$$\frac{-\mathrm{d}[\mathrm{ROOH}]_{\mathrm{T}}}{\mathrm{d}t} = 2k_4K_3K_2[\mathrm{Cu^{II}}_2][\mathrm{ROOH}]^2 + \frac{k_7[k_7{}^2 + 4ac[\mathrm{Cu^{II}}_2]]^{1/2}[\mathrm{ROOH}]^2}{2a} - \frac{k_7{}^2[\mathrm{ROOH}]^2}{2a} \quad \text{(iv)}$$

total copper salt, $[\mathrm{Cu}]_{\mathrm{T}}$, and hydroperoxide, $[\mathrm{ROOH}]_{\mathrm{T}}$, concentration into (iii), with the assumption that the hydroperoxide exists mainly as the dimer, gives eq 9.

The mechanism may be modified to include caged alkoxy radicals ($\overline{2\mathrm{RO}\cdot}$) by replacing eq 6 with eq 10–12. By a similar steady-state treatment, eq iv results, where $a = 2k_8(k_{11} + k_{12})/k_{12}$ and $c = [2(k_{11} + k_{12})k_4K_3K_2 - k_4K_3K_2k_{12}]/k_{12}$. Equation iv could be expressed in terms of total copper salt and hydroperoxide concentrations as was done with eq iii.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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# The Kinetics of Inversion of 2-Methylbutylmagnesium Bromide and Related Compounds

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*Contribution from the Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210.* *Received October 14, 1965*

**Abstract**: The nmr spectra of 2-methylbutylmagnesium bromide and bis(2-methylbutyl)magnesium have been determined as a function of temperature in several ethers. At −30° the $CH_2Mg$ hydrogens are magnetically nonequivalent and give rise to the AB portion of an ABX spectrum. With increasing temperature this pattern progressively collapses to $A_2$ of $A_2X$. Analysis of the results reveals that changes among the nmr spectra are due to different rates of inversion at the $CH_2Mg$ carbon atom. Theoretical line shapes have been calculated as a function of the inversion frequency and compared to the experimental spectra. In diethyl ether the kinetic order of the inversion process is 2.5 in contained Grignard reagent, $\Delta H^*$ and $\Delta S^*$ are 12 ± 0.5 kcal and −11 ± 2 eu, respectively; for the organomagnesium compound the order is 2.0, $\Delta H^*$ is 18 ± 0.5 kcal and $\Delta S^*$ is $5 \pm 2$ eu. Among the series of solvents employed these activation parameters vary widely and obey an isokinetic relationship. The mechanistic consequences of these results are discussed.

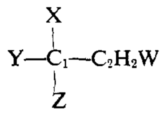
Little is known about the geometry of alkyl carbanions although they are assumed to exist as tetrahedral structures and undergo inversions similar to those found for the isoelectronic amines.[1]

Most previous investigations of carbanion inversion were based on chemical procedures in which organometallic compounds were trapped by carboxylation or hydrolysis and the optical activities of the products observed.[2,3]

It is not possible to determine from such experiments whether inversion took place during the formation of the organometallic reagent or after the reagent had been formed.

Carbanion salts such as organosodium or organopotassium compounds are insoluble in or react with most solvents and are therefore not amenable to nmr or ultraviolet spectroscopic investigation. We have chosen to study organomagnesium and organolithium compounds since these materials behave chemically like carbanionic substances and exhibit in their nmr and ultraviolet absorption spectra properties to be expected of carbanions.[4]

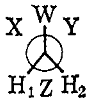
Among the class of compounds in which $CH_2$ is adjacent to an asymmetric center (I) and W is different from hydrogen, there are many examples where the methylene hydrogens ($CH_2W$) are magnetically nonequivalent[5-9] even when rotation about the $C_1$–$C_2$ bond is fast.



$$\mathrm{Y{-}\overset{\overset{\textstyle X}{|}}{\underset{\underset{\textstyle Z}{|}}{C_1}}{-}C_2H_2W}$$

I

Under these conditions the spectrum obtained is a weighted average of those for the three interconverting rotamers, II, III, and IV, the shifts of $H_1$ and $H_2$ ($\delta(H_1)$ and $\delta(H_2)$) being given by expressions a and b below. The $N$ values are mole fractions and the $\delta(-)$ values represent chemical shifts for $H_1$ or $H_2$



II

III

IV

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(1) G. Herzberg, "Infrared and Raman Spectra," D. van Nostrand Co., Inc., Princeton, N. J., 1945.

(2) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Organometallic Substances," Prentice Hall, Inc., New York, N. Y., 1954.

(3) R. E. Dessey and B. Jones, *J. Org. Chem.*, **24**, 1684 (1959); R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950); H. J. Goering and F. H. McCarron, *ibid.*, **80**, 2287 (1958).

(4) G. Fraenkel, D. Williams, and D. G. Adams, *Tetrahedron Letters*, 767 (1963); S. Kobayashi, M. S. Thesis, The Ohio State University, June 1964.

(5) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957); G. Whitesides, F. Kaplan, J. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci., U. S.*, **48**, 1113 (1962); J. J. Drysdale and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 319 (1957).

(6) J. A. Pople, *Mol. Phys.*, **1**, 1 (1958).

(7) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

(8) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).

(9) G. M. Whitesides, D. Holz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

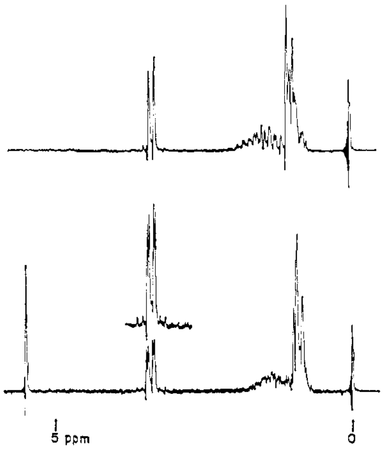

Figure 1. Nmr spectra, 60 Mc, 30°: top, 2-methylbutyl bromide 5% in $CCl_4$; bottom, 2-methylbutanol 5% in $CCl_4$ with 0.1% $CF_3CO_2H$. Both samples contain tetramethylsilane, peaks at right.

$$\delta(H_1) = N_{II}\delta(XZII) + N_{III}\delta(YZIII) + N_{IV}\delta(XYIV) \quad (a)$$

$$\delta(H_2) = N_{IV}\delta(XZIV) + N_{II}\delta(YZII) + N_{III}\delta(XYIII) \quad (b)$$

in different environments where the flanking substituents on $C_2$ and rotamer numbers are indicated in parentheses. Magnetic nonequivalence of the methylene hydrogens arises because $H_1$ and $H_2$ are always in different magnetic environments regardless as to the rate of internal rotation and there may be unequal populations of the three rotamers present. It is not now clear which of these effects is more important.[9]

If the methylene hydrogens in structure I were to simultaneously exchange places rapidly the chemical shift between them would be averaged out. Such a process cannot take place in ordinary covalent compounds but might occur in a Grignard reagent (V) by inversion at $C_2$, followed by a 180° rotation. The nmr absorption for the methylene hydrogens in a Grignard reagent of structure V would change continuously with increasing inversion rate at $C_2$ from AB to $A_2$.[10] Rates of inversion could be calculated from the line shapes for the collapsing AB quartet.[11] It was the object of this work to find a Grignard reagent which would behave in the manner described above and to utilize the change in the nmr line shapes to determine the kinetics of its inversion processes.[12] This paper deals with the nmr spectra of 2-methylbutylmangesium bromide and related organometallic compounds.

V

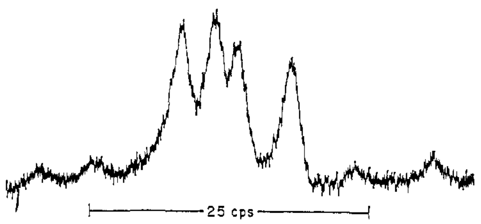

Figure 2. Nmr absorption, 60 Mc, −30°, for $CH_2Mg$ hydrogens in 2-methylbutylmagnesium bromide 2.6 *M* in ether.

## Results and Discussion

Racemic 2-methylbutyl bromide (VI) was prepared by the action of phosphorus tribromide on the corresponding alcohol[13] (VII). The nmr spectra of VI and VII and the parameters obtained from their partial analysis are shown in Figure 1 and Table I, respectively. In these compounds the α-methylene hydrogens are magnetically nonequivalent.

Table I. Nmr Parameters for $CH_3CH_2C(CH_3)H_XCH_AH_BY$

| Y | Solvent | $\delta_A - \delta_B$ ± 0.005 ppm | $J_{AB}$ | $J_{AX}$ ± 0.03 cps | $J_{BX}$ |
|---|---|---|---|---|---|
| OH | $CCl_4$[a] | 0.101 | ±10.38 | +5.62 | +5.42 |
| Br | $CCl_4$ | 0.056 | ±9.60 | +5.70 | +4.51 |

[a] Containing 0.1% $CF_3CO_2H$.

The bromide VI was converted to the Grignard reagent VIII in ether. The nmr absorption for the $CH_2Mg$ hydrogens obtained at −30° is shown in Figure 2. This multiplet forms the AB part of an ABX system, all eight theoretical lines being visible. The spacings of the lines and their relative intensities yield the nmr parameters listed in Table II in excellent fit. The line widths of about 1 cps in Figure 2 do not arise from chemical shifts among slowly exchanging diasteriomeric aggregates in solution since optically active 2-methylbutylmagnesium bromide and the starting material gave the same results; more likely a combination of viscosity and long-range coupling is responsible.

| | | | | |
|---|---|---|---|---|
| RBr | ROH | RMgBr | $R_2Mg$ | $R_2Hg$ |
| VI | VII | VIII | XII | XIII |

$$R = CH_3CH_2CHCH_3CH_2$$

Table II. Nmr Parameters, Organomagnesium Reagents, 1 *M*, R = $CH_3CH_2C(CH_3)H_XCH_AH_B$

| Solute | Solvent | $\delta_{BA}$,[d] ppm | $J_{AB}$,[e] cps | $J_{BX}$,[e] cps | $J_{AX}$,[e] cps |
|---|---|---|---|---|---|
| RMgBr[a] | Ether | 0.170 | ±12.40 | 7.65 | 4.35 |
| $R_2Mg$[b] + $MgBr_2$ | Ether | 0.170 | ±12.40 | 7.65 | 4.35 |
| $R_2Mg$[b] | Ether | 0.234 | ±11.82 | 7.39 | 4.61 |
| $R_2Mg$[b] | Ether, 10% dioxane | 0.197 | ±12.45 | 7.27 | 5.13 |
| $R_2Mg$[c] | Ether, 12% dioxane | 0.235 | ±12.66 | 7.69 | 4.91 |
| $R_2Mg$[b] | Dioxane | 0.168 | ±12.19 | 7.22 | 4.78 |
| $R_2Mg$[b] | THF | 0.171 | ±12.33 | 7.35 | 5.09 |

[a] Formula indicates Grignard reagent by constituents only. [b] $R_2Mg$ prepared from $R_2Hg$, XIIa. [c] Dessey's preparation, XIIb. [d] ±0.003 ppm. [e] ±0.02 cps.

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(10) Notation of Pople, *et al.*, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

(11) S. Alexander, *J. Chem. Phys.*, 37, 966 (1962). This method has been used to obtain inversion frequencies for amines: M. Saunders, and F. Yamada, *J. Am. Chem. Soc.*, 85, 1882 (1963).

(12) (a) Similar experiments have been reported by Roberts and coworkers: J. D. Roberts, Mechanisms Conference, Corvallis, Ore., 1964; (b) G. M. Whitesides, F. Kaplan, and J. D. Roberts, *J. Am. Chem. Soc.*, 85, 2167 (1963); G. M. Whitesides, M. Witanowski, and J. D. Roberts, *ibid.*, 87, 2854 (1965); G. M. Whitesides and J. D. Roberts, prepared for publication; (b) G. Fraenkel, D. T. Dix, and D. G. Adams, *Tetrahedron Letters*, 3155 (1964).

(13) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 2688 (1950).

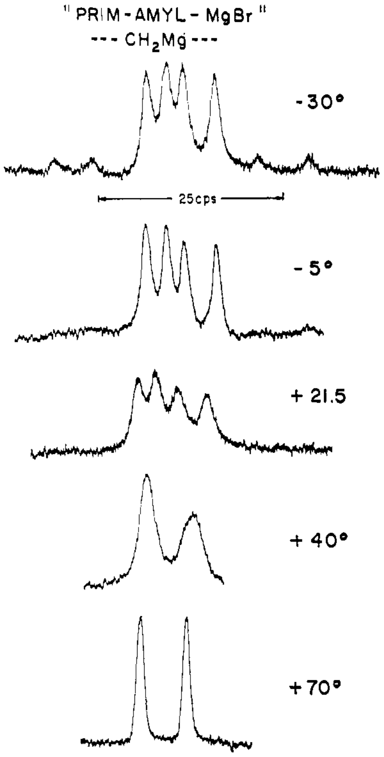
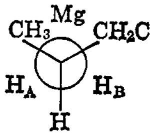


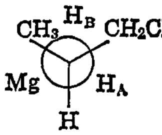
Figure 3. Nmr absorption for $CH_2Mg$ hydrogens in 2-methylbutylmagnesium bromide, 1 *M* in ether at different temperatures.

With increasing temperature the pattern in Figure 2 progressively collapses to $A_2$ of $A_2X$ (see Figure 3), as evidenced by the appearance of an equal doublet by 70° of separation exactly $^1/_2(J_{AX} + J_{BX})$. This behavior is reversible with temperature.

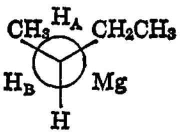
That the average $C_1H$, $C_2H$ vicinal coupling constant in the Grignard reagent VIII does not change over the entire temperature range studied strongly implies that the proportions of the rotamers present, IX, X, and XI, are invariant also.[14]



IX



X



XI

The averaging of the chemical shift between $H_A$ and $H_B$ and $J_{AX}$ with $J_{BX}$ in 2-methylbutylmagnesium bromide at elevated temperatures is best explained by rapid $H_A$, $H_B$ exchange. In this case the exchange would be accomplished by carbanionic inversion at $C_2$ followed by a 180° rotation.

The calculation of exchange rates from nmr line shapes is straightforward when the exchanging nucleii (*e.g.*, $H_A$ and $H_B$) are not coupled to one another,[15,16] and becomes increasingly difficult when $J_{AB} \neq 0$. In the present case a rigorous calculation of the exchange rates from the spectra in Figure 3 has not been attempted; instead an approximate method has been found to yield very satisfactory results.

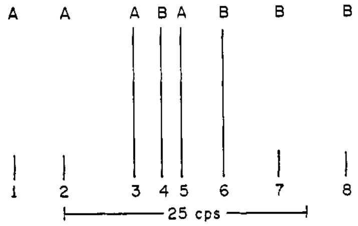


Figure 4. Stick diagram, AB part of ABX system with $\nu_{AB}$ 10.2: $J_{AB} = \pm 12.4$ cps, $J_{AX} = 4.35$ cps, and $J_{BX} = 7.65$ cps, respectively.

The AB portion of an ABX system consists of two overlapping quartets generated by the spin states of $H_X$. In Figure 4 these are lines 1, 3, 4, and 7 and lines 2, 5, 6, and 8. The line separations and intensity ratios of the *new quartets* show them to be essentially AB patterns in which $\nu_A - \nu_B$ has been replaced by $\nu_A - \nu_B \pm {}^1/_2(J_{AX} - J_{BX})$.

The effect of fast $H_A$, $H_B$ exchange on the pattern in Figure 4 is to independently collapse the two new quartets in Figure 4 to single lines at their centers. It is assumed that during an inversion the spin states of $H_X$ do not change[17] and that the values of $T_2$ for the different lines are identical. Theoretical curves for the two collapsing quartets have been calculated for different mean lifetimes between inversions using Saunder computer program for line shapes of AB systems undergoing $H_A$, $H_B$ exchange.[18] The centers of the two calculated curves were spaced apart by $^1/_2(J_{AX} + J_{BX})$ and the curves summed to give the line shapes in Figure 5. The similarities of these graphs to the experimental spectra implies that the treatment outlined here is reasonable and may be used to obtain exchange rates from nmr spectra in the samples under study.

The mean lifetimes between inversions for the reagents reported in this paper were obtained by comparison of the experimental nmr spectra with the calculated line shapes described above.

Following Grunwald, Loewenstein, and Meiboom,[16] the mean lifetime $\tau$ is defined in eq 1 where $G$ denotes the total concentration of contained alkyl groups in the

$$\frac{1}{\tau} \equiv \frac{R_I}{G} \qquad (1)$$

reagent undergoing inversion, $1/\tau$ is the specific rate of exchange, and $R_I$ is the total rate of exchange ($H_A$, $H_B$).

The Eyring plot for a 1 *M* solution of 2-methylbutylmagnesium bromide in ether is shown in Figure 6 and the parameters of activation are listed in Table III. At room temperature the mean lifetime between inversions for this Grignard reagent is $2.4 \times 10^{-2}$ sec.

**Dialkylmagnesium Compound.** Bis(2-methylbutyl)magnesium (XIIa) was prepared by treating the corresponding mercury compound, XIII, with magnesium in diethyl ether. The low-temperature nmr absorption

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[14] Although vicinal coupling constants are some function of dihedral angle (M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); H. Conroy, *Advan. Org. Chem.*, 2, 265 (1960), these models are not a reliable basis for obtaining conformations from nmr data. Furthermore there is evidence that the $\alpha$ CH bonds in primary Grignard reagents are hybridized $s^{0.6}p^{2.5}$, not $sp^3$.[4a] Hence proportions of the rotamers present in 2-methylbutylmagnesium bromide cannot be obtained from the nmr spectra.

[15] H. S. Gutowsky, D. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and A. Saika, *ibid.*, **21**, 1688 (1953); H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

[16] E. Grunwald, A. Loewenstein, and S. Meiboom, *ibid.*, **27**, 1067 (1957).

[17] G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

[18] M. Saunders, Yale University, private communication.

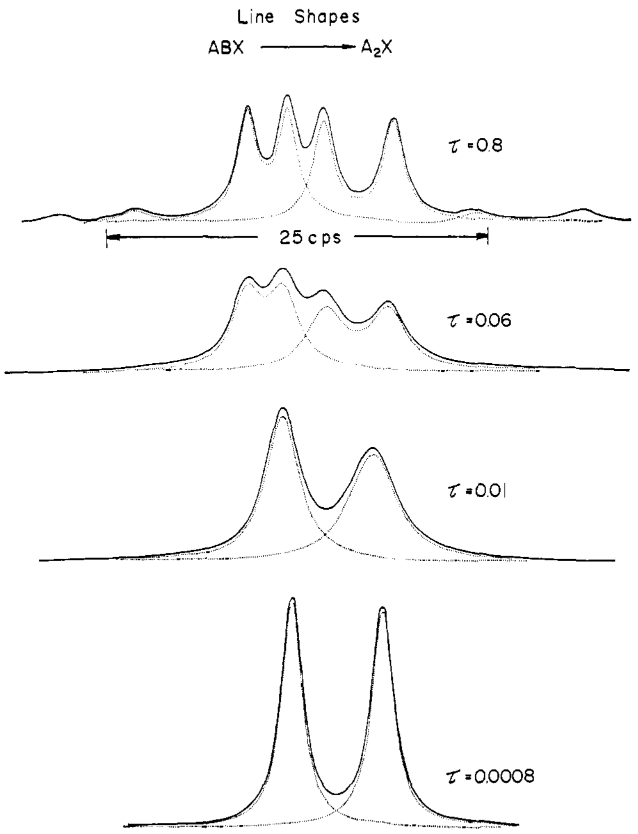

Figure 5. Solid curves indicate theoretical nmr line shapes for $CH_2Mg$ hydrogens in 2-methylbutylmagnesium bromide at different rates of inversion; dotted curves indicate line shapes for component collapsing quartets, $T_2$ = 0.25 sec.

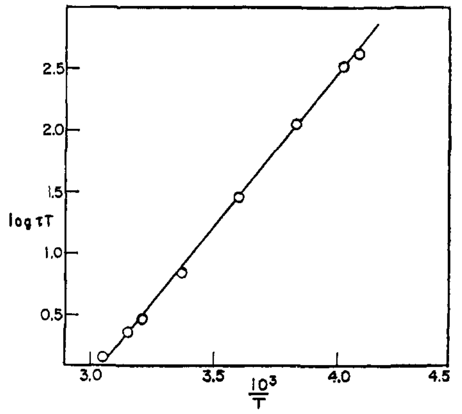

Figure 6. Eyring plot for inversion in 2-methylbutylmagnesium bromide, 1 *M* in ether.

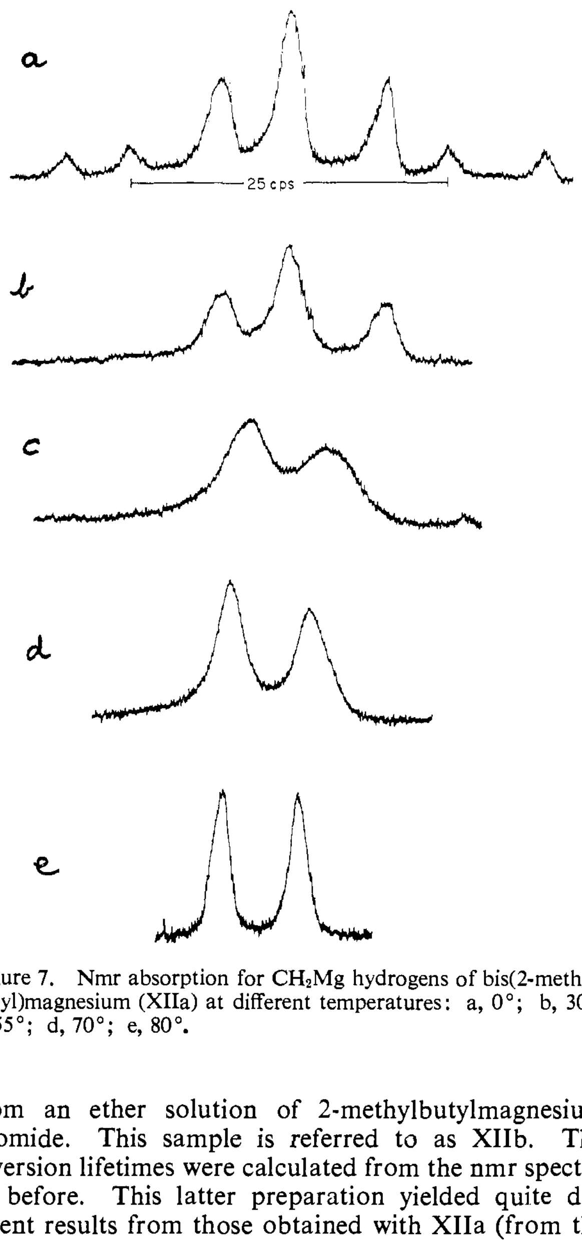

Figure 7. Nmr absorption for $CH_2Mg$ hydrogens of bis(2-methylbutyl)magnesium (XIIa) at different temperatures: a, 0°; b, 30°; c, 55°; d, 70°; e, 80°.

for the $CH_2Mg$ hydrogens of XII in ether is shown in Figure 7a and the analysis is listed in Table II. It is seen that the nmr parameters for XIIa differ markedly from those for the Grignard reagent. When compound XIIa is heated in ether, the nmr absorption for the α hydrogens changes from AB of ABX to $A_2$ of $A_2X$ as shown in Figure 7a–e. Employing the method described above these spectra yielded the activation parameters listed in Table III.

Bis(2-methylbutyl)magnesium also was generated by Dessey's method,[19] precipitating $MgBr_2$ with dioxane from an ether solution of 2-methylbutylmagnesium bromide. This sample is referred to as XIIb. The inversion lifetimes were calculated from the nmr spectra as before. This latter preparation yielded quite different results from those obtained with XIIa (from the mercury compound) as is seen in Tables II and III and Figure 8. Furthermore, addition of dioxane to XIIa in ether yielded nmr and activation parameters

Table III. Activation Parameters for Inversion, 1 *M*, R = 2-Methylbutyl

| Solute | Solvent | $\Delta H^*$, kcal | $\Delta S^*$, eu | $1/\tau$, 25°, $sec^{-1}$ |
|---|---|---|---|---|
| RMgBr | Ether | 12 | −11 | 42 |
| RMgBr | THF | 16.6 | −2 | 1.9 |
| RMgBr | Anisole | 9.6 | −14 | 490 |
| $R_2Mg^a$ | Ether | 18.2 | +5 | 5 |
| $R_2Mg^b$ | Ether, 12% dioxane | 18.3 | −3 | 0.06 |
| $R_2Mg^a$ | Ether, 10% dioxane | 19.5 | +2.5 | 0.13 |
| $R_2Mg^a$ | Dioxane | 4.9 | −40 | 2.5 |
| $R_2Mg^a$ | THF | 10.5 | −25 | 0.57 |
| $R_2Mg$ + $MgBr_2^c$ | Ether | 12.0 | −12 | 42 |

[a] Preparation XIIa. [b] Preparation XIIb. [c] 0.5 *M* each in $R_2Mg$, XIIa, and $MgBr_2$.

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(19) R. E. Dessey, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, 79, 3476 (1957); R. E. Dessey and G. S. Handler, *ibid.*, 80, 5824 (1958).

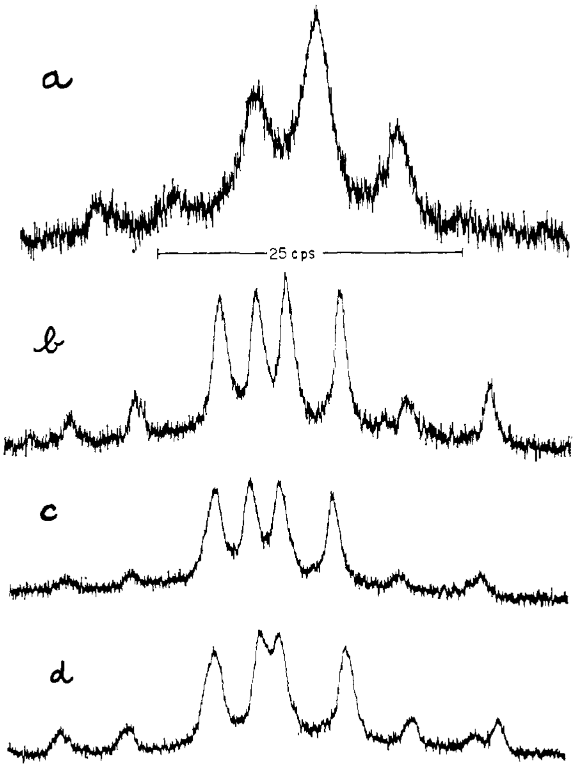

Figure 8. Nmr absorption for $CH_2$ hydrogens of bis(2-methylbutyl)magnesium at 0° in different solvents, all 1 *M:* a, XIIb in ether with 12% dioxane; b, XIIa in THF; c, XIIa in dioxane; d, XIIa in ether with 10% dioxane.

different again from those for the first two samples described above.

As is shown in Figure 8 the lines in the nmr pattern for XIIb are considerably broader than those for XIIa in ether although the two samples had the same viscosity. The Dessey preparation (XIIb) still contained 12% dioxane.[19a] Hence the broad lines in Figure 8a may be attributed mainly to the following factors. There exist small chemical shifts between different organomagnesium species which differ in the arrangement of ether and dioxane molecules coordinated to magnesium. The exchange of these ethers among organomagnesium species must be slow on the nmr time scale.

Thus in this work $R_2Mg$ prepared by Dessey's method does not have the same properties as the reagent prepared from the dialkylmercury compound. Evidently these differences arise from residual dioxane in the Dessey preparations. Previous results obtained with dioxane precipitation techniques should be interpreted in this light.

The low-temperature nmr absorptions for the $CH_2Mg$ hydrogens of XIIa obtained with different solvents are shown in Figure 8 and the corresponding nmr parameters are listed in Table II. Table III contains the thermodynamic activation parameters for inversion. Solvents have a profound influence on the activation parameters. Although $\Delta H^*$ and $\Delta S^*$ undergo violent changes among these samples $\Delta F^*$ changes much less. In fact these data obey the isokinetic relationship[20] (eq 2) which implies that there is a common mechanism responsible for the inversion process in all these solvents (see Figure 9).[21]

$$\Delta H^* = 370\Delta S^* + 19{,}400 \tag{2}$$

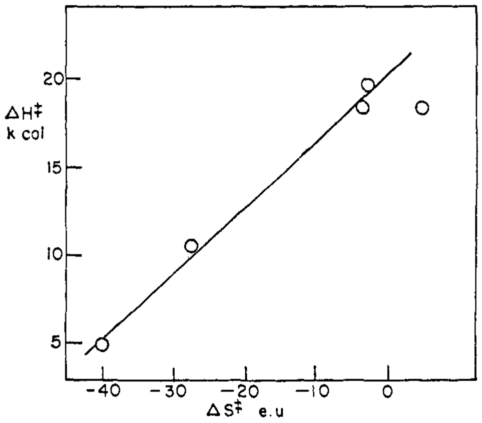

Figure 9. Isokinetic plot for inversion of bis(2-methylbutyl)-magnesium (XIIa) in different solvents.

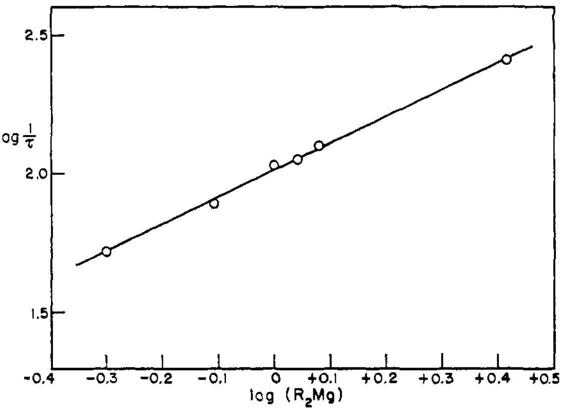

Figure 10. Dependence of $\tau$ on bis(2-methylbutyl)magnesium (XIIa) concentration at 45°.

The inversion rates for bis(2-methylbutyl)magnesium (from the mercury compound) in ether have been studied in some detail. The dependence of $\tau$ on concentration of XII at 45° is illustrated in Figure 10. The concentration range in which these experiments could be performed was necessarily limited by viscosity broadening of the nmr lines at the high end (>3 *M*) and inadequate signal to noise ratios below 0.3 *M*.

In the first approximation it is assumed that the inversion rate $R_I$ has a simple kinetic order, $n$

$$R_I = k[R_2Mg]^n \tag{3}$$

Using the definition for $\tau$[16] with eq 3 gives

$$\frac{1}{\tau} = k[R_2Mg]^{n-1} \tag{4}$$

The slope of the graph in Figure 10 is 1.0 ± 0.05; hence $n$ is 2.0 and the rate law is

$$R_I = 102[R_2Mg]^2 \tag{5}$$

The simplest rationale for these kinetic results is that the slow step in the inversion process involves an inter-

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(20) J. E. Leffler, *J. Org. Chem.*, 20, 1212 (1955).

(21) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9. It is still possble to have two or more interaction mechanisms each with the same value of $\beta$ operating here.

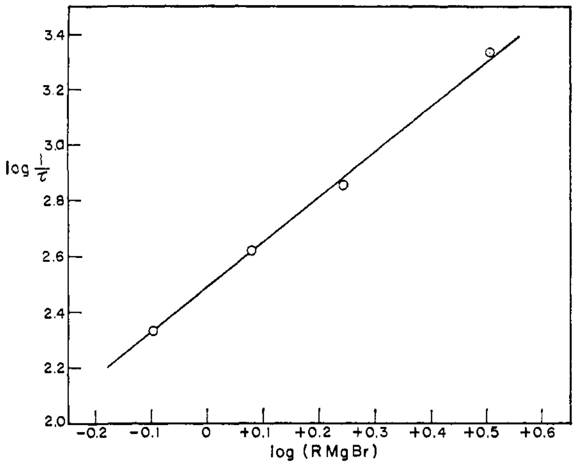
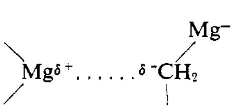


Figure 11. Dependence of $\tau$ on 2-methylbutylmagnesium bromide concentration at 60°.

molecular electrophilic displacement of magnesium on carbon (XIV).[22]

XIV



The number of $R_2Mg$ units in the transition state is twice the now unknown state of aggregation of XIIa in ether. However, dimethyl- and diethylmagnesium have been reported to be monomeric[23] at 0.1 *M* in ether. In the solid state diphenylmagnesium dietherate is monomeric.[24] It is likely that XIIa in ether is monomeric with two ether molecules coordinated per magnesium.

Because the structures of organomagnesium compounds in solution are not known the dependence of these inversion rates on solvents merits only a short comment. Qualitatively it is likely that transition state XIV will have more charge separation than the ground state of XIIa. Also in the course of proceeding from the ground state to XIV the coordination numbers of the two magnesium atoms will change. These factors would be expected to vary radically among different solvents and thus change the rate of inversion.

**Grignard Reagent.** The nmr parameters obtained at low temperatures for 2-methylbutylmagnesium bromide in different solvents are listed in Table II and the activation parameters for inversion appear in Table III. As in the case of the organomagnesium compound XIIa, the rates of inversion depend critically on the nature of the solvent.

An equimolar mixture of XIIa and magnesium bromide in ether gave nmr and activation parameters identical with those for the Grignard reagent (RMgX) of corresponding concentration. Also in similar experiments employing infrared spectral[25] and dielectric constant[26] measurements no differences could be detected between RMgX and $R_2Mg + MgX_2$. Hence, these two preparations are considered to be identical.

The results obtained from the two samples of 2-methylbutylmagnesium bromide desdribed in the preceeding paragraph are independent of the optical activity of the 2-methylbutyl bromide employed as starting material.

The mean lifetimes between inversions of 2-methylbutylmagnesium bromide in ether have been determined as a function of Grignard concentration. The results are shown in Figure 11 and the rate law is

$$R_I = 330[\mathrm{RMgBr}]^{2.5} \qquad (6)$$

The principal conclusion to be drawn here is that the slow step of the inversion process involves electrophilic displacement of magnesium on carbon.

Ashby and Smith find several Grignard reagents to consist of mixtures of monomers and dimers[27] in ether within the concentration range 0.1 to 0.4 *M*. Extrapolation of their results to the concentration range used here suggests that at 1 *M* concentrations these reagents are dimers and that this represents the maximum aggregation of 2-methylbutylmagnesium bromide in ether.

On the basis that 2-methylbutylmagnesium bromide is either monomeric or dimeric in ether the following Schemes I and II, respectively, account for the above results. The solvent coordinated to magnesium has been omitted and the formulas are empirical only.

**Scheme I**

$$2\mathrm{RMgX} \rightleftarrows (\mathrm{RMgX})_2 \qquad \text{fast} \qquad (7)$$

$$\mathrm{RMgX} \rightleftarrows \mathrm{RMg^+} + \mathrm{X^-} \qquad \text{fast} \qquad (8)$$

$$\mathrm{RMg^+} + (\mathrm{RMgX})_2 \longrightarrow \text{inversion} \qquad \text{slow} \qquad (9)$$

(or)

$$\mathrm{RMg^+} + 2\mathrm{RMgX} \longrightarrow \text{inversion} \qquad \text{slow} \qquad (10)$$

**Scheme II**

$$2(\mathrm{RMgX})_2 \rightleftarrows (\mathrm{RMgX})_4 \qquad \text{fast} \qquad (11)$$

$$(\mathrm{RMgX})_2 \rightleftarrows 2\mathrm{RMgX} \qquad \text{fast} \qquad (12)$$

$$\mathrm{RMgX} + (\mathrm{RMgX})_4 \longrightarrow \text{inversion} \qquad \text{slow} \qquad (13)$$

(or)

$$\mathrm{RMgX} + 2(\mathrm{RMgX})_2 \longrightarrow \text{inversion} \qquad \text{slow} \qquad (14)$$

Further elucidation of the mechanism of the inversion process—the relative rates of inversion and carbon–magnesium exchange and the role of solvents—must await more information on the structure of Grignard reagents in solution.

## Conclusions

In this work it has been found that the inversion rates of 2-methylbutylmagnesium bromide and bis(2-methylbutyl)magnesium are fast at 0°. The results are similar to those reported by Roberts and co-workers for neohexylmagnesium halides and bis(neohexyl)-magnesium.[12a] However, it should not be expected that all primary Grignard reagents will behave in a like manner.

It might be argued that since primary alkylmagnesium compound should give the most stable alkyl carbanions they might also be the most likely systems to undergo inversion by unimolecular ionization. In fact no such steps could be detected. Secondary and tertiary

$$\mathrm{RCH_2Mg}- \longrightarrow \mathrm{RCH_2}^{\delta-}\ldots\ldots{}^{\delta+}\mathrm{Mg}- \qquad (15)$$

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[22] Ether coordinated to magnesium has been omitted in XIV.

[23] A. D. Vreudenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).

[24] G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4829 (1964).

[25] H. S. Mosher and R. M. Salinger, *ibid.*, **86**, 1782 (1964).

[26] R. E. Dessey, *J. Org. Chem.*, **25**, 2260 (1960).

[27] E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964).

reagents will be even less likely to invert by such a mechanism and probably also undergo the electrophilic displacement steps. For such a mechanism variations in the rate of inversion among different primary compounds can be chiefly ascribed to steric effects as has been observed for the rates of S$_N$2 solvolysis reactions.[28] The one feature which the systems so far studied, neohexyl-, 2-methylbutyl-, and 2-phenyl-3,3-dimethylbutylmagnesium compounds, all have in common is that they are crowded around the $\alpha$-carbon atoms. Less-substituted reagents would be expected to invert faster.

## Experimental Section

**Chemicals.** The following solvents were distilled from lithium aluminum hydride: dioxane (Matheson Coleman and Bell), anisole (Matheson Coleman and Bell), dimethoxymethane (Eastman Organic Chemicals), and toluene (Matheson Coleman and Bell). Benzene (Matheson Coleman and Bell) was distilled from ethyllithium. Diethyl ether (Mallinckrodt) and tetrahydrofuran (Du Pont) were both distilled from methylmagnesium bromide. Primary active amyl alcohol, $[\alpha]^{21}\text{D}$ $-13.5°$, came from K and K Laboratories and the inactive material was obtained from Eastman Organic Chemicals. The magnesium used in these experiments was triply sublimed highest purity from Dow Chemical Co.; mercuric bromide was from Baker and Adams; phosphorus tribromide was obtained from Matheson Coleman and Bell; helium (highest purity) was from Matheson.

**2-Methylbutyl Bromide (VI).** Crombie's[13] preparation was used. For the optically active preparation of VI $[\alpha]^{21}\text{D}$ (chloroform) was $+4.78°$.

**Bis(2-methylbutyl)mercury (XIII).** A solution of 0.3 mole of 2-methylbutylmagnesium bromide in 200 ml of ether was prepared from 2-methylbutyl bromide. A three-neck, 500-ml flask was equipped with a Soxhlet extractor, a gas inlet tube, and a mechanical stirrer. The assembly was dried by gently flaming the flask in a current of helium. After the flask had cooled off (under helium) the Grignard solution described above was transferred to it in several portions by means of a 50-ml syringe. Mercuric bromide (52 g, 0.144 mole) was placed in the Soxhlet thimble. The ether was refluxed for 4 days extracting all the mercuric bromide from the thimble. The reaction mixture was hydrolyzed with an ice slurry and extracted with ether. The ether layer was washed with 100 ml of 10% aqueous sodium hydroxide and then with four 100-ml aliquots of warm water, 50°. The last water washings and the ether solution were unreactive to alcoholic silver nitrate. The ether layer was dried with calcium chloride and the ether was removed. The remaining oil was distilled at 1 mm and 94–96° to give 32 g of bis(2-methylbutyl)mercury in 65% yield. Both optically active and inactive materials were prepared in this way. For the former material $[\alpha]^{21}\text{D}$ was $+7.82°$ (chloroform).

**Bis(2-methylbutyl)magnesium (XIIa).**[29] A 50-ml, three-neck flask (₸ 14/20) equipped with a mechanical stirrer, reflux condensor, drying tube, and serum cap was dried in a stream of helium with flaming. Triply sublimed magnesium (0.2 g, 0.0083 g-atom) in the form of turnings was placed in the flask and covered with 15 ml of dry ether (distilled from methylmagnesium bromide). Bis(2-methylbutyl)mercury (2 g, 0.0059 mole) was syringed into the flask through the serum cap. The mixture was refluxed gently with rapid stirring for 12 hr. The gray magnesium amalgam and magnesium turnings were allowed to settle out and samples of the solution removed for chemical and nmr analysis. In this way a solution 1.2 *M* in bis(2-methylbutyl)magnesium was obtained. The solution was transferred with a syringe to a glass vial equipped with a 1-mm straight-bore stopcock and serum cap. Selected amounts of ether dried as before were added and after each such addition samples of the solution were removed for transfer to nmr tubes and titration for contained base.

Samples of XIIa in other solvents were prepared by removing ether from the above preparation at $10^{-4}$ mm and 50° and dissolving the resulting solid in the new solvent.

**Bis(2-methylbutyl)magnesium (XIIb) by Dioxane Precipitation Procedure.**[19,30] Into a rapidly stirred 1 *M* solution of 2-methylbutylmagnesium bromide in ether was added 2.8 g of *p*-dioxane. The mixture was refluxed for 5 hr, transferred to a centrifuge tube, and spun at 1000 rpm for 1 hr. Samples of the supernatant liquid were withdrawn with a syringe for chemical and nmr analysis.

Attempts were made to remove all solvents from XIIb in ether by heating at 100° ($10^{-3}$ mm). The resulting powder was only slightly soluble in ether and still contained traces of dioxane.

**Magnesium Bromide.** Magnesium bromide used in these experiments was obtained from the reaction of magnesium with ethylene dibromide in ether.

**Chemical Analysis.** Bromide was determined by the Volhard method. Contained base was measured by acidimetric titration with methyl orange as indicator.

**Nmr Tubes.** Nmr tubes were washed in aqua regia, aqueous trisodium phosphate, distilled water, and 5% ammonia, then baked in an oven at 95° overnight. Immediately before filling, the tube was flamed out in a current of dry helium and stoppered with a rubber serum cap.

**Syringes.** Syringes equipped with syringe stopcocks and 12-in. 18-gauge needles were flushed with helium before use. The nmr tubes were filled with these syringes through the serum caps. Then the bottoms of the tubes were cooled with liquid nitrogen and the tops were pulled off in a hot flame without removing the serum caps.

**Grignard Reagents.** The apparatus consisted of a 25-mm o.d. Pyrex tube 6 in. long attached to an outer ₸ 24/40 joint at one end and sealed off at the other. A side arm equipped with a 2-mm straight-bore Teflon stopcock and serum cap was attached to the main tube at an oblique angle. The assembly was flamed out in a current of helium. About 0.2 g of sublimed magnesium in the form of turnings was placed in the tube together with a magnetic stirring bar. The assembly was attached to a stillhead and 15 g of the ether to be used was distilled onto the magnesium from methylmagnesium bromide. 2-Methylbutyl bromide (0.25 ml) was slowly syringed through the Teflon stopcock into the magnetically stirred reaction vial at such a rate as to give mild refluxing. No initiator was needed. After the bromide was added, the stopcock was closed and the reaction was stirred for 2 hr. Excess magnesium was allowed to settle and samples withdrawn as previously described for nmr and chemical analysis. Over 95% conversion was achieved in these runs.

**Nmr Spectrometer.** All spectra were determined with the Varian A-60 nmr spectrometer equipped with variable-temperature probe. Line shapes used for determination of $\tau$ were obtained on a scale of 1 cps/cm at a sweep rate of 0.1 cps/sec.

**Analysis of Spectra.** All ABX spectra reported in this work were analysed in the standard manner.[31] Among the organometallic compounds the X parts of the spectra were buried under solvent absorption.

**Acknowledgment.** This research was generously supported by the Petroleum Research Fund of the American Chemical Society Grant No. 943-A5 and the Air Force Office of Scientific Research Grant No. AF-AFOSR 251-63. We are endebted to Professor Martin Saunders, Yale University, for a copy of his computor program used in this work. We would like to thank Professor John D. Roberts, California Institute of Technology, for copies of his papers prior to their publication, and also Dr. M. Scheinblatt and Dr. Z. Luz, Weizmann Institute of Science, for valuable discussions.

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(31) Reference 10, p 134.