaction Product from Methylmagnesium Bromide and Benzonitrile in Ether

Fractions	Sample wt, g	Mg, %	Br, %	Mg:Br ratio
1	1.6297	7.31	24.71	1.00:1.03
2	0.3374	10.14	31.44	1.00:0.94
3	0.0637	8.35	27.60	1.00:1.01
Calcd for $C_6H_5C(CH_3)NMgBr \cdot Et_2O$		8.20	26.95	1.00:1.00
Calcd for $C_6H_5C(CH_3)NMgBr$		10.93	35.93	1.00:1.00

Redistribution of $C_6H_5C(CH_3)NMgCH_3$ with $MgBr_2$. A solution containing 0.0159 mol of $C_6H_5C(CH_3)NMgCH_3$ in 50 ml of diethyl ether was prepared by the reaction of $(CH_3)_2Mg$ and C_6H_5CN in a 1:1 ratio. $MgBr_2$ (0.0166 mol) was dissolved in 150 ml of freshly distilled diethyl ether and added to the solution of $C_6H_5C(CH_3)NMgCH_3$. A light yellow precipitate formed immediately after mixing. The solid was filtered through a fine porosity fritted glass funnel under vacuum in the drybox, dried under vacuum, and

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[12] Personal communication with Ventron Electronics Corp.

[13] E. C. Ashby and R. Arnott, *J. Organometal. Chem.*, 14, 1 (1968).

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

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

Table II. Reaction of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ in Diethyl Ether

	Sample wt, g	Mg, %	Br, %	Mg:Br ratio
Precipitate	3.7449	9.79	34.88	1.00:1.08
Calcd for $C_6H_5C(CH_3)NMgBr$		10.93	35.93	1.00:1.00
Filtrate	0.7270	13.10	38.78	1.00:0.90
Calcd for $CH_3MgBr \cdot Et_2O$		12.57	41.32	1.00:1.00

analyzed (Table II). The infrared and nmr spectra of the filtrate were consistent with that observed earlier for methylmagnesium bromide. Ether was then removed from a portion of the filtrate under vacuum and the resulting solid analyzed (Table II).

Procedures for Kinetic Studies. The kinetic flasks, syringes, and needles were rinsed with ether, heated in an oven at 150° for at least 2 hr, and then placed in the entry port of an inert atmosphere box which was subsequently evacuated to a pressure of 0.25 mm. After filling the chamber with prepurified nitrogen, the equipment was transferred into the drybox and assembled after a thorough purge *via* a needle with a stream of prepurified nitrogen and passed through a 90-cm tube of Linde 4A Molecular Sieves. All of the solutions were sampled *via* syringe through a three-way Teflon stopcock under a flow of prepurified nitrogen in the drybox. Since the solubility of the reaction product was found to be about 3×10^{-2} *M*, all kinetic studies were carried out at concentrations below this value.

For the kinetic studies in excess Grignard reagent, concentrated organomagnesium reagent was added to diethyl ether in order to dilute to the desired concentration. A 70-ml portion of dilute organomagnesium solution was transferred from the dilution flask *via* syringe to the reaction flask. Neat *n*-tetradecane was then added to the reaction flask as an internal standard. The reaction flask was wrapped with aluminum foil and placed in a constant-temperature water bath (25 ± 0.02°). The flask and its contents were allowed to reach temperature equilibrium before a nitrogen line was attached to the stopcock at the top of the reaction flask. After turning the stopcock in a manner to by-pass the opening to the solution, the line and stopcock were purged with nitrogen. The stopcock was then turned to accept a syringe needle from the top with the nitrogen flow from the side, and the desired amount of benzonitrile standard solution was added *via* a 50-μl syringe. A 2-ml sample was withdrawn immediately and quenched in a vial with a septum cap containing 6 ml of saturated ammonium chloride solution. This sample was used as the zero-time reading. Other samples were quenched in the same manner at appropriate intervals of time. Samples were obtained over the range 5-80% reaction. The quenched samples were analyzed by following the disappearance of nitrile by gas chromatography. The time was recorded after the sample was injected into the ammonium chloride solution.

After withdrawing the needed amount of dilute organomagnesium solution for the kinetic studies, three 5-ml samples of dilute organomagnesium solution were withdrawn for concentration determination. An excess of 0.01 *N* H_2SO_4 was added to the sample followed by ether removal under aspirator pressure on a steam bath. The excess H_2SO_4 was back titrated with 0.01 *N* NaOH solution to a phenolphthalein endpoint. The average value was adopted as the concentration of organomagnesium solution.

Kinetic studies in excess benzonitrile were also carried out. Although concentrated solutions of benzonitrile (0.5 *M*) absorb strongly at wavelengths shorter than 280 mμ, negligible absorbance in the region between 320 and 370 mμ is observed. Diethyl ether solutions of methylmagnesium bromide show no absorbance in the ultraviolet spectrum above 270 mμ. Ultraviolet spectra of mixtures of methylmagnesium bromide with excess benzonitrile were obtained in the following fashion. Quartz 10-mm uv cells, glass-sealed with a 1-mm bore, two-way, Kimax Teflon stopcock, were dried for a few seconds by heating and then transferred to the drybox. The 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 the routine procedures. The 25-ml flasks and uv cells were purged with prepurified nitrogen *via* a needle before loading the samples. The desired amount of standard benzonitrile solution was added to the 25-ml volumetric flask under nitrogen flow, and diethyl ether was added to the mark. A 4-ml portion of dilute benzonitrile solution was transferred from the volumetric flask to the uv cell *via* a calibrated syringe. The uv cells were removed from the drybox along with a 50-μl syringe containing the Grignard reagent. The uv cells were placed in a constant-temperature water bath. After time was allowed for the cells to come to temperature equilibrium, a known amount of standard Grignard reagent was injected into the cell. The cell was rapidly shaken to ensure mixing. The rate of the reaction was followed by measuring the increase in absorbance at 344 mμ, λ_{max} of the product. The cells remained in the constant-temperature bath at all times except when taking a reading. Generally, 25-30 sets of time-absorbance values were taken in each kinetic experiment.

For the kinetic studies using a low ratio of reactants, a 70-ml portion of freshly distilled diethyl ether was transferred to a reaction flask. A calibrated syringe was used to transfer the desired amount of methylmagnesium bromide to the reaction flask. The concentration of organomagnesium solution determined by titration agreed within 2% with that computed from dilution. The initial concentration of benzonitrile was determined by quenching the reaction mixture at zero time in 10% H_2SO_4 and measuring the absorbance of benzonitrile at 277.5 mμ. The remainder of the procedures were similar to those described for the kinetic study in excess methylmagnesium bromide. Kinetic data were obtained by gas chromatographic analysis.

Spectral Evidence for Complexation. Evidence for complexation between methylmagnesium bromide and benzonitrile was sought using both uv and ir measurements. When the concentrations of methylmagnesium bromide and benzonitrile in one case were 1.07×10^{-3} and 9.13×10^{-4} *M*, respectively, and in another were 2.56×10^{-3} and 7.99×10^{-3} *M*, respectively, the uv spectrum of each mixture was the same as the sum of the spectra of the two components. However, when the concentrations of methylmagnesium bromide and benzonitrile were 8.48×10^{-3} and 9.74×10^{-3} *M*, the absorption of the mixture in the region 240-285 mμ was somewhat larger than the sum of the components.

Attempts were also made to find evidence for a complex with $MgBr_2$, since $MgBr_2$ is a stronger Lewis acid than CH_3MgBr. The spectrum of a mixture 8.84×10^{-3} *M* in benzonitrile and 0.119 *M* in $MgBr_2$ was scanned from 6000 to 2000 Å. The absorption of the mixture in the region 240-265 mμ was somewhat greater than the sum of the components.

Evidence for complexation was also sought using infrared spectroscopy. The spectrum of a mixture of methylmagnesium bromide and C_6H_5CN, each 0.166 *M* in concentration, was scanned from 800 to 3500 cm^{-1}. In the C_6H_5CN diethyl ether solution the C≡N stretch band appears at 2236 cm^{-1}. A new band was formed after CH_3MgBr and C_6H_5CN were mixed at 1633 cm^{-1} which was attributed to the C=N in the product. The region of the spectrum from 2150 to 2350 cm^{-1}, in which bands due to a complex would be expected, was examined carefully. However, no additional band nor any change in the absorption band attributed to C_6H_5CN was observed.

Results

General Features of Rate Studies. It is important that kinetic studies of Grignard reactions be carried out at concentrations at which the organomagnesium species are monomeric. If not, associated species are present and the analyzed concentration of the Grignard solution does not represent the concentration of monomeric species. This point is crucial if the reaction proceeds through the monomeric species. In general, other workers in the field have not taken this factor into account or have alternatively explained their results by salt effects[16] and other phenomena. Our association measurements[10b] have indicated the Grignard reagent concentration at which association becomes appreciable and we have carried out our studies below this concentration.

The reaction of benzonitrile with methylmagnesium bromide in diethyl ether was studied in two ways: (1) in excess Grignard reagent, by quenching the reaction mixture with saturated ammonium chloride solution

(16) S. G. Smith and G. Su, *J. Amer. Chem. Soc.*, **88**, 3995 (1966).

and then measuring the disappearance of benzonitrile by glpc using *n*-tetradecane as an internal standard; (2) in excess benzonitrile, by following directly the appearance of the product [$C_6H_5C(CH_3)NMgBr$] at 344 mμ. Since the absorbance of acetophenone, the product after hydrolysis, appears in the same region in the uv as benzonitrile (240–280 mμ), it is not possible to use spectrophotometric methods to follow the appearance of acetophenone. In the first case, the data were recorded generally between 5 and 80% reaction for each individual run. In the second case, each individual run was allowed to reach completion. Under pseudo-first-order conditions the kinetic dependence is simplified, the dependence on the reactant in excess being eliminated. The dependence on benzonitrile was determined by using an excess of organomagnesium reagent and *vice versa.*[17]

Magnesium Purity. The purity of magnesium used in these studies is crucial because there is evidence that rates of reactions of Grignard compounds with organic substrates are quite sensitive to trace impurities of transition metals.[11,18] Thus, several different grades of magnesium were used in an attempt to determine the effect of magnesium metal purity. When triply sublimed magnesium (99.95% pure) was used to prepare the Grignard reagent, 2–13% by-product formation was observed when excess Grignard reagent was used in the reaction. The by-product formed immediately when the reactants were mixed, and thus, the amount formed was nearly constant throughout the entirety of the reaction. The per cent by-product changed with the ratio of $[G]_0/[N]_0$ as shown in Table III. No by-product was formed when the Grignard:nitrile ratio was 1:1. Each individual run in excess Grignard followed a well-behaved first-order pattern in benzonitrile; however, a plot of k_G *vs.* $[G]_0$ did not produce a straight line. In addition, faster rates were observed when methylmagnesium bromide prepared from triply sublimed magnesium was allowed to react with benzonitrile as compared to those cases when the Grignard reagent was prepared from single crystal magnesium.

Table III. The Relationship of Per Cent By-Product to the Ratio of Methylmagnesium Bromide[a] to C_6H_5CN

$[G]_0$, M	$[N]_0 \times 10^4$, M	$[G]_0/[N]_0$	By-product, %
0.101	7.02	144	13.0
0.101	9.33	108	9.7
0.117	41.12	28	2.5

[a] Methylmagnesium bromide prepared from triply sublimed magnesium.

A small amount of Grignard solution was prepared from an ultrapure grade of magnesium[19] used earlier.[18] In the one run performed with this Grignard reagent, using an excess of the Grignard reagent, no by-product was found. Further kinetic studies were carried out using Grignard reagent prepared from zone-refined magnesium.[20] Although no by-product was formed under conditions of excess Grignard reagent and each individual run exhibited well-behaved first-order kinetics, k_G was found to be dependent on the initial benzonitrile concentration.

The most consistent kinetic results were obtained from Grignard reagent prepared from single crystal magnesium.[21] No by-product was formed in the reaction in excess Grignard reagent, and k_G was only very slightly dependent on the initial concentration of benzonitrile. The data obtained in this study are summarized in Table IV.

Table IV. Observed Rate Constants for the Reaction of a Constant Concentration of Methylmagnesium Bromide (5.82×10^{-2} M) with a Variable Initial Concentration of Benzonitrile

Run	$[N]_0 \times 10^4$, M	$[G]_0/[N]_0$	$k_G \times 10^4$, min^{-1}
1	5.90	99	1.41
2	10.07	58	1.39
3	13.78	42	1.36
4	17.48	33	1.33
		Av	1.37 ± 0.037

Reaction Product and Its Properties. The reaction product of methylmagnesium bromide with C_6H_5CN in diethyl ether has been studied by fractional crystallization. The data show that the product has the empirical formula $C_6H_5C(CH_3)NMgBr$. More information about the physical properties of the reaction mixture could not be obtained due to the low solubility of the product ($<3 \times 10^{-2}$ M). When the ratio of Grignard : nitrile was 2:1 the product precipitated from solution essentially quantitatively leaving 1 mol equiv of Grignard reagent in solution.

Kinetics in Excess Grignard Reagent. Reactions using excess Grignard reagent were performed in diethyl ether at 25° at Grignard:nitrile ratios ranging from 20:1 to 70:1. The maximum concentration of methylmagnesium bromide employed was 0.1 M since association studies have shown that the former is predominantly monomeric at and below this concentration. The kinetic data were obtained by quenching individual samples of the reaction mixture in saturated ammonium chloride solution at appropriate intervals of time and following the disappearance of nitrile by glpc. Under these conditions, the reaction was found to be first order in benzonitrile (Figure 1). The significance of the linearity will be discussed later. Pseudo-first-order rate constants were calculated from each of the eight to ten sets of % reaction–time values obtained in a given experiment, and the average value taken. The results obtained are summarized in Table V.

The values of k_G increase with $[G]_0$ as expected. If the reaction is first order in Grignard, then $k_G/[G]_0$ should be constant for this series of experiments. The values are observed to be constant (Table V). The

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(17) For reactions in excess Grignard, the pseudo-first-order rate constant is designated k_G; for reactions in excess nitrile the pseudo-first-order rate constant is designated k_N. Concentrations of Grignard and nitrile at time t during a reaction are designated as [G] and [N], respectively; with $[G]_0$ and $[N]_0$ being the initial concentrations.

(18) (a) E. C. Ashby, F. Walker, and H. M. Neumann, *Chem. Commun.*, 330 (1970); (b) E. C. Ashby, H. M. Neumann, F. W. Walker, J. Laemmle, and L.-C. Chao, *J. Amer. Chem. Soc.*, **95**, 2597 (1973).

(19) This magnesium, prepared by zone refining techniques, was kindly provided by Professor Royal W. Stark, The University of Chicago.

(20) Kindly provided by Professor T. Chaudron, Center Etudes Chim. Met., Vitry-sur-Seine, Fr.

(21) See Experimental Section.

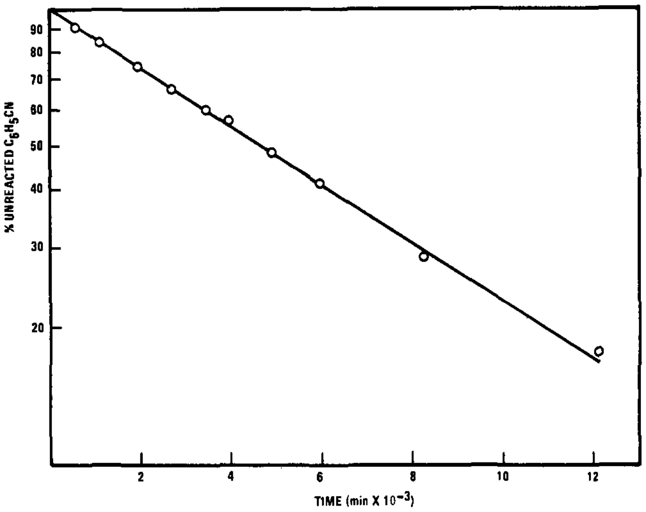

Figure 1. Plot demonstrating pseudo-first-order behavior of benzonitrile (1.49×10^{-3} *M*) with excess methylmagnesium bromide (5.67×10^{-2} *M*) in diethyl ether at 25°.

Table V. Observed Rate Constants for the Reaction of Benzonitrile with Excess Grignard Reagent at 25°

Run	$[G]_0 \times 10^2$, *M*	$[G]_0/[N]_0$	$k_G \times 10^4$, min^{-1}	$k_G \times 10^4$, min^{-1} (calcd)	$k_G/[G]_0 \times 10^3$, l. mol^{-1} min^{-1}
5	2.19[a]	37	0.533	0.47	2.43
6	2.98	20	0.715	0.63	2.44
7	4.63	31	1.13	0.93	2.45
8	5.67	38	1.45	1.12	2.55
	5.82[b]		1.37	1.14	2.35
9	6.80	46	1.66	1.30	2.43
10	8.44	57	1.95	1.56	2.31
11	9.98	67	2.30	1.78	2.31
				Av	2.41 ± 0.06

[a] In the reaction of C_6H_5CN with excess methylmagnesium bromide, the C_6H_5CN concentration was 1.49×10^{-3} *M* except in this case when it was 6.00×10^{-4} *M*. [b] Average of four runs from Table IV.

rate law for the reaction in excess Grignard is then given by the expression

$$\text{rate} = k[C_6H_5CN][\text{Grignard}] \qquad (6)$$

The value of k obtained from these experiments is $(2.41 \pm 0.06) \times 10^{-3}$ l. mol^{-1} min^{-1} at 25°.

If a significant amount of complex between C_6H_5CN and Grignard were present in these systems the value of $k_G/[G]_0$ should show a decreasing trend with increased $[G]_0$. Since such a trend is not evident it can be concluded that $K[G]_0 < 1$, where K is the equilibrium constant for complex formation, and further, that $K < 10$.

Kinetics in Excess of Nitrile. The rate of the reaction in excess benzonitrile was followed spectrophotometrically, by observing the increase in the absorption band at 344 mμ characteristic of the product. The absorbance increased rapidly initially, then reached an almost constant value for a period of time, and finally increased rapidly again. Typical behavior is shown in Figure 2. The rapid increase in absorbance in the final stage is attributed to a condensation product[22] with a high molar extinction coefficient.

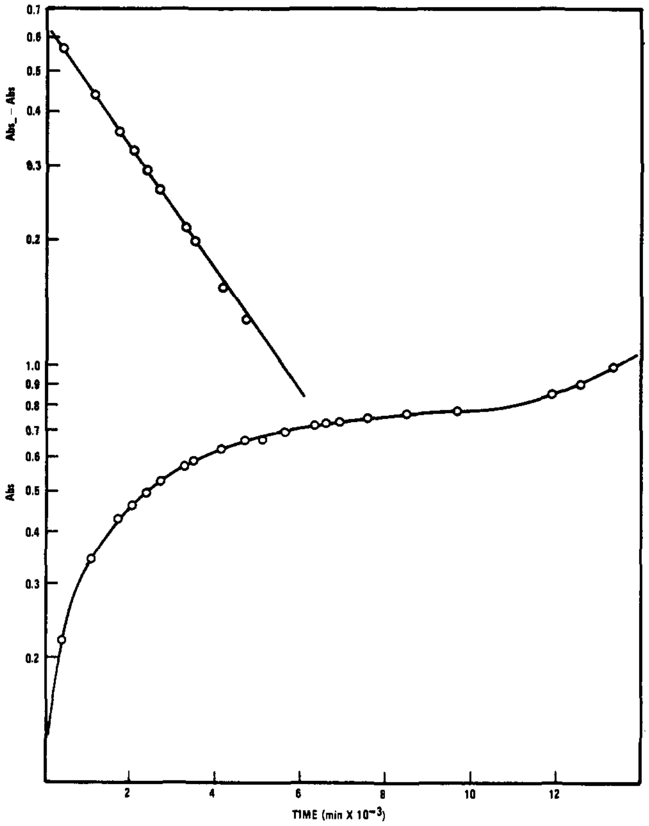

Figure 2. The reaction of methylmagnesium bromide (5.94×10^{-3} *M*) with excess benzonitrile (0.127 *M*) in diethyl ether.

Further information was obtained by quenching the reaction mixtures in the uv cell with saturated ammonium chloride and measuring the amount of acetophenone by gas chromatography analysis. A number of determinations were carried out when the absorbance readings were leveling out, before the period of rapidly increasing absorbance. At this stage glpc analysis indicated acetophenone in about 85% yield, and did not reveal the presence of condensation product.

The initial rise in absorbancy to the leveling off value suggested the behavior associated with a single first-order reaction. In this case the variation of absorbancy with time is given by the expression

$$\text{Abs} = \text{Abs}_\infty - (\epsilon_B - \epsilon_A)[A]_0 e^{-k_N t} \qquad (7)$$

and a plot of log (Abs_∞ – Abs) *vs.* t should produce a straight line with a slope of $k_N/2.303$. Plots of log (Abs_∞ – Abs) *vs.* t showed the expected linearity, and allowed determination of k_N, the pseudo-first-order rate constant.

If the reaction is first order in benzonitrile, in addition to being first order in Grignard, the second-order rate constant is $k_N/[N]_0$. The results from several experiments are summarized in Table VI. The results include one set (runs 16–19) using constant excess nitrile concentration with variable methylmagnesium bromide concentration.

For nitrile concentrations less than 0.2 *M* the rate law can be expressed by eq 8 with the value of k equal to

$$\text{rate} = k[C_6H_5CN][\text{Grignard}] \qquad (8)$$

$(2.52 \pm 0.12) \times 10^{-3}$ l. mol^{-1} min^{-1}. This value is the

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

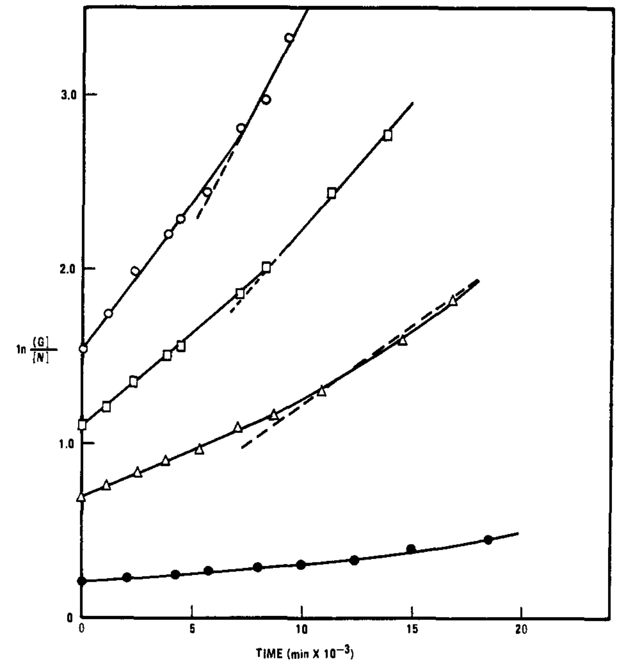

Figure 3. Second-order plot of the reaction of methylmagnesium bromide with benzonitrile at low ratio in diethyl ether: ○, fivefold excess of G; □, threefold excess of G; △, twofold excess of G; ●, equivalent amount. Dotted lines correspond to slope expected for $k = 2.45 \times 10^{-3}$ l. mol^{-1} min^{-1}.

Table VI. Rate Constants for the Reaction of Methylmagnesium Bromide in Excess Benzonitrile at 25°

Run	$[N]_0$	$[G]_0 \times 10^3$, M	$k_N \times 10^4$, min^{-1}	$k_N \times 10^4$, min^{-1} (calcd)	$k_N/[N] \times 10^3$, l. mol^{-1} min^{-1}
12	0.0637	2.92	1.56	1.41	2.44
13	0.0729	2.87	1.80	1.60	2.47
14	0.0780	2.92	2.12	1.71	2.71
15	0.101	4.33	2.72	2.18	2.69
16	0.128	3.33	2.91	2.72	2.27
17	0.128	4.07	2.83	2.72	2.21
18	0.127	4.67	3.21	2.70	2.53
19	0.127	5.94	3.34	2.70	2.63
20	0.150	2.01	3.62	3.14	2.42
21	0.230	3.93	4.43	4.59	Av 2.52 ±
22	0.459	3.93	7.83	8.05	0.12
23	0.640	3.93	7.75	10.31	
24	0.822	3.93	11.71	12.29	

same, within experimental error, as the value obtained in the experiments with excess Grignard. This excellent agreement leads to the conclusion that the same mechanism is operative both in excess Grignard and in excess nitrile.

For nitrile concentrations greater than 0.2 M values of $k_N/[N]_0$ become smaller as the nitrile concentration becomes larger. This is the behavior expected if complexation between nitrile and Grignard is appreciable. The trend in the values indicates an equilibrium constant of magnitude about 2–3.

Low Ratio of Reactants. Since the same rate law was observed in large excess of nitrile and in large excess of Grignard, it was reasonable to expect that the same rate law should hold when the two reactants are in approximately equal concentrations. Figure 3 and Table VII show the results of several such experiments. When the Grignard reagent was in fivefold excess, a standard second-order plot was linear for 80% of the reaction; with a threefold excess of Grignard reagent, the second-order plot was linear for 70% of the reaction; with a twofold excess, the second-order plot was linear for 55%; and in equal molar ratios the second-order plot was linear for 40% reaction. The reactions do not follow the simple second-order behavior for the entirety of the reaction. The standard second-order plots are initially linear, but the second-order rate constants obtained (designated as k_{app}) were about 25% smaller than those obtained under pseudo-first-order conditions. Only in the later stages of the reaction did the rates approach the expected values.

Table VII. Rate of Reaction at Low Reactant Ratios

Run	$[N]_0$	$[G]_0$	k_{app}[a] $\times 10^3$, l. mol^{-1} min^{-1}	$k_{app} \times 10^3$ (calcd), l. mol^{-1} min^{-1}
25	0.02667	0.1262	1.69	1.71
26	0.02897	0.0885	1.70	1.84
27	0.03092	0.0627	1.65	1.94
28	0.03375	0.0272	1.47	2.10

[a] Calculated from the first several points using the equation

$$k_{app} = \frac{1}{t([G]_0 - [N]_0)} (\ln ([G]/[N]) - \ln ([G]_0/[N]_0))$$

The fact that the rate is initially slower than expected would be consistent with the presence of significant amounts of complex at that time. In the later stages, with decreased amounts of both Grignard and nitrile, the amount of complex could become negligible and the rate thus reach the expected value. Assuming that complexation accounts for the observed effects, an equilibrium constant of magnitude 2–5 is calculated.

Effect of Magnesium Bromide on Reaction Rate. The addition of magnesium bromide in reaction mixtures involving organomagnesium compounds has been reported to affect the course or rate of a variety of reactions. Addition of magnesium bromide decreases the rate of reaction of diphenylmagnesium with benzonitrile in THF.[9] A similar decrease has been reported numerous times in the reaction of Grignard reagents with ketones or esters.[23-29]

Although it may have other effects on the reaction system, the addition of magnesium bromide to methylmagnesium bromide must cause a shift in the Schlenk equilibrium producing more of the CH_3MgBr species and decreasing the amount of $(CH_3)_2Mg$. The reaction rate should decrease markedly on addition of magnesium bromide if the reaction of methyl bromide Grignard reagent proceeds to a significant extent through the $(CH_3)_2Mg$ species. If the reaction proceeds predominantly through the CH_3MgBr species the reaction rate should increase slightly on addition of magnesium bromide. The results of experiments in which magnesium bromide was added to the Grignard

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

(24) M. Anteunis, *J. Org. Chem.*, 27, 596 (1962).

(25) R. D'Hollander and M. Anteunis, *Bull. Soc. Chim. Belg.*, **74**, 71 (1965).

(26) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1963).

(27) H. O. House and D. D. Traficante, *J. Org. Chem.*, **28**, 355 (1963).

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(29) T. Holm, *Acta Chem. Scand.*, **21**, 2753 (1967); **23**, 579 (1966).

Table VIII. Effect of Addition of $MgBr_2$ on the Reaction of Methylmagnesium Bromide with Benzonitrile

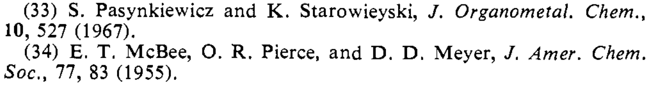
Run	[Methylmagnesium bromide]$_0$	$[C_6H_5CN]_0 \times 10^3$, *M*	$[MgBr_2]_0 \times 10^3$, *M*	$MgBr_2$, %	$k_G \times 10^4$, min^{-1}	$k_G \times 10^4$, min^{-1} (calcd)
a	0.0283			0	0.682	0.60
29	0.0283	0.993	2.87	10.2	0.279	0.45
30	0.0277	0.970	5.54	20.1	0.285	0.39
b	0.0886			0	2.13	1.62
31	0.0886	1.595	8.95	9.9	0.971	1.19
32	0.0886	1.596	17.8	20.1	0.906	1.01
33	0.0885	1.593	26.9	30.4	0.816	0.89

[a,b] Data were obtained from the reaction of C_6H_5CN in excess methylmagnesium bromide; $k_G = 2.41 \times 10^{-3}[G]_0$.

reagent are summarized in Table VIII. The behavior observed (*i.e.*, a marked decrease in rate when 10% $MgBr_2$ is added, followed by a smaller decrease on adding 20–30% $MgBr_2$) is qualitatively that expected when reaction proceeds through both CH_3MgBr and $(CH_3)_2Mg$. The results further indicate that the bimolecular rate constant for reaction of CH_3MgBr with nitrile must be about 1.0×10^{-3}, thus considerably smaller than the 17.7×10^{-3} value found[30] for the reaction of $(CH_3)_2Mg$ with benzonitrile.

Complex Formation. The behavior of related systems suggests that complex formation between organomagnesium compounds and benzonitrile should occur. Complexation between benzonitrile and organoaluminum compounds has been intensively studied.[31–33] A 1:1 complex between acetonitrile and magnesium bromide in phenetole as solvent has been reported.[34] Vapor pressure lowering was interpreted in terms of a strong 1:1 complex, but the concentration employed in the experiments was not stated. Some of our kinetic results, *viz.*, those in low ratio of reactants, and those in high concentration of nitrile, provide indirect evidence of complex formation. Attempts to get direct evidence by uv and ir measurements were not conclusive.

Redistribution of $C_6H_5C(CH)_3NMgCH_3$ and $MgBr_2$. The redistribution of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ was investigated by simply mixing ether solutions of both components. Both $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ are more soluble in diethyl ether than $C_6H_5C(CH_3)NMgBr$. When equivalent amounts of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ were mixed, a yellow precipitate formed immediately. Elemental analysis showed the Mg:Br ratio to be 1.00:1.09; a result which would be consistent with the precipitate being $C_6H_5C(CH_3)NMgBr$, or its being the adduct $C_6H_5C(CH_3)NMgCH_3 \cdot MgBr_2$. The filtrate was identified as CH_3MgBr by ir and nmr measurements. These results indicate that the redistribution has occurred rapidly and extensively.



$$C_6H_5{-}\underset{CH_3}{\underset{|}{C}}{=}N{-}MgCH_3 + MgBr_2 \longrightarrow C_6H_5{-}\underset{CH_3}{\underset{|}{C}}{=}NMgBr\downarrow + CH_3MgBr \quad (9)$$

Discussion

In dealing with reactions of Grignard reagents, the rate law is commonly expressed in terms of the concentration of "Grignard reagent." Thus, to this point we have written the rate law describing the reaction of methylmagnesium bromide with benzonitrile as

$$\text{rate} = k[\text{nitrile}][\text{Grignard}] \qquad (10)$$

However, the results reported above suggest that R_2Mg and $RMgX$ each react by separate paths. The reaction rate should then be expressed as

$$\text{rate} = k_2[R_2Mg][\text{nitrile}] + k_1[RMgX][\text{nitrile}] \qquad (11)$$

The results also suggest that $RMgX$ and MgX_2 form complexes with the nitrile. The overall behavior of the system can then be described by a model similar to that which proved successful for describing the reaction of methylmagnesium bromide with benzophenone.[11] If this model is satisfactory, it should be possible to calculate the measured rate constants k_G, k_N, and k_{app} for the various experiments from the fundamental rate and equilibrium constants of this model.

The appropriate methods of calculation for the four kinds of experiments are as follows.

(1) For experiments in excess Grignard

$$k_G = \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1Q[G]_0 + [K_3\sqrt{(1 + K_3[N])K_s}/(1 + K_3[N])]Q[G]_0}\,Q[G]_0 \qquad (12)$$

where

$$Q = \frac{1}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \qquad (13)$$

Since [N] is small under these conditions, the approximation $[N] = [N]_0$ was made in this case.

(2) For experiments in excess nitrile

$$k_N = \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}}[N] \qquad (14)$$

(3) For experiments with low ratio reactants

$$k_{app} = \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}}\,\frac{[N]}{[N]_0} \qquad (15)$$

The value of [N] was obtained by successive approximations using eq 16.

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

[31] K. Starowieyski and S. Pasynkiewicz, *Rocz. Chem.*, **40**, 47 (1966).

[32] K. Starowieyski, S. Pasynkiewicz, and M. Boleslawski, *J. Organometal. Chem.*, **10**, 393 (1967).

[33] S. Pasynkiewicz and K. Starowieyski, *J. Organometal. Chem.*, **10**, 527 (1967).

[34] E. T. McBee, O. R. Pierce, and D. D. Meyer, *J. Amer. Chem. Soc.*, 77, 83 (1955).

$$[N] = [N]_0 - \frac{K_1[N] + K_1K_3[N]^2 + K_3[N]\sqrt{(1 + K_3[N])K_s}\,[G]_0}{(1 + K_3[N])(1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \qquad (16)$$

(4) For experiments in excess Grignard with added $MgBr_2$ the concentration of R_2Mg was first calculated using eq 17. Concentrations of CH_3MgBr and

$$[R_2Mg] = \frac{\sqrt{[X]_0{}^2 + 4K_s[G]_0{}^2 + 8K_s[X]_0[G]_0} - ([X_0] + 4K_s[G]_0)}{2(1 - 4K_s)} \qquad (17)$$

$MgBr_2$ were calculated from $[R_2Mg]$, $[X]_0$, and $[G]_0$. The rate constant is then given by

$$k_G = \frac{k_1[RMgX] + k_2[R_2Mg]}{1 + K_1[G] + K_3[X]} \qquad (18)$$

In attempting to obtain the best fit to the constants k_1, k_2, K_1 (the equilibrium constant for complexation with RMgX), K_3 (the equilibrium constant for complexation with MgX_2), and K_s (the constant for the Schlenk equilibrium) of the model, while allowing all five constants to vary, it was found that the best fits were obtained with unreasonably large values of either k_2 or K_s, which are known from other experiments. A compromise set of constants are: $k_1 = 1.3 \times 10^{-3}$ l. mol^{-1} min^{-1}, $k_2 = 20.0 \times 10^{-3}$ l. mol^{-1} min^{-1}, $K_1 = 2.5\ M^{-1}$, $K_3 = 10\ M^{-1}$, and $K_s = 0.0040$. Calculated values of the measured rate constants, corresponding to this set, are given in all of the tables for comparison with the measured values.

Since R_2Mg is an important reactive species in this system, a comment is necessary in relation to the linearity of the pseudo-first-order plots (such as Figure 1) for reactions in excess Grignard, since we have reported curvature in the analogous reaction with benzophenone.[19]

From eq 10 and 11 it follows that

$$k = k_2[R_2Mg]/[\text{Grignard}] + k_1[RMgX]/[\text{Grignard}] \qquad (19)$$

$$= k_2F_{R_2Mg} + k_1F_{RMgX} \qquad (20)$$

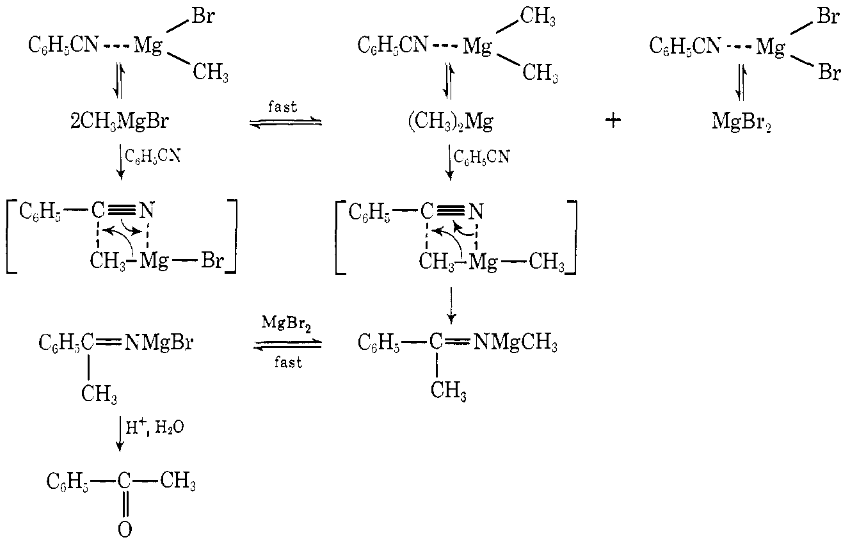
where F_{R_2Mg} and F_{RMgX} are the fractions of the Grignard reagent that are R_2Mg and RMgX, respectively. The pseudo-first-order plots will be strictly linear (and this will hold both for reaction in excess Grignard and in excess nitrile) only if k remains constant during the course of the reaction. The latter depends, in turn, primarily on whether F_{R_2Mg} remains constant.

The reaction of R_2Mg with C_6H_5CN would be expected to lead to $C_6H_5RC{=}NMgR$ as the initial product. As R_2Mg reacts, it is replenished *via* the mobile Schlenk equilibrium

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (21)$$

If these are the only reactions occurring in the system, the concentration of MgX_2 will increase with time, and F_{R_2Mg} will decrease with time rather than remain constant. It is this mass action effect on the position of equilibrium, rather than any slowness in the rate of formation of R_2Mg,[35] that accounts for curvature in the pseudo-first-order plots.

Scheme I



(22)

Any redistribution reaction which tends to keep $[R_2Mg]$ and $[MgX_2]$ of equal value will tend to keep F_{R_2Mg} constant. The reaction given in eq 9 is important in this regard. If it is rapid and complete, F_{R_2Mg} will be constant during the reaction. The redistribution reaction was observed to occur within seconds when the reactants were at 0.08 *M* concentration. The kinetic evidence suggests that redistribution is rapid even at the lower concentrations used in the kinetic experiments. The experiments in excess benzonitrile would be most sensitive to a slow or incomplete redistribution because of the low concentrations of product and Grignard species. The linearity of the pseudo-first-order plots (such as Figure 1), and the agreement of the rate constants so obtained with those obtained in excess Grignard, provide strong evidence that redistribution is rapid and essentially complete in all of our experiments.

According to all the information presented, the detailed mechanism for the reaction of methylmagnesium bromide with benzonitrile is as shown in Scheme I. Even though the reaction of methylmagnesium bromide with benzonitrile follows two distinct reaction paths, the reaction kinetically still obeys the simple second-order rate equation.

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[35] S. E. Rudolph and S. G. Smith, *Chem. Commun.*, 1428 (1970).