

$3 \times 10^{-5} M$ concentration of radicals, while similar treatment of a solution of *cis*-2-decalone produced $2 \times 10^{-5} M$ concentration of radicals.

Study of Enolization and Oxidation of Ketones by Infrared Spectroscopy. A study of the changes occurring during a typical oxidation reaction by infrared spectroscopy was undertaken to obtain some idea of the extent and speed of enolization and the subsequent oxidation of the enolate.

A thoroughly degassed solution of 0.05 *M* *trans*-2-decalone in DMSO was placed in an IRTRAN-II cell, and the change in the spectrum with time upon the addition of 0.1 *M* potassium *t*-butoxide in the absence of air was followed (only the region between about 1800 and 1600 cm^{-1} was scanned). The strong absorption of the carbonyl group at 1717 cm^{-1} decreased rapidly and a new broader band at 1597 cm^{-1} appeared. Three minutes after the addition of the base, about 77% of the ketone was calculated to have ionized, while after 20 min., there was barely any absorption at 1717 cm^{-1} . At this stage, the basic solution was exposed to air for a short time (14 sec.)

whereupon a new, strong band appeared immediately at 1665 cm^{-1} (shoulders at 1677 and 1654 cm^{-1}) along with a weaker band at 1577 cm^{-1} (shoulders at 1588 and 1566 cm^{-1}). When air was admitted for a longer period (2 min.), these two bands became stronger (increase of about 30% in absorbance), but some absorption in the region of 1597 cm^{-1} persisted.

Acknowledgment. We are grateful to Professor R. L. Augustine for samples of *cis*- and *trans*-2-decalones; to Professor W. S. Johnson for 7; to Professor R. Sciaky for 6; to Drs. R. Burtner, F. Colton, and W. F. Johns, G. D. Searle and Co., for 8, 12, 14a, and 15; to Dr. R. T. Rapala, Eli Lilly and Co., for 11 and 17a; to Drs. R. Konaka, T. Komeno, and K. Takeda of Shionogi and Co., Ltd., for 11a; to Drs. L. Velluz and G. Amiard for 12a, 12b, and its acetate, 15a, 15b, and its acetate; to Professor C. Chen for 14 and 17; to Dr. J. A. Edwards, Syntex Laboratories, Palo Alto, Calif., for 20; to Professor O. L. Chapman and Dr. T. A. Rettig for 4,4-dimethyl-2-cyclohexen-1-one; and to Professor W. C. Wildman for the use of the Chromalab gas chromatograph.

Nuclear Magnetic Resonance Spectroscopy. The Configurational Stability of Primary Grignard Reagents. Structure and Medium Effects¹

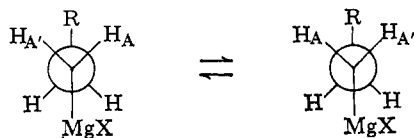
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Contribution No. 3172 from the Gates and Crellin Laboratories of Chemistry,
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Qualitative and semiquantitative examination of the temperature dependence of the RCH_2 -Mg proton n.m.r. spectra of several Grignard reagents indicates that the rate of inversion at this center is relatively insensitive to the structure of the group R. Secondary Grignard reagents invert much more slowly, if at all. The dependence of the inversion rate of the primary organometallic compounds on solvent character and on added salts suggests that inversion proceeds by means of a mechanism having kinetic order greater than one.

Introduction

The preceding paper² presented n.m.r. spectral evidence demonstrating that 3,3-dimethylbutylmagnesium chloride³ in diethyl ether solution undergoes rapid inversion of configuration at the CH_2 -Mg center.



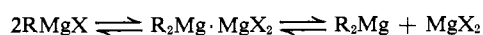
(1) Supported in part by the Office of Naval Research and the National Science Foundation.

(2) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 2854 (1965).

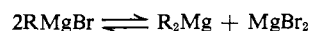
(3) For convenience, the organometallic compound formed by reaction of an alkyl halide with magnesium in an ethereal solvent will again be called an alkylmagnesium halide.

This observation suggests that careful examination of the spectrum of this and related compounds in different solvents and at different concentrations might provide data pertinent to the mechanism of this inversion and to the nature of Grignard reagents in solution.

Much of the modern work concerned with the structure of Grignard reagents has centered around attempts to evaluate the importance of the so-called Schlenk equilibrium in describing the Grignard reagent. In several well-known experiments, Dessy and co-workers examined the exchange reaction between labeled magnesium bromide and diethyl-⁴ and diphenyl-



magnesium,⁵ and concluded from these experiments that the equilibrium



was not important in the Grignard reagents studied. In addition, conductometric measurements were reported to give identical⁵ values for the dielectric constant of a 1:1 mixture of diethylmagnesium and magnesium bromide and of an equivalent concentration of "ethylmagnesium bromide."⁶ It was therefore con-

(4) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 3476 (1957).

(5) R. E. Dessy and G. S. Handler, *ibid.*, **80**, 5824 (1958).

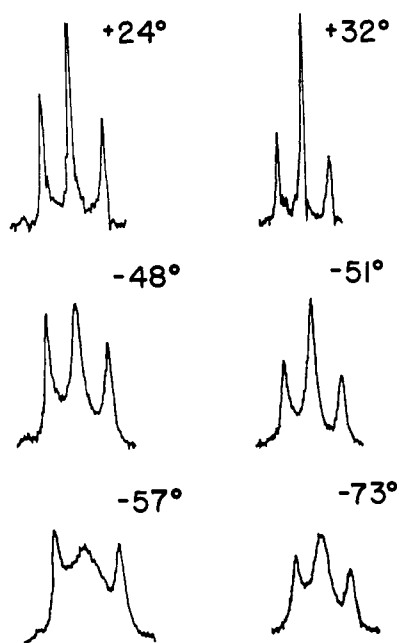


Figure 1. Spectra of the CH_2 -Mg protons of 3-methylbutylmagnesium chloride and *n*-butylmagnesium chloride in diethyl ether as a function of temperature.

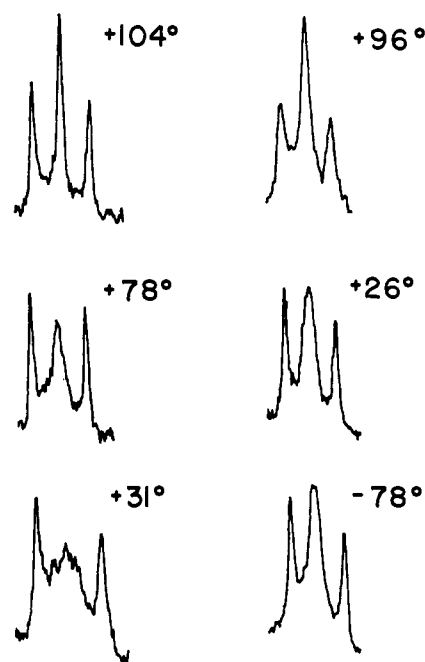


Figure 2. Spectra of the CH_2 -Mg protons of bis(3-methylbutyl)magnesium and di-*n*-butylmagnesium in diethyl ether as a function of temperature.

cluded that the Grignard reagents studied were best represented by the equilibrium and that no species represented by the formula "RMgX" is present in solution.⁷

Recently however, Stucky and Rundle⁸ and Ashby and Becker⁹ have presented data suggesting that Dessy's conclusion may have been premature. Stucky and Rundle demonstrated by the X-ray crystal structure determination of phenylmagnesium bromide dietherate that the magnesium atom was tetrahedrally coordinated to one phenyl group, one bromide atom, and two oxygen atoms; that is, that this Grignard reagent was in fact "RMgBr·2Et₂O" in the solid state.

Ashby and Becker were able to obtain a crystalline solid from a tetrahydrofuran solution of ethylmagnesium chloride whose empirical formula corresponded to EtMg₂Cl₃·THF. This fact, and their observation that ethyl Grignard reagent was monomeric in tetrahydrofuran, led them to conclude that the most important species in solution was actually EtMgCl.

Both of these studies depended on compounds existing in the solid state, and in consequence neither is necessarily pertinent to the structure of the Grignard reagent in solution. However, the X-ray study in particular provides evidence that "RMgX" may exist under suitable conditions, and suggests that further

work on the structure of Grignard reagents in solution must take into consideration the possibility of its existence.

Results

Organomagnesium compounds derived from halides similar in structure to 3,3-dimethylbutyl chloride show an analogous temperature dependence in their spectra. Thus, the spectra of the CH_2 -Mg protons of 3-methylbutylmagnesium chloride and *n*-butylmagnesium chloride are triplets at room temperature; at -50° , the spectra become more complicated (Figure 1). The degree of complexity is unfortunately sufficiently great to discourage attempts to analyze the spectra explicitly. The 3,3-dimethylbutyl group provides a particularly simple system for analysis, because the four protons of the ethylene fragment are not coupled to the protons of the *t*-butyl group. In the 3-methylbutyl and *n*-butyl derivatives however, the chemical shift between the methyl protons and the adjacent methylene protons is of the same order of magnitude as the coupling constant between them, and the α -proton spectrum is consequently complicated.¹⁰

Although little quantitative information can be obtained from the spectra of these Grignard reagents, or from the spectra of the corresponding dialkylmagnesium compound (Figure 2), qualitative comparison with the 3,3-dimethylbutylmagnesium compounds makes clear two similarities in their temperature dependence. The first of these is that the low-temperature spectra of the Grignard reagents are very similar to the room-temperature spectra of the corresponding dialkylmagnesium compounds. The second is that the

(6) The contradiction with a previous report is unexplained: R. E. Dessy and R. M. Jones, *J. Org. Chem.*, **24**, 1685 (1959).

(7) R. E. Dessy, *ibid.*, **25**, 2260 (1960). However, see R. E. Dessy, S. E. I. Green, and R. M. Salinger, *Tetrahedron Letters*, **21**, 1369 (1964), and D. O. Cowan, J. Hsu, and J. D. Roberts, *J. Org. Chem.*, **29**, 3688 (1964), for evidence that in fact the Schlenk equilibrium may be rapidly established.

(8) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(9) E. C. Ashby and W. E. Becker, *ibid.*, **85**, 118 (1963).

(10) F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961); J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

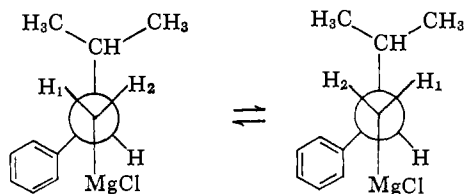
Grignard reagent spectra do not seem to change at temperatures below approximately -70° , and the dialkylmagnesium spectra change little below $+30^{\circ}$.

Both of these observations are compatible with the explanation previously proposed for the temperature dependence of the spectrum of 3,3-dimethylbutyl Grignard reagent based on the rate of inversion. Moreover, the second of these observations would be difficult to reconcile with important changes in populations of rotational conformations with temperature. If changes in the populations of the *trans* and *gauche* conformations were important in determining the temperature dependence of these spectra, the broadening observed in the central line for di-*n*-butylmagnesium compared with *n*-butylmagnesium chloride would be the consequence of an increase in the energy difference between *trans* and *gauche* conformations of these compounds. Decreasing the temperature of the Grignard reagent produces a broadening of the central line of its spectrum. If this change were a reflection of changes in conformer populations, lowering the temperature of the dialkylmagnesium compound should result in an analogous change in its spectrum. In fact, little change in the spectrum of the latter compound is observed on decreasing the temperature. Therefore, changes in conformer populations are probably not important in determining the temperature dependence of the spectra.

An analogous argument can of course be applied to the 3-methylbutylmagnesium and 3,3-dimethylbutylmagnesium compounds studied.

The high-temperature spectral behavior of bis(3-methylbutyl)magnesium and di-*n*-butylmagnesium appears comparable with that observed for bis(3,3-dimethylbutyl)magnesium. Each changes from its "low-temperature" form to a triplet over the temperature range $+50$ to $+110^{\circ}$.

The similarity in the spectral behavior of these three structurally similar Grignard reagents suggests that the rates and thermodynamic parameters for the processes which result in the simplification of their spectra are approximately the same. This qualitative observation that all the primary Grignard reagents examined exhibit the same spectral behavior is further supported by analysis of the temperature dependence of the spectrum of 2-phenyl-3-methylbutylmagnesium chloride as will be described below.



Discussion of the Grignard reagents considered up to this point has centered on the observation of a temperature-dependent averaging of vicinal coupling constants between α - and β -methylene protons. The same kinds of information can in principle be obtained from chemical-shift data. The two primary Grignard reagents examined for evidence of chemical-shift averaging were selected in the expectation that their α -methylene group would have an AB-type spectrum if inversion at the CH_2 -Mg center were slow, and an A_2 -type spectrum if inversion were rapid.

The protons of a methylene group near a center of molecular asymmetry may be magnetically nonequivalent and display AB-type n.m.r. spectra.¹¹ Recent investigations indicate that conformational preference is responsible for the major part of the magnetic nonequivalence of the methylene protons.^{11,12} A primary Grignard reagent which might be expected to have magnetically nonequivalent methylene protons would thus be one in which one rotational conformation around the α,β -carbon-carbon bond would be significantly lower in energy than the other two. The CH_2 Mg protons of two Grignard reagents, 2-phenylpropylmagnesium bromide and 2-phenyl-3-methylbutylmagnesium chloride, were examined for evidence of magnetic nonequivalence. The α -methylene hydrogens of the former in diethyl ether solution had an A_2 -type spectrum from $+33$ to -80° (viscous broadening prevented measurement below this temperature). The methylene protons of the latter had a spectrum characteristic of the AB part of an ABX spectrum at room temperature; at $+110^{\circ}$, the spectrum collapsed to an A_2X type (Figures 3 and 4).

The most plausible interpretation of the temperature dependence of the spectrum of 2-phenyl-3-methylbutylmagnesium chloride is the same as that proposed for 3,3-dimethylbutylmagnesium chloride. The magnetic nonequivalence of the methylene hydrogens at $+33^{\circ}$ demonstrates clearly that inversion of configuration at the CH_2 -Mg center is slow on the n.m.r. time scale. The loss of the magnetic nonequivalence as the temperature is increased is taken as evidence that a rapid inversion of configuration, analogous to that proposed previously, averages the magnetic environments of the methylene hydrogens.

Quantitative discussion of these spectra is more difficult than that of the spectra of the 3,3-dimethylbutylmagnesium derivatives,² because the chemical shifts and coupling constants obtained on analysis of the former compound are less precise. The AB part of an ABX spectrum theoretically consists of eight lines, of which four may be of low intensity. The positions of these low-intensity lines are unfortunately difficult to determine exactly in the room temperature spectra of either 2-phenyl-3-methylbutylmagnesium chloride or bis(2-phenyl-3-methylbutyl)magnesium. These lines are necessary for accurate determination of the geminal methylene coupling constant. The spectrum in ether solution is further confused by the accidental near degeneracy of two of the intense lines and by the high-field ^{13}C -ether satellites. Moreover, no information can be obtained from the X part of the spectrum, due both to its low intensity and to its complexity.

Therefore, although agreement can be obtained between the observed and calculated spectra, the values obtained from analysis cannot be regarded as highly precise. Coupling constants and chemical shifts for a solution of this Grignard reagent in diethyl ether solution at -14° , and in tetrahydrofuran solution at $+33^{\circ}$, and for the corresponding dialkylmagnesium compound in ether at $+33^{\circ}$ are reported in Table I. The starting halide has an A_2X type spectrum in carbon tetrachloride solution.

(11) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964), and references therein.

(12) See, however, H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

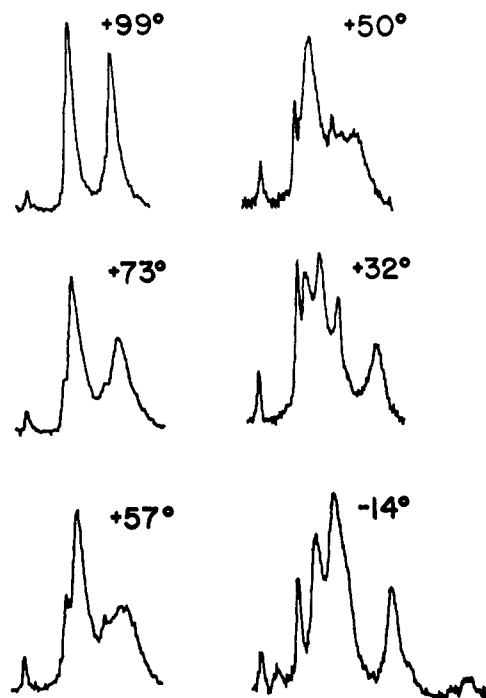


Figure 3. Spectra of the $\text{CH}_2\text{-Mg}$ protons of 2-phenyl-3-methylbutylmagnesium chloride in diethyl ether as a function of temperature. The spectrum of the organometallic compound is superimposed on that of the ether ^{13}C satellite.

The temperature dependence of the α -proton spectrum of 2-phenyl-3-methylbutylmagnesium chloride depends on the response of the ABX spectrum to the exchange rate of a process interchanging the A and B protons. The AB part of the observed ABX spectrum consists of two overlapping quartets, arising from transitions within two separate sets of energy levels

Table I. Spectral Parameters (c.p.s.) for the Methylene Protons of 2-Phenyl-3-methylmagnesium X Treated as an ABX System^a

	X = Cl ^b	X = Cl ^c	X = R ^d
$\nu_A - \nu_B$	12.9	9.2	14.2
$\nu_A - \nu_X$	150 ^e	150 ^e	150 ^e
J_{AB}	± 12.1	± 12.5	$\pm 12.2^e$
J_{AX}	∓ 10.3	∓ 9.7	∓ 10.2
J_{BX}	∓ 4.3	∓ 5.6	∓ 3.2

^a Accuracy in the chemical shift and coupling constant values is estimated to be ± 0.5 c.p.s. ^b Diethyl ether solution at -14° . ^c Tetrahydrofuran solution at $+33^\circ$. ^d Diethyl ether solution at -14° . ^e This value was assumed.

(i.e., the two sets of transitions have no energy levels in common). Figure 5 indicates the transitions which are expected to collapse under the influence of an exchange process averaging states 3' and 4', and 5' and 6'.¹³ It can be shown that each of these quartets behaves approximately as an AB quartet with "effective chemical shifts" of $\nu_B - \nu_A + J_{BX} - J_{AX}$ or $\nu_B - \nu_A - J_{BX} + J_{AX}$, respectively,¹⁴ and coupling

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

(14) These calculations, based on the method of Alexander and Kaplan, will be published in detail elsewhere: S. Alexander, *J. Chem. Phys.*, **37**, 967, 974 (1962), and references therein.

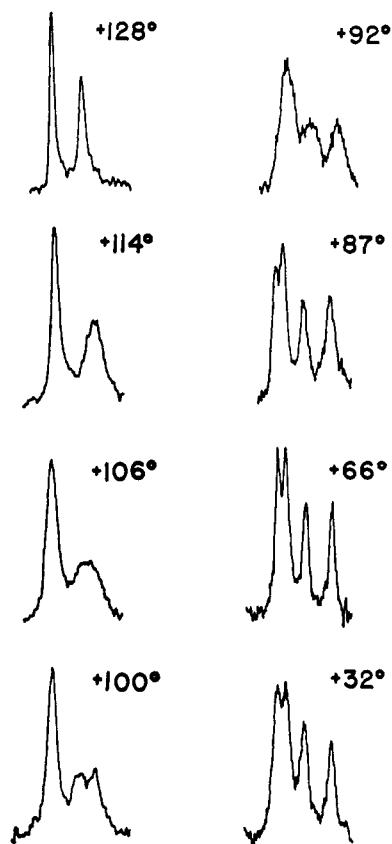


Figure 4. Spectra of the $\text{CH}_2\text{-Mg}$ protons of 2-phenyl-3-methylbutylmagnesium chloride in tetrahydrofuran as a function of temperature.

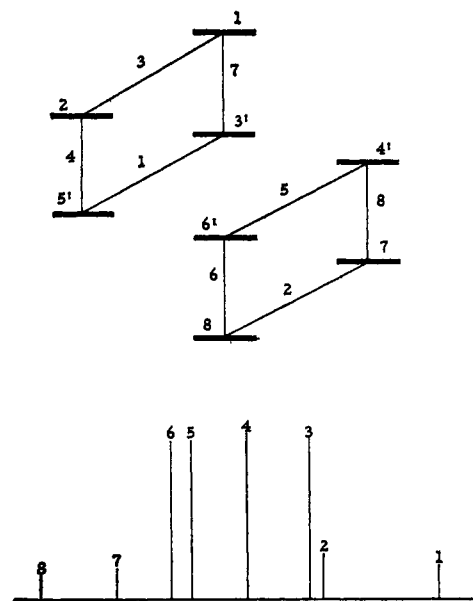


Figure 5. Schematic energy level diagram and spectrum for the AB part of an ABX spectrum. The illustrated order of energy levels holds for $\nu_A > \nu_B$, $J_{AB} > 0$, and $J_{AX} < J_{BX} < 0$. Transitions 1, 2, 3, and 4 are A transitions; 5, 6, 7, and 8 are B transitions.

constant J_{AB} , under the influence of the exchange process.

Analysis of the temperature dependence of the α -proton spectrum of 2-phenyl-3-methylbutylmagnesium chloride is complicated by the fact that only the four

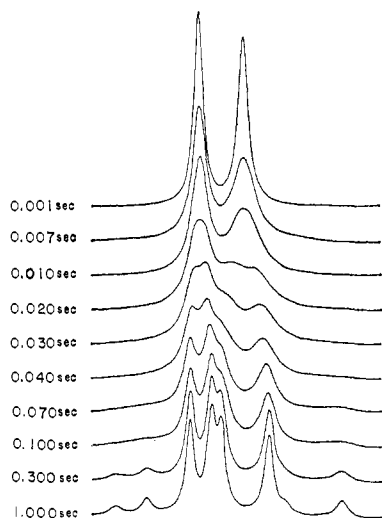


Figure 6. Calculated line shapes for the $\text{CH}_2\text{-Mg}$ part of the spectrum of 2-phenyl-3-methylbutylmagnesium chloride in diethyl ether solution, at different values of the pre-exchange lifetime τ . The parameters used and the method of calculation are described in the text.

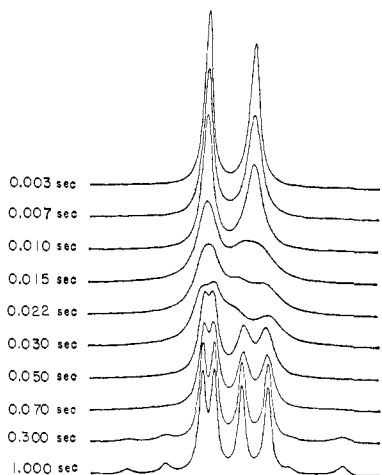


Figure 7. Calculated line shapes for the $\text{CH}_2\text{-Mg}$ part of the spectrum of 2-phenyl-3-methylbutylmagnesium chloride in tetrahydrofuran solution, at different values of the pre-exchange lifetime τ .

intense central lines of the AB part of the ABX spectrum can be observed, in the region of intermediate exchange rates. In order to obtain values for the rate of exchange of the A and B protons at each observed temperature, a series of theoretical spectra were calculated at values of the pre-exchange lifetime which spanned the region in which the spectrum changed from its ABX form to an A_2X form. Each of the theoretical spectra was obtained by summing two AB type spectra using "effective chemical shifts" and an "effective coupling constant" obtained using the parameters of Table I¹⁵ and the relations given above (Figures 6 and 7). Comparison of the observed and calculated spectra permitted the assignment of a value for the pre-exchange lifetime τ to each observed spectrum. Following the well-known relation between τ and the Arrhenius parameters for the exchange process, a plot

(15) These spectra were computed using programs developed for this purpose by Jesse L. Beauchamp and J. Thomas C. Gerig.

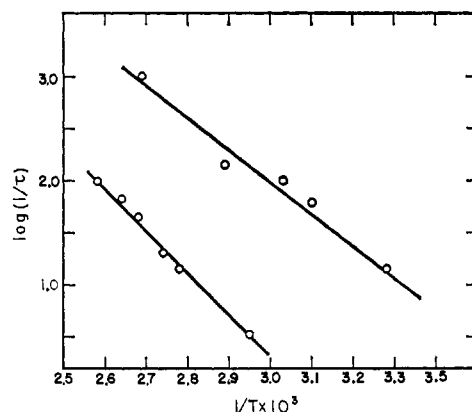


Figure 8. Plot of $\log(1/\tau)$ as a function of $1/T$ for 2-phenyl-3-methylbutylmagnesium chloride. The data of the upper curve are from diethyl ether solution; the data of the lower curve are from tetrahydrofuran solution. Arrhenius parameters derived from these plots are listed in the text.

$$k = 1/\tau$$

$$k = Ae^{-E_a/RT}$$

of $\log(1/\tau)$ vs. $1/T$ yielded E_a and A (Figure 8). For 2-phenyl-3-methylbutylmagnesium chloride in diethyl ether the values obtained for the activation energy and pre-exponential factor were $E_a \cong 12$ kcal./mole and $A \cong 10^{10}$ sec.⁻¹; for 2-phenyl-3-methylbutylmagnesium chloride in tetrahydrofuran, the corresponding values were $E_a \cong 18$ kcal./mole and $A \cong 10^{14}$ sec.⁻¹. The spectrum of bis(2-phenyl-3-methylbutyl)magnesium does not collapse in the accessible temperature range (see Table II).

Table II. Temperatures and Pre-exchange Lifetimes Used to Obtain the Dependence of $1/\tau$ on $1/T$ for 2-Phenyl-3-methylbutylmagnesium Chloride

Temp., °K.	τ , sec.
Diethyl ether solution	
305	0.070
323	0.020
330	0.010
346	0.007
372	0.001
Tetrahydrofuran solution	
339	0.300
360	0.070
365	0.050
373	0.022
379	0.015
387	0.010
401	0.007

Two further points related to the spectral behavior of this compound deserve brief comment. First, the line broadening observed in the region of intermediate exchange rate for 2-phenyl-3-methylbutylmagnesium chloride again confirms that exchange and not changes in the populations of the rotational conformations open to the molecule is responsible for the temperature dependence of the spectrum.² Second, the absence of a temperature dependence on the spectrum of the related compound 2-phenylpropylmagnesium bromide does not necessarily imply that inversion of configura-

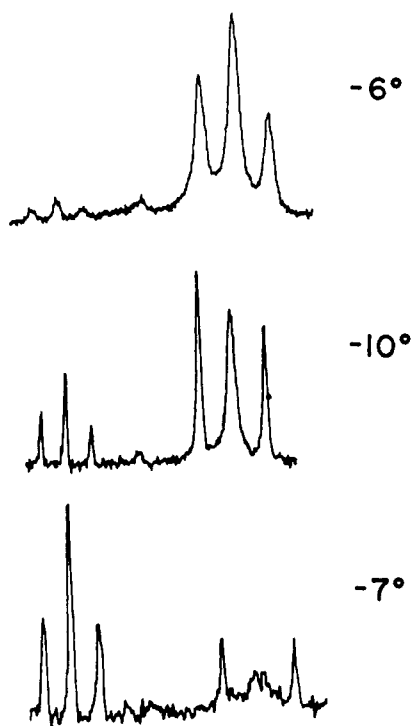


Figure 9. Spectra of 3,3-dimethylbutylmagnesium chloride in diethyl ether as a function of concentration. The sharp triplet at lower field is the ether methyl ^{13}C satellite.

tion is rapid.¹⁶ We have examined the spectrum of this latter compound and of bis(2-phenylpropyl)magnesium from $+33^\circ$ to -75° (viscous broadening prevents observation below this temperature) and find that the CH_2Mg protons of both compounds remain magnetically equivalent. The preceding discussions have demonstrated clearly that other, structurally similar primary Grignard reagents have very similar activation parameters for the inversion process. There is no obvious reason to expect the rate of inversion of the 2-phenylpropylmagnesium compounds to be anomalous. We believe that these compounds are inverting at approximately the same rates as those discussed previously, but that the 1-phenylethyl group produces only a small magnetic nonequivalence in the adjacent methylene group.¹⁷

At this point it is of interest to describe briefly certain of the variables which have pronounced effects on the rate of inversion at the CH_2Mg center of the organometallic compound. Those most pertinent are the effects of concentration of the organometallic compound, structure of the solvent, and nature of the halogen anion(s) present in solution.

Decreasing the concentration of 3,3-dimethylbutylmagnesium chloride in solution decreases the rate of

(16) The conclusions reached by Fraenkel and co-workers concerning the interpretation of similar observations are probably incorrect. The magnitude of a chemical-shift difference resulting from molecular asymmetry is difficult to predict under the best of circumstances. Although the interpretation of a *nonzero* chemical shift in terms of configurational stability is fairly straightforward, meaningful interpretation of a *zero* chemical shift requires caution: cf. G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, 767 (1963).

(17) The chemical shift between the $\text{CH}_2\text{-C}_6\text{H}_5$ protons of 1-phenyl-2-methylbutyl benzyl ether is 16.0 c.p.s. in carbon tetrachloride solution and 9.8 c.p.s. in acetone. In contrast, the corresponding chemical shifts in 1-phenylethyl benzyl ether are 9.1 and 2.5 c.p.s., respectively: G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 1058 (1965).

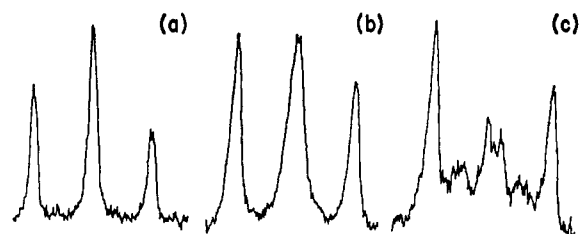


Figure 10. Room temperature spectra of the $\text{CH}_2\text{-Mg}$ protons of 3,3-dimethylbutylmagnesium chloride as a function of solvent: (a) diethyl ether, (b) tetrahydrofuran, (c) diglyme.

inversion. Figure 9 indicates that at -8° a decrease in Grignard reagent concentration of approximately tenfold changes the spectrum from one characteristic of rapid inversion to one characteristic of slow inversion. In these spectra, the triplet at lower field is the upfield ^{13}C satellite of the ether methyl group, and may be used to judge both the concentration of the organometallic compound and the natural line width in the solution.

The effect of solvent on the spectrum of the Grignard reagent is equally dramatic (Figure 10). In diethyl ether solution at room temperature, the spectrum of the $\text{CH}_2\text{-Mg}$ protons is a triplet; in tetrahydrofuran at approximately the same temperature and concentration, the central line is broadened noticeably; in diglyme, the spectrum is the typical $\text{AA}'\text{XX}'$ type. The tetrahydrofuran spectrum was examined as a function of temperature and found to collapse to a relatively sharp triplet at $+57^\circ$. The spectrum became more complicated at temperatures below 0° (unfortunately viscous broadening prevented detailed comparison with the low-temperature diethyl ether solution spectrum). The effect of temperature on the spectrum in diglyme was not examined.

The type and quantity of halide ion present in solution is also important in determining the appearance of the spectrum. In all cases we have examined, inversion of configuration is slower when bromide ion is the halogen in solution than when chloride ion is present. Thus, the spectrum of 3-methylbutylmagnesium chloride changes from its "high-temperature" triplet to the more complicated "low-temperature" form between -30 and -70° ; in contrast, the central line of 3-methylbutylmagnesium bromide shows appreciable broadening at room temperature, and the spectrum changes to a slow inversion spectrum at -15° . Qualitatively the same spectral behavior is observed for *n*-butylmagnesium chloride and *n*-butylmagnesium bromide.

Addition of magnesium bromide to a solution of 3,3-dimethylbutylmagnesium chloride appears to slow the rate appreciably. A solution prepared by reaction of 0.1 ml. of ethylene dibromide and 0.01 ml. of 3,3-dimethylbutyl chloride with excess magnesium turnings in ether reaches its low-temperature form at -7° ; a solution containing the same concentration of Grignard reagent but one-tenth as much added magnesium bromide has a corresponding spectrum only at -40° , and the Grignard reagent itself has this spectrum at approximately -50° (Figure 11).

These last experiments indicate that halide ion is probably involved in some specific manner in the rate-determining step for the process averaging the vicinal

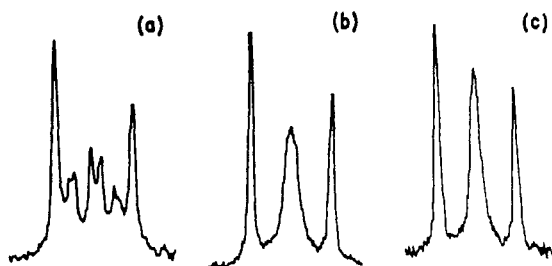
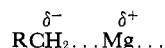


Figure 11. Spectra of 3,3-dimethylbutylmagnesium chloride in diethyl ether at -7° as a function of added magnesium bromide. The approximate molar ratios of magnesium bromide to 3,3-dimethylbutylmagnesium chloride in the solutions are: (a) 1.5, (b) 0.15, (c) 0.00.

coupling constants. That is, the effect of the halide ion is not merely to influence properties of the solution such as dielectric constant or ionic strength, but rather to change the activation energy for the inversion process by its effect on the structure or solvation of the organometallic compound. It might be possible in the absence of these observations to rationalize the decrease in rate of inversion with decreasing concentration as the result purely of changes in the bulk properties of the solution. In particular, if the transition state for inversion involves charge separation, the dielectric constant of the solvent will be important in determining



the rate. Dessy and Jones have examined the dielectric constant of solutions of ethylmagnesium bromide and of diethylmagnesium and found a pronounced concentration dependence.⁶ The concentration of the Grignard reagent in solutions used for n.m.r. samples was ordinarily 0.2 to 3 *M*. If the samples examined by Dessy are a fair model, the dielectric constant of the solution in this concentration range should be quite sensitive to changes in concentration. Consequently, the tenfold change in concentration in the samples in Figure 9 might have been accompanied by a fivefold change in dielectric constant. A decrease in dielectric constant of this magnitude should significantly decrease the rate of a process depending primarily on charge separation.

However, addition of magnesium bromide to a Grignard reagent solution can reasonably be expected to increase the dielectric constant of the solution.⁶ If dielectric constant were the most important factor in determining the rate of inversion of 3,3-dimethylbutylmagnesium chloride, the order in Figure 11 should be the opposite of that observed.

It is important to notice that the spectrum observed for solutions containing both chloride and bromide ion is not a superposition of the spectra of two separate species "RMgCl" and "RMgBr" but rather an average spectrum. Similar averaging is also observed in mixtures of dialkylmagnesium and magnesium halide in ether. If, for example, a solution of 3,3-dimethylbutylmagnesium chloride is treated with less than a stoichiometric amount of dioxane, the magnesium chloride present in solution is only partially removed. The spectrum observed for such a solution is not a superposition of the spectra of the Grignard reagent and the dialkylmagnesium compound separately, but an

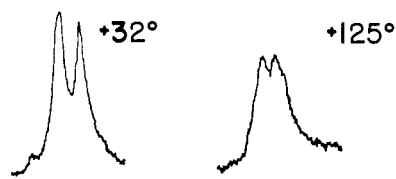


Figure 12. Spectrum of the methyl protons of 3,3-dimethylcyclobutylmagnesium bromide in tetrahydrofuran. The separation between the two peaks is approximately 4 c.p.s. at $+32^\circ$.

averaged spectrum corresponding to an intermediate rate of inversion. Correspondingly, addition of an excess of magnesium bromide to a solution of bis(3,3-dimethylbutyl)magnesium produces a sample whose vicinal coupling constants are averaged; addition of less than a stoichiometric amount of magnesium bromide results in partial averaging.

These observations suggest that none of the species involved in the Schlenk equilibrium, "RMgX," " R_2Mg ," and " $\text{R}_2\text{Mg} \cdot \text{MgX}_2$," have prolonged separate existence in solution. It is not presently possible to decide whether the partial averaging of vicinal coupling constants observed for samples containing less than a stoichiometric quantity of magnesium chloride is the result of rapid migration of halide ion from magnesium to magnesium, of rapid migration of magnesium chloride as a separate species, or of some other process occurring in solution.

The results discussed so far have dealt entirely with primary Grignard reagents. Although a limited number of examples have been examined, these results define clearly the rates of inversion which may be expected for this class of organometallic compound.

A comparison of the rate of inversion of suitably chosen primary and secondary Grignard reagents might be expected to be useful, in light of the probable pertinence of such data to considerations of the mechanism of inversion. Unfortunately application of the techniques used in examination of the primary Grignard reagents to several secondary Grignard reagents has been less successful. It is not proved possible to measure the rate of inversion of a secondary Grignard reagent; however, it is possible to establish a lower limit on this rate from the experiments described below.

The spectrum of the Grignard reagent prepared from 3,3-dimethylcyclobutyl bromide in tetrahydrofuran solution at room temperature shows a doublet for the methyl protons (Figure 12). The magnetic non-equivalence of the methyl groups can reasonably be explained only as the consequence of slow inversion of configuration at the *CH*-Mg center. If the Grignard reagent is inverting slowly, two types of methyl groups are present; one *cis* to the magnesium atom, one *trans*. The absence of a chemical shift between the two methyl groups would not have allowed an unambiguous interpretation, because either rapid inversion of configuration at the *CH*-Mg center or an accidental degeneracy of the chemical shifts of a slowly inverting Grignard would give the same result. However, the observation of two kinds of methyl protons indicates clearly that inversion is slow with this molecule.

Similarly, the two isopropyl methyl groups of 2,3-dimethylbutyl Grignard reagent are magnetically non-equivalent at room temperature in both tetrahydro-

furan and deuteriodiethyl ether solution (Figure 13). The carbon atom bearing the magnesium atom in this compound is a center of molecular asymmetry. The observation that the adjacent isopropyl methyl groups are magnetically nonequivalent indicates that inversion of configuration at the $\text{CHCH}_3\text{-Mg}$ center is slow on the n.m.r. time scale.¹³

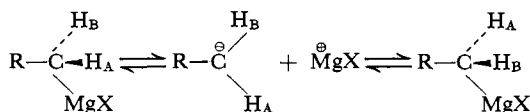
Neither of these compounds shows significant temperature dependence in its spectrum. The chemical shift between the methyl protons of 3,3-dimethylcyclobutylmagnesium bromide does not change over the temperature range $+33$ to $+120^\circ$. The chemical shift between the methyl protons in the isopropyl group of 2,3-dimethylbutylmagnesium chloride does decrease by approximately 0.7 c.p.s. between $+33$ and $+120^\circ$; however, this decrease occurs gradually over the indicated temperature range, and is probably due to changes in the rotational conformation populations of the isopropyl group rather than to a change in the rate of inversion.

The absence of a significant temperature dependence in the spectra of these two compounds suggests that the barrier to inversion of configuration is higher in the secondary than in the primary Grignard reagents. It might be argued that 3,3-dimethylcyclobutyl Grignard reagent is not a representative secondary Grignard reagent, since the ring strain of the molecule and hybridization of the carbon atoms are atypical. However, 2,3-dimethylbutyl Grignard reagent seems a reasonable model for a secondary Grignard reagent.

It should be noted in connection with these observations that the reaction of a dialkylmercurial with mercuric bromide proceeds at the same rate for diisopropyl- and di-*n*-propylmercury compounds and faster for dicyclopropylmercury and diphenylmercury.¹⁸ This dissimilarity between the influence of the alkyl group on the rate of this reaction and on that of the Grignard inversion suggests that the well-established $\text{S}_\text{E}2$ mechanism for the mercurials and the mechanism of inversion in the Grignard reagents are probably not closely related.

Discussion

The experimental observations presented in this and previous² papers indicate that inversion of configuration of several primary Grignard reagents occurs with similar activation parameters. An important question to be asked concerning the mechanism of the inversion reaction concerns its kinetic order. If inversion proceeds by an uncomplicated ionization-recombination pathway, the inversion rate should be approximately



independent of the concentration of organometallic compound or magnesium salts in solution, if salt effects and the effect of concentration on the dielectric constant of the medium are neglected. If inversion is a process of higher kinetic order, its rate should vary with the concentration of the reactants. It is observed experimentally that the inversion rate does depend in a very striking manner on the concentration of the Grig-

(18) R. E. Dessy and Y. K. Lee, *J. Am. Chem. Soc.*, **82**, 689 (1960).

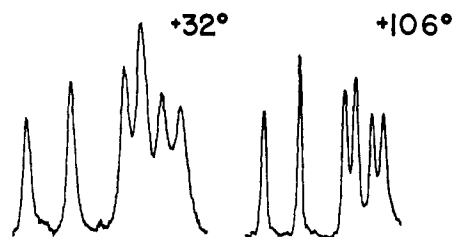


Figure 13. Spectrum of the methyl protons of 3-methylbutylmagnesium chloride in tetrahydrofuran solution. The four lines at highest field are the isopropyl methyl proton resonances.

nard reagent in solution, being slower in dilute than in concentrated solution. The actual decrease accompanying a decrease in concentration can be estimated for 3,3-dimethylbutylmagnesium chloride from Figure 9, which indicates that a change in the concentration of the organometallic compound from approximately 15% to approximately 1% at -6° is sufficient to change the spectrum from its fast exchange form to its slow exchange form. The fast exchange and slow exchange forms of the Grignard reagent spectra correspond to inversion rates differing by approximately a factor of 100.²

This observed dependence of inversion rate on the concentration of the Grignard reagent is in reasonable qualitative agreement with that which might be expected using a bimolecular mechanism as a model. The observed change in inversion rate might also be within the range which would be predicted on the basis of unimolecular mechanism, provided the transition state for the inversion in the mechanism has very much more charge separation than the ground state. In this case, the change in rate would be a consequence of the change in the bulk dielectric constant of the solvent, accompanying the change in concentration.

The effect of the concentration and kind of halogen anion present in solution is best discussed by considering the influence the anion might have on the transition state for uni- and bimolecular reactions.

In a unimolecular ionization-recombination reaction, the anion would probably exert its influence by its effect on the carbon-metal bond strength and the effect would, of course, be largest for halide ion bonded directly to the magnesium atom. An increase in the electronegativity of a substituent X bonded to magnesium should increase the p-character of the magnesium bonding orbital directed toward X.¹⁹ An increase in the p-character of the Mg-X bond will be accompanied by a decrease in the p-character of the magnesium bonding orbital directed toward carbon and an increase in the ionic character of the C-Mg bond. The ease of ionic dissociation of the R-Mg bond of organomagnesium compounds is thus predicted to be $\text{R-MgCl} > \text{R-MgBr} > \text{R-MgI} > \text{R-MgR}$, in agreement with the observed order.

If the mechanism of inversion is bimolecular, it probably involves electrophilic attack on the Grignard reagent by some species containing the fragment MgX : either RMgX , $\text{MgX}_2 \cdot \text{R}_2\text{Mg}$, or some more complicated magnesium-containing species. The rate of inversion would then be expected to increase with increasing electrophilicity of the attacking species.

(19) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

The more electronegative the halogen atom attached to the magnesium, the more electrophilic the MgX fragment should be. Hence, using a bimolecular model for the reaction and assuming that the rate depends primarily on the electrophilicity of the fragment MgX, one would predict that the rate of inversion should also increase in the observed order $R-MgCl > R-MgBr > R-MgI > R-MgR$.

It is likely that the anion present in solution influences the inversion reaction in some manner other than through its effect on electrophilicity or on the bulk dielectric constant of the solution. Magnesium bromide added to a solution of 3,3-dimethylbutylmagnesium chloride in ether slows the rate of inversion. It would be inconsistent to assume that electrophilicity of the MgX fragment were the sole important factor in determining the rate of inversion, and then to say that adding a weak electrophile to a strong electrophile should decrease the over-all electrophilicity of the MgX fragments in solution.

The spectrum observed for the mixture of Grignard reagent and magnesium bromide does not consist of two superimposed spectra corresponding to "RMgCl" and "RMgBr" but rather of an averaged spectrum intermediate between the two. This observation suggests that migration of halide ion (or magnesium halide) between organometallic centers occurs rapidly in solution.²⁰ In consequence, the solution of "RMgCl" with added magnesium bromide probably contains an equilibrium concentration of "RMgBr." It seems possible that the anion present in solution might influence the inversion rate both through its effect on electrophilicity of the MgX fragment in solution and through its effect on the carbon-magnesium bond strength.

This same approach may be used to rationalize the dependence of the inversion rate on solvent. Ethers are electron-donor solvents, by virtue of their non-bonding oxygen electrons; as such, they are known to be capable of forming strong dative bonds to positively charged magnesium species. In an ionization-recombination mechanism, solvation in the transition state should be more important than solvation to the ground state because charge separation in the transition state will be greater. Inversion should therefore proceed more rapidly in a basic ether such as tetrahydrofuran than in a relatively nonbasic ether such as diethyl ether because of the greater capability of the former to solvate the positively charged magnesium fragment in the transition state.

If, on the other hand, the rate of inversion is primarily dependent upon the electrophilicity on the MgX fragment, inversion should be slowest in the most basic ether; the ability of the basic ether to donate electrons to the magnesium atom should considerably reduce the electrophilicity of this atom.

The spectra of Figure 10 indicate that inversion is fast in diethyl ether, slower in tetrahydrofuran, and slowest in diglyme. Consequently, the dependence of inversion rate on solvent character also provides

(20) In this connection, it should be noted that while the results mentioned so far do not exclude the possibility that all the inversion observed in the dialkylmagnesium compounds takes place through catalytic action of small quantities of magnesium halide left unprecipitated by dioxane, with bis(3,3-dimethylbutyl)magnesium, at least, inversion takes place with halide-free preparations derived from the mercury compound.²

qualitative support for the suggestion that the inversion mechanism is characterized by a molecularity higher than one.

The effect of structure on the rate of inversion has not been investigated carefully. The activation parameters obtained for inversion of 3,3-dimethylbutylmagnesium chloride and 2-phenyl-3-methylbutylmagnesium chloride in ether suggest that inversion occurs at approximately the same rate in both compounds; the secondary Grignard reagents examined definitely invert more slowly. This difference in rate may reflect the difference in the relative stabilities usually ascribed to primary and secondary carbanions, or major differences in the geometry of the molecules near the C-Mg bonds.

The possibility of inversion involving rapid elimination and addition of magnesium hydride²¹ is ruled out by the fact that this would be expected to give *intermolecular* hydrogen exchanges which would affect the spin-spin splitting patterns; however, there is no definite evidence which excludes some sort of homolytic cleavage recombination mechanism for the inversion process.

If the mechanism of the inversion reactions bears any resemblance to the electrophilic substitution reactions of organomercury compounds, it is interesting to speculate on the possible rate of alkyl-group migration with *retention* of configuration. The organomercury compounds commonly exchange through a four-center transition state and the rate of exchange with retention of configuration is much greater than that with inversion. If this type of transition state is also favorable with organomagnesium compounds, the rate of metal-metal exchange with retention of configuration may be very much faster than the rate of inversion.

Experimental Section²²

Nuclear magnetic resonance spectra were obtained with the spectrometers described previously.² Analyses of the ABX spectra of the 2-phenyl-3-methylbutylmagnesium derivatives were considerably more uncertain than those for the AA'XX' systems² because the low-intensity outer lines of the AB part of the spectrum frequently could not be distinguished from noise in the spectrum and because the X part of the spectrum could not be analyzed at all.

To obtain the activation energies for the 2-phenyl-3-methylbutylmagnesium derivatives, the observed spectra were compared with those calculated as described previously. The comparison in the region of intermediate exchange rate is a fairly subjective procedure and consists of visual comparison of the "shape" of the observed and calculated spectra. This estimation procedure, coupled with the dependence of the calculated line shape on the value chosen for $1/T_2$, combine to introduce a certain arbitrary character to the analysis of these spectra. The values chosen for $1/T_2$ were 0.20 and 0.25 sec. for 2-phenyl-3-methyl-

(21) Isomerization of vinylaluminum compounds proceeds at a moderate rate at 100° by a similar elimination-addition mechanism: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **85**, 2165 (1963).

(22) Boiling points are uncorrected. Vapor chromatograms were obtained using Perkin-Elmer vapor fractometers Models 154-C and 800. Infrared spectra were determined with a Perkin-Elmer Model 237 double-beam grating spectrometer, using an 8-min. scan. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

butylmagnesium chloride in ether and tetrahydrofuran, respectively.

The samples of the Grignard reagents were prepared as described previously.² Grignard reagents and dialkylmagnesium compounds containing $\text{CH}_2\text{-Mg}$ groups were identified by the characteristic chemical shift and spin-coupling patterns of their α -protons. The resonances of protons adjacent to a strongly electropositive metal occur at significantly higher field than those of any of the other compounds likely to occur in the solution; these protons could consequently be recognized and examined without difficulty. The α -proton resonances of the secondary Grignard reagents were usually complicated by spin coupling and of lower intensity than those of the primary Grignard reagents, and were frequently difficult to locate. These Grignard reagents were characterized by addition of a slight excess of water to the sample tube followed by centrifugation to remove the precipitated magnesium salts. Comparison of the spectrum of the organometallic solution and that of the hydrolyzed solution with the spectra of solutions in the same solvent of the starting halide and of the hydrocarbon expected from hydrolysis (when available) usually allowed the resonances due to Grignard reagent to be identified without difficulty.

The quantity of solids produced during the preparation depended primarily on the type of halide used: bromides frequently produced no solids at all; chlorides often gave small quantities of a white flocculent precipitate.

Grignard reagents prepared in tetrahydrofuran were occasionally pale yellow after heating, and showed a tendency to precipitate larger amounts of solids than the corresponding ether solutions. Occasionally, a tetrahydrofuran solution of an alkylmagnesium chloride would give such heavy deposits of crystals as to fill the liquid phase; however, sufficient sample for n.m.r. examination could usually be recovered by centrifugation. The signal intensity in such samples was usually slightly less than that of the same solutions before crystallization.

Tetrahydrofuran solutions occasionally gave broad spectra immediately after their preparation; resolution always improved after the sample had aged for several days.

Solutions prepared in diglyme had approximately the same characteristics as those prepared in tetrahydrofuran, except that the viscosity of the final diglyme solution was significantly greater.

The yields of Grignard reagent prepared in diethyl ether solution were estimated to be 70–95% by comparison with the ^{13}C satellites of solvent, based on starting halide.

2-Phenyl-3-methyl-1-butanol. Diisopropylmagnesium was prepared by addition of 66 g. (0.75 mole) of dry dioxane to a Grignard solution prepared from 92 g. (0.75 mole) of 2-bromopropane and 18 g. (0.75 mole) of magnesium in 300 ml. of ether in a 1-l., three-necked, round-bottomed flask equipped with mechanical stirrer, condenser, and pressure-equalized dropping funnel. The precipitated magnesium bromide dioxanate was not separated from the dialkylmagnesium solution to which was then added 60 g. (0.50 mole) of styrene oxide at such a rate as to maintain gentle refluxing. The reaction mixture was stirred for 4 hr. at room tem-

perature, heated under reflux for 1 hr., and hydrolyzed with saturated aqueous ammonium chloride solution to the point at which the solids conglomerated on the sides of the flask. The ether layer was decanted from the salts and dried over calcium sulfate. Removal of the ether on a rotary evaporator and distillation of the residue through a 20-cm., wire-spiral-packed column yielded 53 g. of product, b.p. 84–87° at 2 mm. (lit.²³ b.p. 93° at 4 mm.); the purity of the product was estimated to be 90–95% from the n.m.r. spectrum.

2-Phenyl-3-methylbutyl chloride was prepared by addition of 50 ml. of thionyl chloride to a solution of 25 ml. of 2-phenyl-3-methyl-1-butanol and 50 ml. of dimethylformamide in a 200-ml. erlenmeyer flask immersed in an ice bath. The temperature of the solution was maintained at $15 \pm 5^\circ$ during the addition. The solution was allowed to stand at room temperature for 6 hr. after addition of the thionyl chloride, then hydrolyzed by pouring into 200 ml. of cold water. The organic layer was separated and the aqueous layer was extracted twice with 50-ml. portions of ether. The combined extracts were dried over calcium chloride, then distilled twice through a 20-cm., wire-packed column at reduced pressure to yield 12 g. (approximately 45%) of product, b.p. 67–74° (0.8 mm.).

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{Cl}$: C, 72.32; H, 8.28; Cl, 19.41. Found: C, 72.55; H, 8.26; Cl, 19.18.

2-Phenyl-3-methylbutylmagnesium chloride could be prepared from the chloride only with difficulty. The most successful procedure involved mixing 0.1 ml. of the chloride and 0.1 ml. of ether with magnesium turnings in an n.m.r. tube. The magnesium turnings were then broken up with a Nichrome wire. Onto this mixture was poured 0.4 ml. of ether *without mixing the layers*. The tube was sealed and heated in the usual² manner; after approximately 1 hr. at 100° reaction between magnesium and the halide occurred. The remainder of the preparation was unexceptional.

1,3-Dibromo-2,2-dimethylpropane. The procedure used was a modification of that of Schurink.²⁴ In a 500-ml., round-bottomed, three-necked flask equipped with a pressure-equalized dropping funnel and air-cooled condenser was placed 183 g. (0.92 mole) of 2,2-dimethyl-1,3-propanediol. The flask was heated on the steam bath and 500 g. of freshly opened phosphorus tribromide was added over the course of 2 hr. The steam bath was exchanged for an oil bath and the temperature was increased to 160°. The temperature was maintained at this level for 24 hr. The heterogeneous mixture resulting was then cooled and poured into 1 l. of water. The lower layer was separated and dried over calcium sulfate. The n.m.r. spectrum indicated that this material was approximately 70% the desired bromide. The yield was 200 g., and the product was used without further purification.

3,3-Dimethylcyclobutanecarboxylic acid was prepared following the procedure of Campbell and Rydon,²⁵ substituting the crude 1,3-dibromo-2,2-dimethylpro-

(23) C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, **77**, 369 (1955).

(24) H. B. Schurink, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 476.

(25) A. Campbell and H. N. Rydon, *J. Chem. Soc.*, 3002 (1952).

pane prepared above for the 1,3-diiodo-2,2-dimethylpropane used by these workers. The yield of acid was 22 g., b.p. 75–103° at 12 mm. (lit.²⁵ b.p. 105–106° at 15 mm.).

Silver 3,3-dimethylcyclobutanecarboxylate was prepared from 3,3-dimethylcyclobutanecarboxylic acid following the procedure of Cason and Way.²⁶ The silver salt was air dried at room temperature, and then dried at 0.5 mm. for 4 days prior to its use in the brominative decarboxylation.

3,3-Dimethylcyclobutyl Bromide from Silver 3,3-Dimethylcyclobutanecarboxylate. The procedure was modeled after that described for the preparation of cyclobutyl bromide.²⁶ The reaction flask was dried by distilling 50 ml. of carbon tetrachloride from it immediately before use. Bromine and carbon tetrachloride were dried by distillation from phosphorus pentoxide.

The silver salt (38.9 g., 0.17 mole) was added over the course of 1 hr. to 250 ml. of carbon tetrachloride and 28.9 g. (0.18 mole) of bromine in a 500-ml., three-necked, round-bottomed flask equipped with mechanical

stirrer and thermometer and immersed in a Dry Ice–acetone bath. The salt was added through a piece of Gooch tubing connecting one inlet of the reaction flask directly to the erlenmeyer flask in which the salt had been dried. No carbon dioxide evolution was observed until the solution had been warmed briefly to +20°; after the reaction had started, the solution was cooled to 0° and the remainder of the silver salt was added. When gas evolution had ceased, the reaction mixture was allowed to stand overnight and then filtered, washed once with aqueous sodium bisulfite, once with 2 *N* potassium hydroxide solution, and once with water. The organic layer was dried over calcium sulfate, and the carbon tetrachloride was removed through a 10-cm. glass-helix packed column. The bromide was distilled under slightly reduced pressure through a 30-cm. Vigreux column. The product (12 g., 45%) had b.p. 132° by the capillary boiling point method. The purity of the product was approximately 95% as estimated by v.p.c. (column K, 110°). The n.m.r. and infrared spectra were consistent with the desired structure.

Anal. Calcd. for C₆H₁₁Br: C, 44.19; H, 6.80; Br, 49.01. Found: C, 44.13; H, 5.94; Br, 48.80.

(26) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

Mass Spectrometry in Structural and Stereochemical Problems. LXXIX.¹ Aliphatic and Alicyclic Nitro Compounds²

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Contribution from the Department of Chemistry, Stanford University, Stanford, California. Received June 7, 1965

The mass spectra of several aliphatic and alicyclic nitro compounds were measured by low- and high-resolution techniques. In contrast to the results with aromatic nitro compounds, no significant amount of rearrangement to nitrites was encountered. With the exception of nitromethane, the molecular ion peak is either very small or not at all discernible. The nitro group is not a charge-stabilizing moiety (in the sense for instance that the amino group is) as is shown by the nature of the fragment ions. The loss of an NO₂ radical and the subsequent decomposition of alkyl fragments constitute one important process. Another is the loss of both oxygen atoms (apparently by the sequential elimination of an oxygen atom and of water) to yield the equivalent of nitrile species. Rearrangement of one oxygen atom with the generation of ions containing only C, H, and O is of no importance in nitroalkanes. The loss of the elements of nitrous acid and the subsequent decomposition of the resulting olefins (M – HNO₂)⁺ represent the most significant feature of the mass spectra of tertiary nitroalkanes.

(1) For Paper LXXVIII see C. Djerassi, J. Karliner, and R. T. Aplin, *Steroids*, **6**, 1 (1965).

(2) Financial help by the National Institutes of Health (Grant No. AM-04257) of the U. S. Public Health Service is gratefully acknowledged. We wish also to thank Professor H. Feuer and Dr. J. Hooz of Purdue University for samples of various nitroalkanes.

(3) (a) Recipient of a Fulbright Travel Scholarship. (b) Recipient of a fellowship from the "Stiftung Volkswagenwerk." (c) Recipient of a NATO fellowship.

One of the most recent attempts to interpret mass spectra of structurally unknown organic compounds is the computer-aided analysis of high-resolution spectra which allows the conclusion that certain heteroatoms are located within a given number of carbon atoms.⁴ This approach, however, can only be useful if no rearrangements of functional groups occur prior to fragmentation. While hydrogen shifts⁵ are a well-established and virtually ubiquitous phenomenon in mass spectrometry, alkyl^{6a} and aryl^{6b} migrations seem to be less common. Little appears to be known about possible rearrangements of functional groups with one noticeable exception, namely, aromatic nitro compounds,⁷ which upon electron impact are transformed extensively to the isomeric nitrite esters. In view of this observation, it seemed to us of interest to investigate whether aliphatic nitro compounds underwent a similar process and, if so, whether any mechanistic conclusions could be reached by high-resolution

(4) K. Biemann, *Pure Appl. Chem.*, **9**, 95 (1964); see also J. W. Daly, B. Witkop, P. Bommer, and K. Biemann, *J. Am. Chem. Soc.*, **87**, 124 (1965).

(5) See C. Djerassi, *Pure Appl. Chem.*, **9**, 159 (1964).

(6) (a) F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965); P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S. O. Lawesson, *ibid.*, **87**, 4559 (1965), and references cited therein; (b) P. Funke, K. G. Das, and A. K. Bose, *ibid.*, **86**, 2527 (1964).

(7) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, 311 (1964).