

- I. CONFIGURATIONAL STABILITY
 AND REDISTRIBUTION EQUILIBRIA
 IN ORGANOMAGNESIUM COMPOUNDS
- II. REDISTRIBUTION EQUILIBRIA IN
 ORGANOCADMIUM COMPOUNDS

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ABSTRACT

I. CONFIGURATIONAL STABILITY AND REDISTRIBUTION
EQUILIBRIA IN ORGANOMAGNESIUM COMPOUNDS

The dependence of the rate of inversion of a dialkylmagnesium compound on the solvent has been studied.

Examination of the temperature dependence of the nuclear magnetic resonance spectrum of 1-phenyl-2-propylmagnesium bromide in diethyl ether solution indicates that inversion of configuration at the methylene group of this Grignard reagent occurs with an approximate rate of 2 sec^{-1} at room temperature. This is the first example of a rapid inversion rate in a secondary Grignard reagent.

The rates of exchange of alkyl groups between dineopentylmagnesium and di-s-butylmagnesium, bis-(2-methylbutyl)-magnesium and bis-(4,4-dimethyl-2-pentyl)-magnesium respectively in diethyl ether solution were found to be fast on the nmr time scale. However, the alkyl group exchange rate was found to be slow in a diethyl ether solution of dineopentylmagnesium and bis-(2-methylbutyl)-magnesium containing N,N,N',N'-tetramethylethylenediamine. The unsymmetrical species neopentyl-2-methylbutyl-magnesium was observed at room temperature in the nmr spectrum of the solution containing the diamine.

II. REDISTRIBUTION EQUILIBRIA IN ORGANOCADMIUM
COMPOUNDS

The exchange of methyl groups in dimethylcadmium has been

studied by nuclear magnetic resonance spectroscopy. Activation parameters for the methyl group exchange have been measured for a neat sample and for a solution in tetrahydrofuran. The exchange is faster in the basic solvent tetrahydrofuran relative to the neat sample and in tetrahydrofuran solution is retarded by the solvating agent N,N,N',N'-tetramethylethylenediamine and greatly increased by cadmium bromide. The addition of methanol to a solution of dimethylcadmium in tetrahydrofuran appears to have very little effect on the rate of exchange. The exchange was found to proceed with retention of configuration. The rate-limiting step for the exchange of methyl groups in a basic solvent appears to be the dissociation of coordinating solvent from dimethylcadmium.

The equilibrium between methylcadmium bromide, dimethylcadmium and cadmium bromide in tetrahydrofuran solution has also been studied. At room temperature the interconversion of the species is very fast on the nmr time scale but at -100° distinct absorptions for methylcadmium bromide and dimethylcadmium are observed.

The species ethylmethylcadmium has been observed in the nmr spectrum.

The rate of exchange of vinyl groups in a solution of divinylcadmium in tetrahydrofuran has been found to be fast on the nmr time scale.

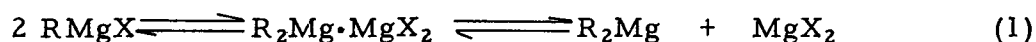
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INTRODUCTION

The Grignard reagent has been known (1) for over sixty years; however, its constitution is only now becoming clear (2). This structural problem has been complicated by conflicting reports in the literature and by the limited number of physical methods available to earlier workers.

A Grignard solution ("RMgX" will be used to indicate the Grignard compounds formed from RX and Mg) may contain three or more species: 1) an alkylmagnesium halide, 2) a dialkylmagnesium compound, 3) magnesium halide and association complexes of these species. Schlenk and Schlenk (3) found that essentially all of the halogen present as MgX_2 could be removed from Grignard compounds in ether solution by the addition of dioxane. Based on this observation and on an earlier finding (4) that the molecular association of methylmagnesium iodide varied with concentration, Schlenk and Schlenk proposed the following equilibrium to explain the composition of Grignard reagents.



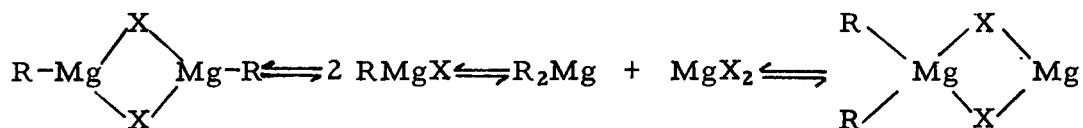
Recent studies (5-10) have indicated the importance of association of "RMgX" in solution and the dimeric $(\text{RMgX})_2$ is now usually included in the Schlenk equilibrium. Table I (2c) shows some selected data on the degree of association of Grignard reagents in ether and tetrahydrofuran.

Table I

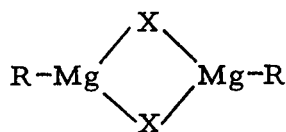
Selected Data on the Degree of Association of Grignard Reagents

Organic group	Halogen	Concn. (moles "RMgX" per l. of soln.)	i (mol. wt. / form. wt.)	Ref.	Notes
In diethyl ether					
Me	I	0.037	1.09	7	(a)
Me	I	0.245	1.59	7	(a)
Et	Cl	0.086	1.87	7	(a)
Et	Cl	0.196	1.92	7	(a)
Et	Br	10^{-2} - 10^{-3}	1.01 ± 0.01	10	(b)
Et	Br	0.035	1.00	7	(a)
Et	Br	0.249	1.37	7	(a)
Et	I	0.055	1.00	7	(a)
Et	I	0.204	1.36	7	(a)
iPr	Cl	0.042	1.85	7	(a)
iPr	Cl	0.260	2.02	7	(a)
cyclohexyl	Br	0.324	2.05	42	(c)
Ph	Br	0.042	1.07	7	(a)
Ph	Br	0.326	1.71	7	(a)
Ph	Br	0.331	1.67	42	(c)
p-tolyl	Br	0.566	1.65	42	(c)
mesityl	Br	0.059	1.06	7	(a)
mesityl	Br	0.275	1.77	7	(a)
In tetrahydrofuran					
Et	Cl	0.1-0.3	1.01	17	(d)
Et	Br	10^{-2} - 10^{-3}	1.00 ± 0.01	8	(e)
Et	Br	0.1-0.3	1.04	17	(d)

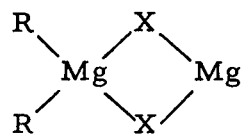
(a) Measurements at b. p. of ether at 760 mm. Magnesium/halogen ratio 1/1.00 \pm 0.04. (b) Measurements at 27.3°. Recrystallized reagent, with magnesium/halogen ratio 1/1.006. (c) Measurements at 20°. Magnesium/halogen ratio 1/1.06 to 1/1.25. (d) Measurements at 30°. Magnesium/halogen ratio not given. (e) Measurements at 27.3°. The reagent was recrystallized from diethyl ether, freed from diethyl ether, and dissolved in tetrahydrofuran; magnesium/halogen ratio 1/1.029. Crystallization of ethylmagnesium bromide from tetrahydrofuran leads to crystals enriched in magnesium bromide [6, 8].



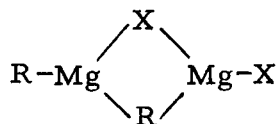
The dimeric species can be formulated in various ways (I - V); however, I and II appear to be the most reasonable because halogen bridges are preferred to alkyl bridges (7, 11).



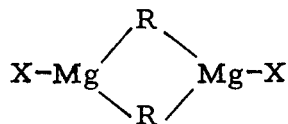
I



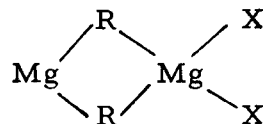
II



III



IV



V

The most effective method of studying the constitution of the Grignard reagent in solution is to determine the rate and equilibrium constants of the Schlenk equilibrium for various Grignard reagents and in various solvents. The special problem concerning the configurational stability of the Grignard reagent will be discussed later.

In 1957 Dessy and coworkers (12) found no exchange between $^{28}\text{MgBr}_2$ and Et_2Mg . They reported further that an equimolar mixture of MgBr_2 and Et_2Mg has the same properties as the Grignard reagent prepared from ethyl bromide and magnesium. It thus appeared that

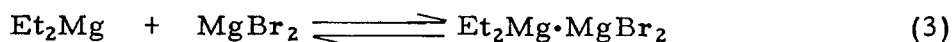
the structure $R_2Mg \cdot MgX_2$ was the best representation of the Grignard reagent and that the Schlenk equilibrium (equation 2) did not proceed to the left, and hence alkyl group exchange did not take place in ether solution. The fact that $MgBr_2$ prepared from ^{25}Mg (from a different source than the ^{28}Mg) did show complete exchange was attributed by Dessy to impurities in the metal.

Further work by Dessy (13) showed that a plot of dielectric constant against composition displayed a break in the curve at a ratio of $Et_2Mg/MgBr_2$ of 1/1 and that, at this concentration, the dielectric constant was the same as for a solution of ethylmagnesium bromide at an equivalent concentration. However, Vreugdenhil and Blomberg (14) have reported that the conductance in ether solution of an equimolar mixture of diethylmagnesium and magnesium bromide was lower than that of an equivalent concentration of ethylmagnesium chloride except for concentrations above 0.4 molar.

Reaction product studies (15) and infrared studies (16) have indicated that an equimolar mixture of a dialkylmagnesium compound and magnesium halide is identical to a solution containing an equivalent concentration of an alkylmagnesium halide. However, association studies indicated (14) that the two mixtures are not identical, because ethylmagnesium bromide was found to be monomeric, whereas a mixture of diethylmagnesium and magnesium bromide was found to exhibit some association. It would seem then that the reaction between magnesium halide and dialkylmagnesium compounds can be slow or fast depending on the exact conditions involved.

Ashby and Becker in 1963 (17) provided strong evidence for the existence of an RMgX species and the presence of alkyl group exchange in tetrahydrofuran. These authors demonstrated that crystallization of a Grignard reagent from tetrahydrofuran (in which Grignard compounds are monomeric) gave crystalline solids with the empirical formulas, RMg_2X_3 and MgR_2 . RMg_2X_3 was then redissolved in tetrahydrofuran in which its molecular association was determined to be 0.62. This association factor was taken as evidence that RMg_2X_3 is extensively dissociated into RMgX and MgX_2 . Hence, contrary to Dessy's exchange experiments (12), it now appeared that ethylmagnesium chloride, at least in tetrahydrofuran, was best described by the equilibrium first reported by Schlenk (equation 1). Solids of formula RMg_2X_3 have also been crystallized from diethyl ether. Unfortunately these solids would not redissolve in ether and consequently their molecular association could not be determined.

The very careful association studies of Vreugdenhil and Blomberg (10) disproved the existence of the equilibrium below, in 10^{-3} to 10^{-2} molar diethyl ether solutions.



These authors determined the association numbers of the following: magnesium bromide, 1.13 ± 0.04 ; diethylmagnesium, 1.00 ± 0.02 ; mixtures of the two preceding compounds, 1.05–1.06; and the Grignard prepared from magnesium and ethyl bromide, 1.00 ± 0.02 . Thus evidence began to accumulate that Dessy's original contention that the Grignard reagent was best represented as $\text{R}_2\text{Mg} \cdot \text{MgX}_2$ was incorrect.

X-ray studies of crystalline phenylmagnesium bromide (18) have shown that a phenyl group, a bromine atom, and two ether molecules are tetrahedrally bonded to one magnesium atom. The molecular configuration of ethylmagnesium bromide in the crystalline state is similar to phenylmagnesium bromide (19).

Dessy (20) has recently repeated his exchange experiments and now finds statistical exchange in the system $^{28}\text{MgBr}_2$ plus R_2Mg . However, Dessy reports that an impure grade of magnesium (Dow atomized shot) gave no exchange. Cowan, Hsu, and Roberts (21) have also reported statistical exchange of magnesium in an experiment where high-purity $^{25}\text{MgBr}_2$ was added to ethylmagnesium bromide. Hence, it now appears certain that alkyl group exchange takes place in Grignard solutions.

Ashby (22) observed that when ethyl bromide reacts with magnesium in triethylamine, a single solvated monomer $\text{EtMgBr}\cdot\text{NEt}_3$ crystallizes. When triethylamine was added to a 1.95 molar solution of ethylmagnesium bromide in diethyl ether, the precipitate $\text{EtMgBr}\cdot\text{NEt}_3$ was isolated in over 90% yield. The magnesium bromide-triethylamine complex was not isolated although it is the most insoluble of the possible products. Hence ethylmagnesium bromide in diethyl ether is solvated by triethylamine faster than it equilibrates with magnesium bromide.

Smith and Becker (23) recently measured the heat of mixing of diethylmagnesium and magnesium bromide. The heat of mixing, ΔH , was plotted against moles of MgBr_2 added and a break in the curve was

found for an equimolar mixture of diethylmagnesium and magnesium bromide. The results indicated that in diethyl ether the equilibrium (equation 3) lies predominantly to the right. Smith and Becker (24, 25) also carried out similar thermochemical experiments in tetrahydrofuran. The equilibrium constant for equation 3 in this solvent was found to be 4, which corresponds to statistical distribution, and which is in agreement with the results of Salinger and Mosher (26) who obtained the same equilibrium constant from infrared studies.

Until very recently nuclear magnetic resonance spectroscopy has not been very fruitful in studies of the Schlenk equilibrium (27, 28). Although Maher and Evans (29) have reported nmr evidence for the $R_2Mg \cdot MgX_2$ representation, their conclusions have been found to be contradictory to the association evidence that is now available.

However, nmr has been very useful in understanding the configurational stability of Grignard reagents (29-32). Neohexylmagnesium chloride and dineohexylmagnesium have been shown (29) to undergo inversion at the alpha carbon with the respective energy barriers $E_a = 11 \pm 2$ kcal/mole and $E_a = 20 \pm 2$ kcal/mole. Approximately the same activation parameters were found by Fraenkel and co-workers (32) for the inversion process in 2-methylbutylmagnesium bromide and bis(2-methylbutyl) magnesium. The question of the exact mechanism for the inversion process is still unsettled, but it should be clearly recognized that it may be a process distinct from alkyl exchange. Any nmr study of exchange in organomagnesium compounds must allow for the inversion process, because inversion can produce equivalence at

otherwise magnetically nonequivalent sites. It has been one of the purposes of the research described herein to further elucidate the mechanism of this inversion process.

The research described in Part I of this dissertation was begun with the ultimate goal of 1) providing evidence for an unsymmetrical dialkylmagnesium compound, 2) carrying out direct solution studies of the Schlenk equilibrium, 3) determining if any alkyl group exchange occurs apart from the Schlenk equilibrium, and 4) elucidating further the mechanism of inversion.

When this research was begun it was argued by Hamelin (33) that there was no evidence for the existence of any unsymmetrical organomagnesium compound in solution. While the present research was in progress, House, Latham, and Whitesides (34) successfully prepared methylcyclopentadienylmagnesium, phenylcyclopentadienylmagnesium, methylphenylmagnesium, and 3,3-dimethylbutylcyclopentadienylmagnesium. Their work was greatly aided by their finding that the exchange of alkyl groups was especially retarded by the use of N,N,N',N'-tetramethylethylenediamine. These authors, however, have not provided evidence for the existence of a completely aliphatic unsymmetrical dialkylmagnesium compound.

Magnuson has observed extra splittings in the methylene resonances of diethylmagnesium in tetrahydrofuran containing magnesium bromide and N,N,N',N'-tetramethylethylenediamine, and he has attributed this to the presence of two ethylmagnesium species which are interconverting slowly on the nmr time scale. The splittings were

observed at -50° , but were found, however, to disappear at temperatures below -50° . No extra resonances were observed when diethylmagnesium prepared from diethylmercury was mixed with ethyl bromide, treated with magnesium, and finally with diamine to produce a mixture in which the molar ratio of diethylmagnesium to ethylmagnesium bromide was 1.0. It appears to the present author that the conclusion, that the extra resonances are due to ethylmagnesium bromide and diethylmagnesium, is on very shaky ground, since the splittings were not observed in a solution containing both ethylmagnesium bromide and diethylmagnesium. Is it possible that exchange between ethylmagnesium bromide and diethylmagnesium is rapid in the absence of magnesium bromide and slow in its presence? House (34) reports that alkyl group exchange is catalyzed by the presence of magnesium bromide.

It is well known that the protons of a methylene group which are in close proximity to an asymmetric center may be magnetically nonequivalent. Whitesides, Holtz, and Roberts (36) have shown that conformational preferences are responsible for the major part of this magnetic nonequivalence.

In the present work, attempts have been made to employ magnetic nonequivalence in the study of unsymmetrical dialkylmagnesium compounds. An unsymmetric dialkylmagnesium compound having the structure RMgR' with a center of molecular asymmetry in the R group may display magnetic nonequivalence at either an isopropyl group or a methylene group in the R' moiety provided that both

inversion and alkyl exchange are slow on the nmr time scale.

It was hoped the magnetic nonequivalence could be used to study the exchange of alkyl groups in an unsymmetrical dialkylmagnesium compound as well as the rate of establishment and position of the Schlenk equilibrium (equation 3) because the nonequivalence would be destroyed either if the equilibrium lies far on the right or is rapidly established on the nmr time scale.

RESULTS AND DISCUSSION

A. Inversion in Organomagnesium Compounds

The nmr spectrum of 3,3-dimethylbutylmagnesium chloride in ether solution at 35° (normal probe temperature) shows an A_2X_2 pattern for the methylene protons. At -50°, however, the methylene protons of the carbon bonded to magnesium (hereafter referred to as the alpha carbon) form half of an $AA'XX'$ system. Whitesides, Witanowski, and Roberts (29) have attributed these spectral variations with temperature to an inversion process occurring at the alpha carbon. Bis-(3,3-dimethylbutyl)-magnesium also shows inversion in ether solution, but at a significantly lower rate than the corresponding Grignard reagent. Dialkylmagnesium compounds generally appear to invert more slowly than the corresponding Grignard reagents under the same conditions. Table II lists the activation parameters that have been found for Grignard reagents and dialkylmagnesium compounds in various solvents.

Grignard reagents invert more rapidly in ether than in tetrahydrofuran solution. Although Table II indicates that the inversion rate of the dialkylmagnesium compound, bis-(2-methylbutyl)-magnesium, is also greater in ether than in tetrahydrofuran, we have found that the same is not true for bis-(3,3-dimethylbutyl)-magnesium. In Figure 1a the nmr spectrum of the CH_2Mg protons of bis-(3,3-dimethylbutyl)-magnesium in ether solution is shown; Figure 1b shows the nmr spectrum of the same compound in tetrahydrofuran solution.

Table II

Activation Parameters for Inversion in Organomagnesium Compounds.

Organomagnesium Compound	Solvent	ΔH^\ddagger kcal/mole	ΔS^\ddagger e. u.	$\frac{1}{\tau}$ at 25°	Ref.
3, 3-dimethylbutyl-magnesium chloride	Ether	11 ± 2			29
Bis(3, 3 dimethyl-butyl)-magnesium	Ether	20 ± 2			29
2-methylbutylmagnesium bromide	Ether	12	-11	42	32
2-methylbutylmagnesium bromide	THF	16.6	-2	1.9	32
2-methylbutylmagnesium bromide	Anisole	9.6	-14	490	32
Bis(2-methylbutyl)-magnesium	Ether	18.2	+5	5	32 38
Bis(2-methylbutyl)-magnesium	Ether 12% Dioxane	18.3	-3	0.06	32 39
Bis(2-methylbutyl)-magnesium	Ether 10% Dioxane	19.5	+2.5	0.13	32 38
Bis(2-methylbutyl)-magnesium	Dioxane	4.9	-40	2.5	32 38
Bis(2-methylbutyl)-magnesium	THF	10.5	-25	0.57	32 38
Bis(2-methylbutyl)-magnesium + magnesium bromide	Ether	12.0	-12	42	32

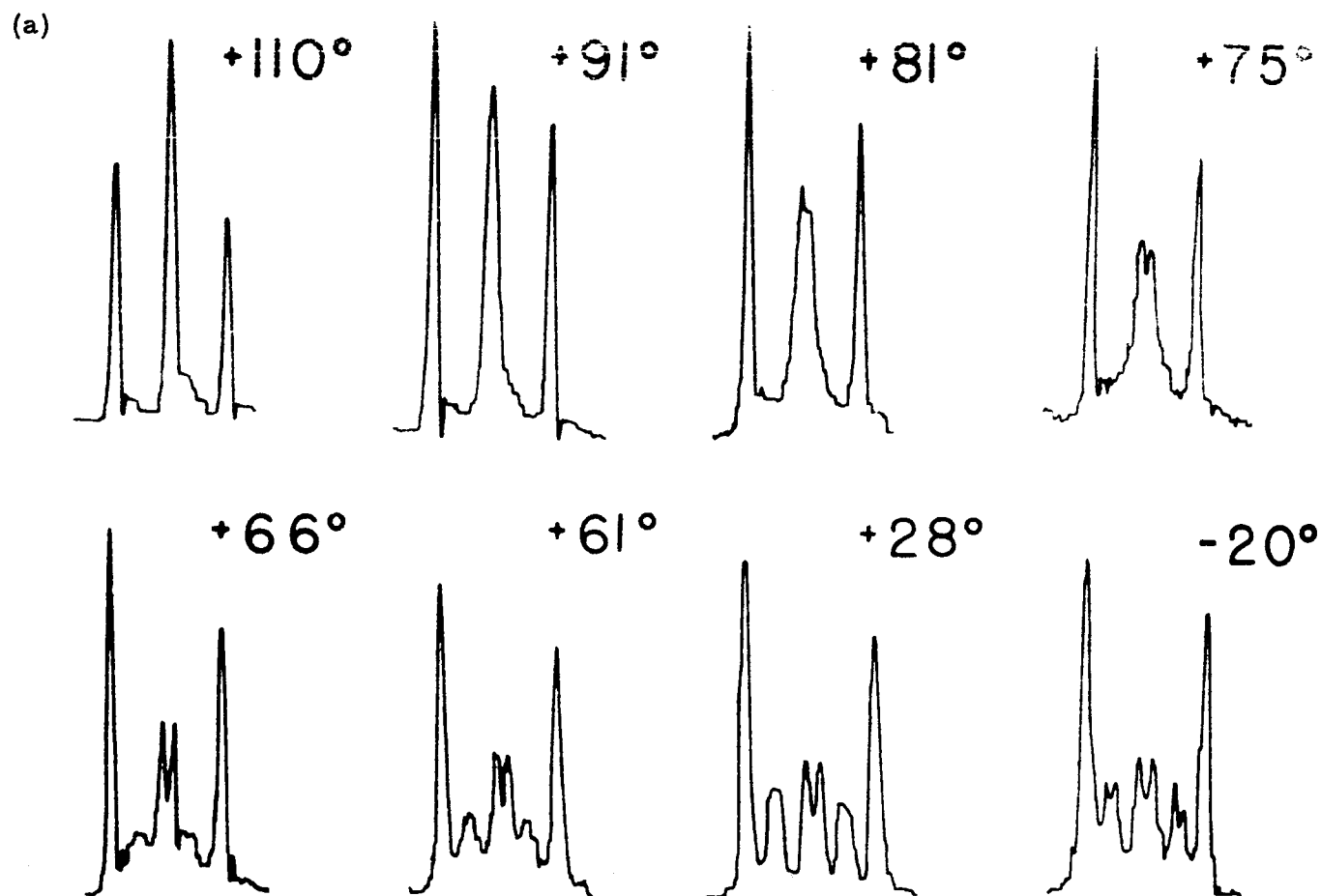


Figure 1a. Nmr spectra (60 MHz) of bis-(3,3-dimethylbutyl)-magnesium in diethyl ether as a function of temperature. Only the spectra of the $\text{CH}_2\text{-Mg}$ protons are shown.

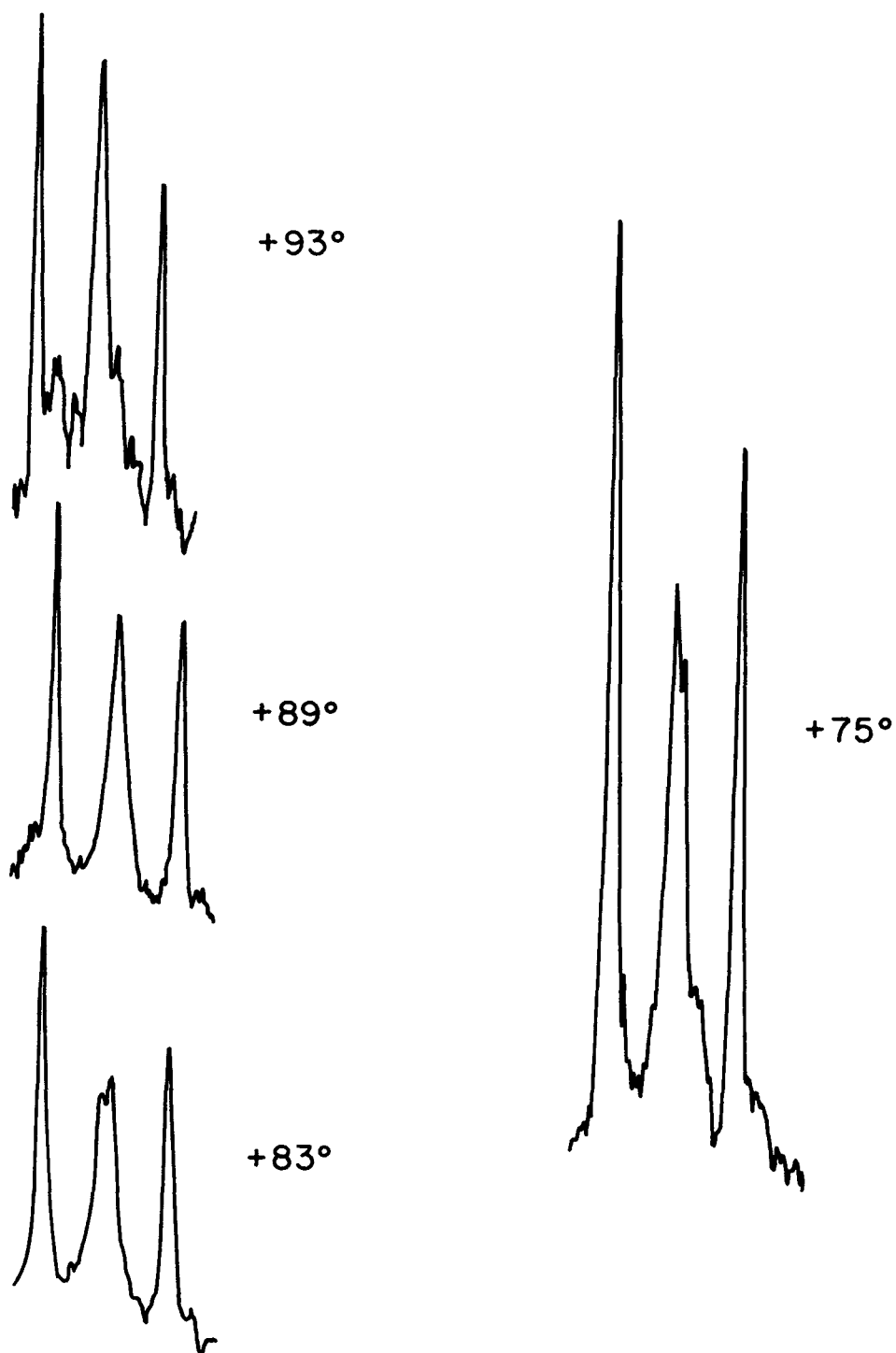


Figure 1b. Nmr spectra (60 MHz) of bis-(3,3-dimethylbutyl)-magnesium in tetrahydrofuran as a function of temperature. Only the spectra of the CH₂-Mg protons are shown.

The inversion rate is approximately the same in both solvents at the same temperatures.

The effect of the concentration of organomagnesium compounds on their inversion rates has been studied. Whitesides and Roberts (30) have reported that decreasing the concentration of 3,3-dimethylbutylmagnesium chloride in solution decreased the rate of inversion. Fraenkel and Dix (32) have reported that the kinetic order of the inversion process for 2-methylbutylmagnesium bromide is 2.5. In the present study, the effect of the addition of a second Grignard reagent on the inversion rate of a Grignard has been observed.

In Figure 2a is shown the nmr spectrum of 2-phenyl-3-methylbutylmagnesium chloride in ether solution (the spectrum of the organometallic compound is superimposed on that of the ^{13}C satellites of the solvent ether). To the sample tube containing this Grignard was added 0.05 ml of neopentyl bromide and excess magnesium. Figure 2b shows the nmr spectrum of 2-phenyl-3-methylbutylmagnesium chloride after the formation of neopentylmagnesium bromide in the same sample tube. In Figure 2c the variation of the nmr spectrum of the original 2-phenyl-3-methylbutylmagnesium chloride (sample of Fig. 2a) with temperature is shown. The important result is that the inversion rate of 2-phenyl-3-methylbutylmagnesium chloride is increased by the addition of neopentylmagnesium bromide. It should be noted that this increase in the inversion rate does not arise from a change in the concentration of 2-phenyl-3-methylbutylmagnesium chloride because the effective volume change between the samples was very small. However, the total

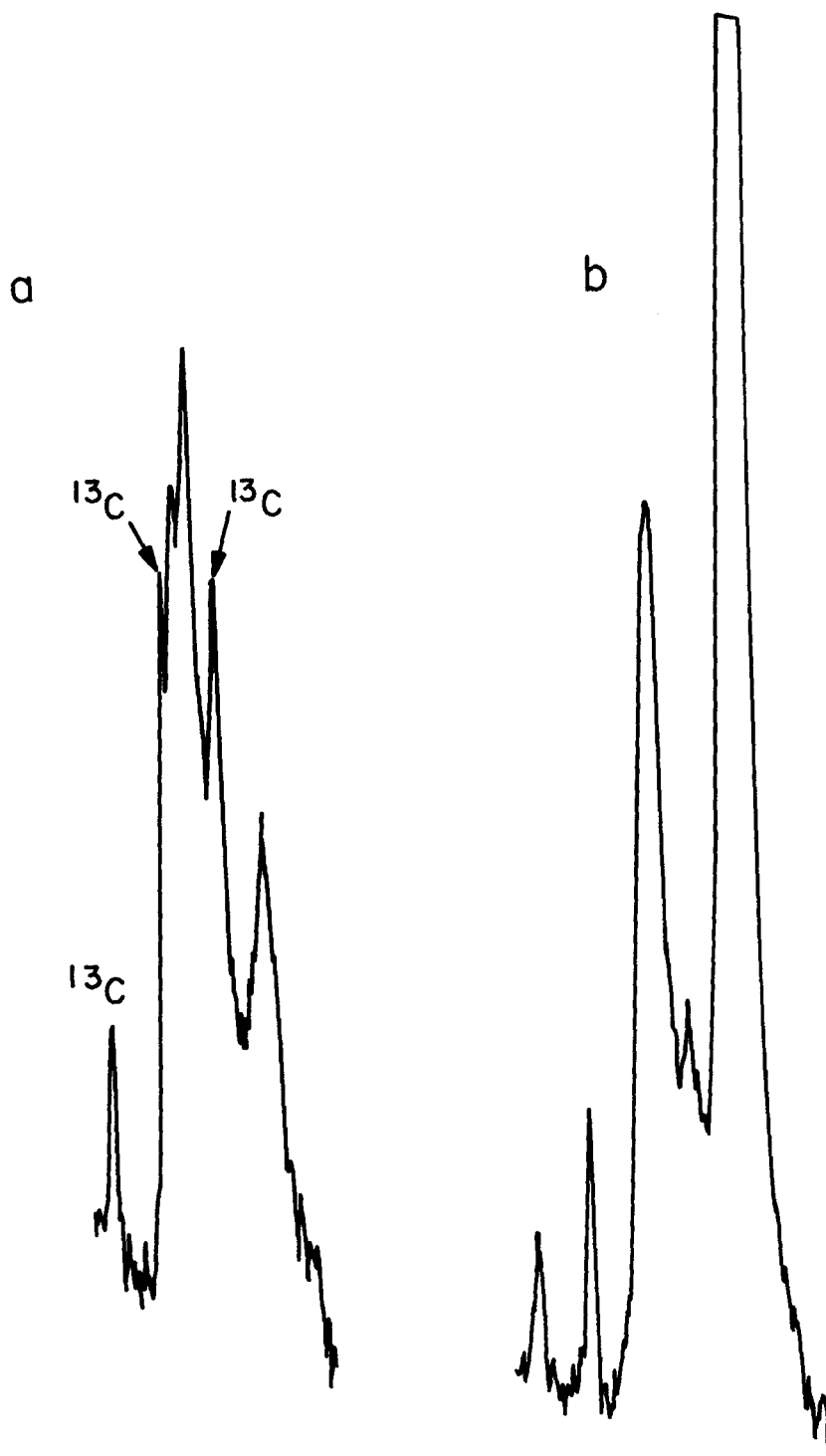


Fig. 2a. Spectra (60 MHz) of the $\text{CH}_2\text{-Mg}$ protons of 2-phenyl-3-methylbutylmagnesium chloride in diethyl ether.

Fig. 2b. Spectra (60 MHz) of the $\text{CH}_2\text{-Mg}$ protons of 2-phenyl-3-methylbutylmagnesium chloride after the formation of neopentylmagnesium chloride. The off-scale peak belongs to the $\text{CH}_2\text{-Mg}$ protons of neopentylmagnesium chloride.

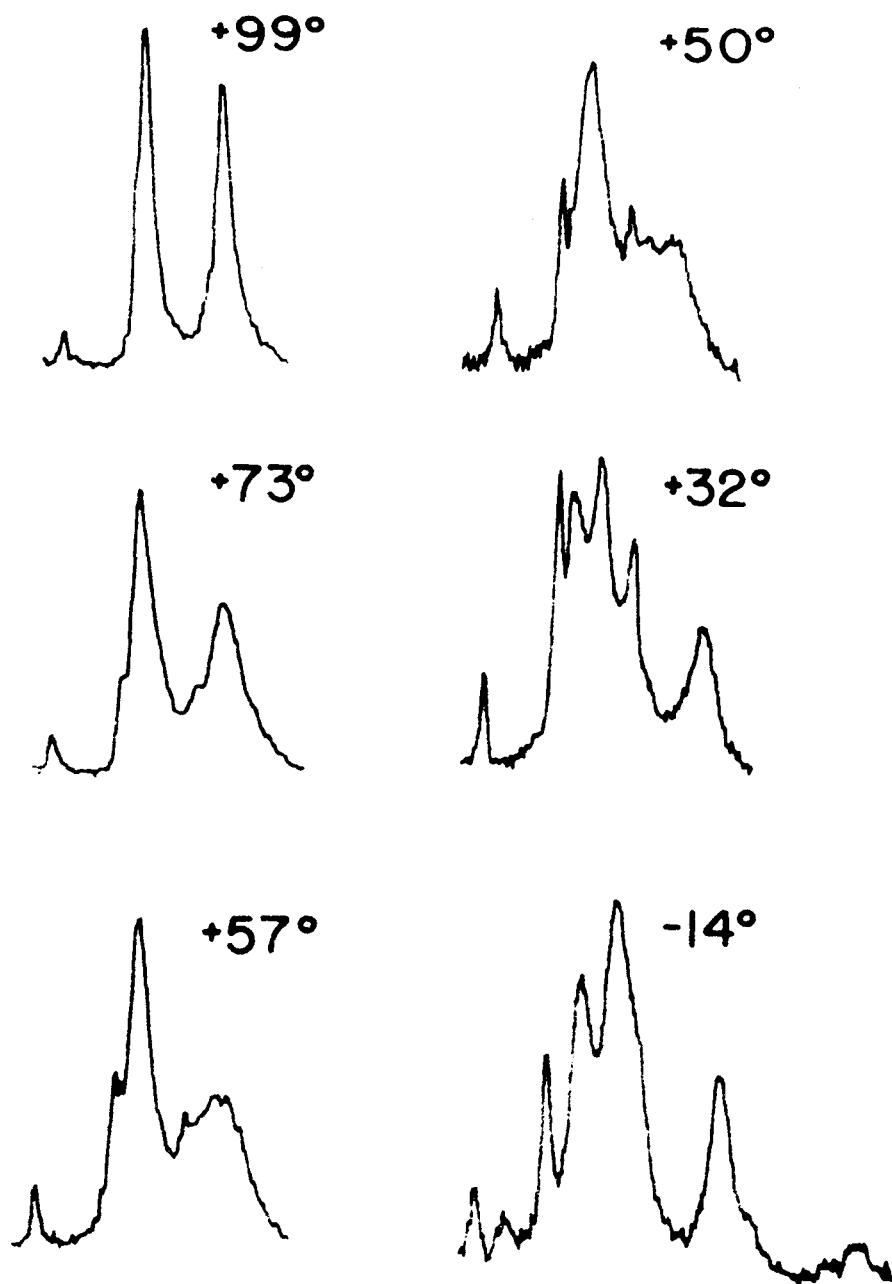


Figure 2c. Spectra (60 MHz) of the CH_2 -Mg protons of 2-phenyl-3-methylbutyl-magnesium chloride in diethyl ether, as a function of temperature. The spectrum of the organometallic compound is superimposed on that of the ether ^{13}C satellite.

concentration of Grignard species was increased in 2b. This result indicates that inversion of Grignard reagents in ether solution takes place by the attack of one Grignard molecule on another. The alternate explanation that a change in the inversion rate is a result of a change in dielectric constant of the solution has been substantially ruled out by Whitesides and Roberts (30) in the case of 3,3-dimethylbutylmagnesium chloride.

The nmr spectrum of the HC-Mg proton of s-butylmagnesium bromide in ether solution is shown in Figure 3. Because of the complexity of the spectrum no attempt at analysis has been made. The complexity of this spectrum arises from the fact that the methylene protons are nonequivalent, and the nonequivalence of the methylene protons indicates that inversion is slow in s-butylmagnesium bromide. The slow inversion rate persists in this Grignard reagent at temperatures as high as 100°C. Whitesides and Roberts (30) have also observed slow inversion with other secondary Grignard reagents, such as 3,3-dimethylcyclobutylmagnesium bromide and 3-methyl-s-butylmagnesium chloride in tetrahydrofuran solution.

The Grignard, 1-phenyl-2-propylmagnesium bromide was prepared from magnesium and 1-phenyl-2-propyl bromide which had been purified by preparative gas chromatography. In Figure 4a the nmr spectrum of the methylene protons of this Grignard reagent in ether solution is shown. The nmr absorptions (at 35°) for these methylene protons form the AB part of a deceptively simple ABX spectrum (40). Figure 4b shows a theoretical spectrum for the same methylene

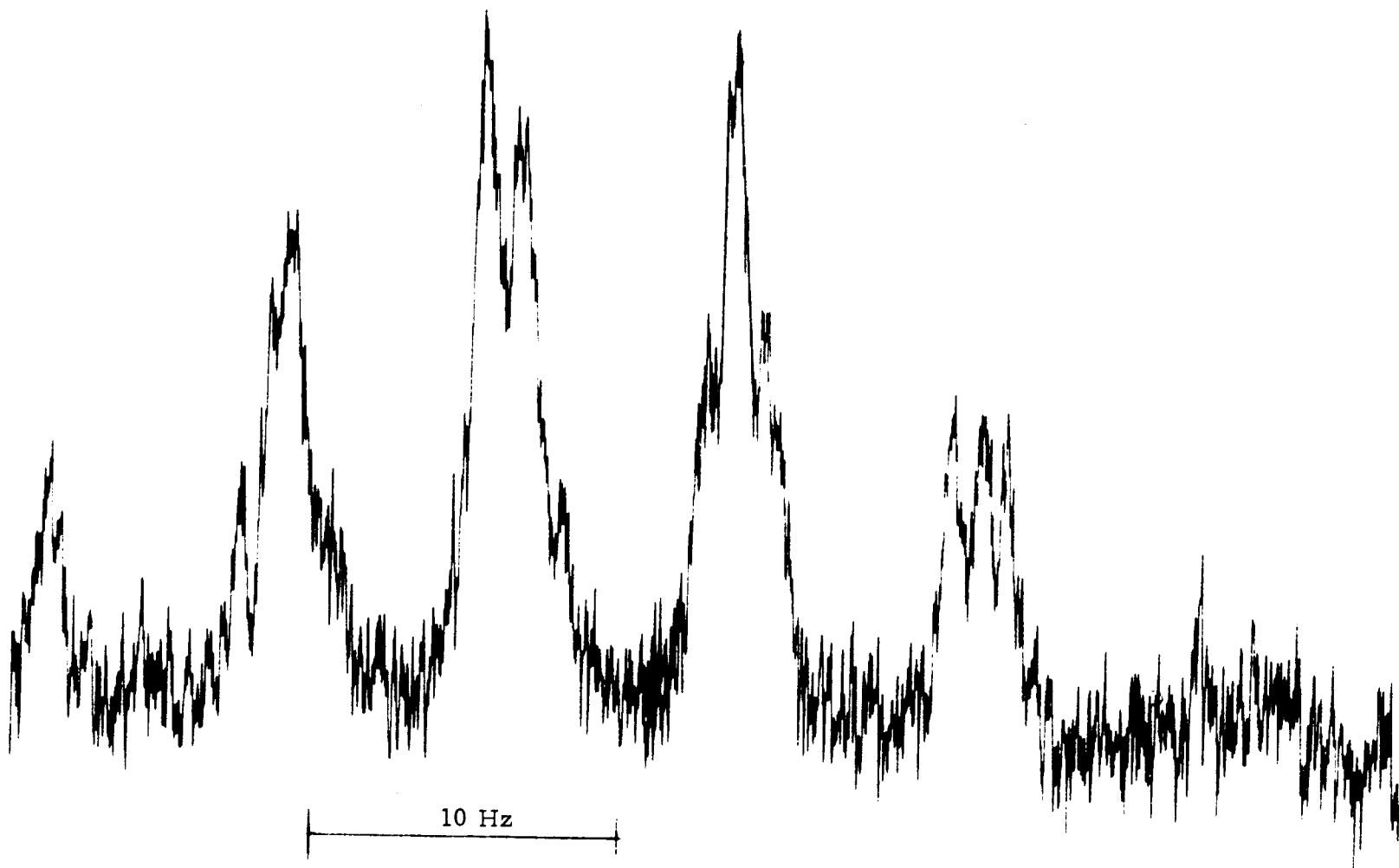


Figure 3. Spectrum (60 MHz) of the CH-Mg proton of s-butylmagnesium bromide in diethyl ether.

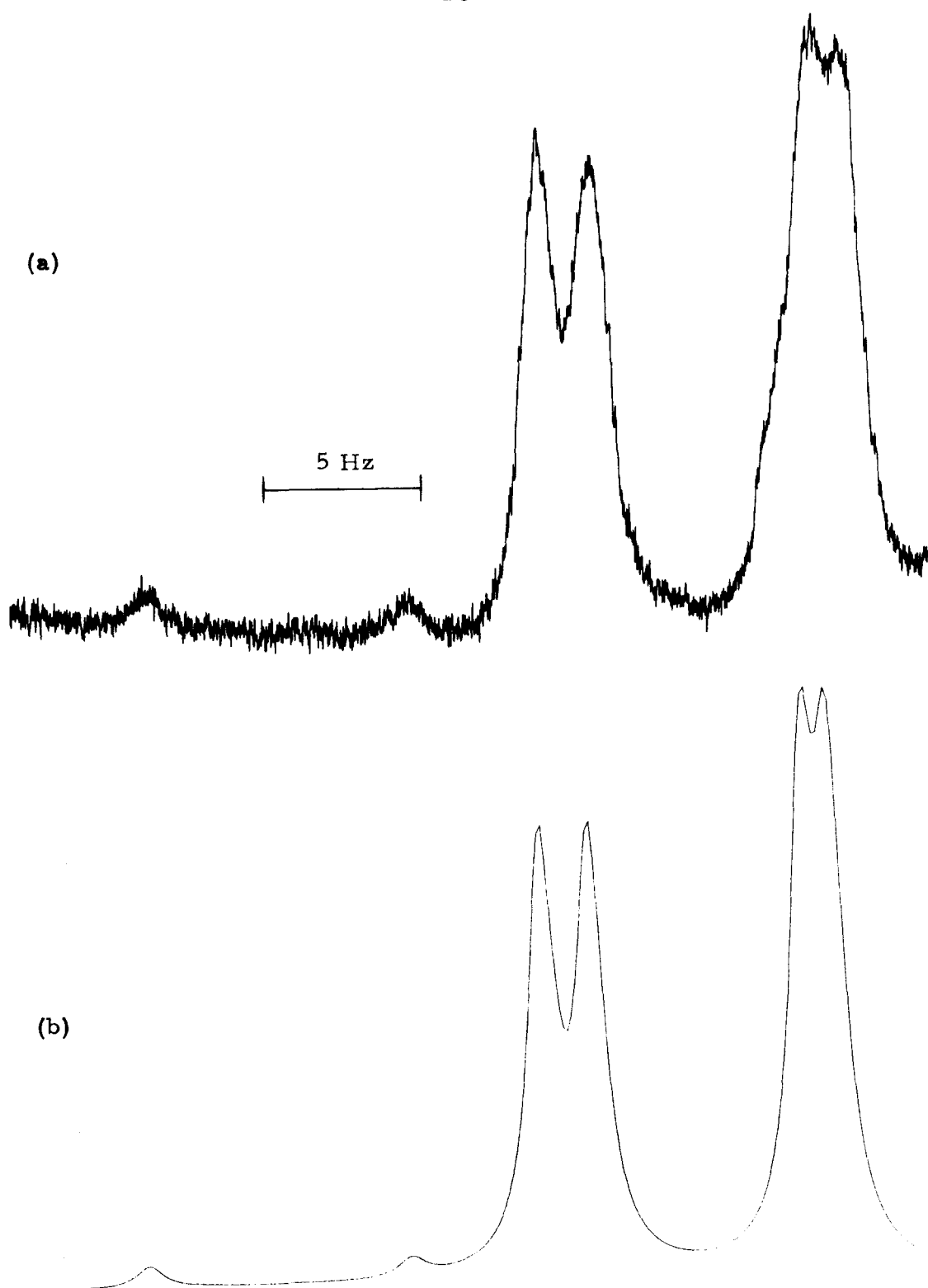


Figure 4. Spectrum (60 MHz) of the $\text{CH}_2\text{-}\phi$ protons of 1-phenyl-2-propylmagnesium bromide: (a) experimental spectrum (b) theoretical spectrum. The "wings" on the upfield side of the ABX spectrum are not shown.

protons calculated using the chemical shifts and coupling constants given in Table III. The report by Adams (41) that these protons are equivalent can possibly be explained by differences in concentration leading to different inversion rates, but is more likely due to poor spectrometer resolution.

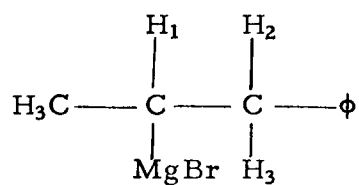
In Figure 5 is shown the nmr spectra of the $\text{CH}_2\phi$ protons over a temperature range from $+40$ to $+103^\circ$. As the temperature is increased the splittings disappear and the spectrum becomes the A_2 part of an A_2X system. The change in the spectrum upon heating can be explained by an increase in the inversion rate at the HCMg center. This is the first example of rapid inversion in a secondary Grignard reagent.

Unfortunately the changes in the experimental spectra are very small and hence any attempt to match the experimental spectra with theoretical spectra is subject to large error. Nonetheless, in Figure 6 is shown theoretical spectra of the $\text{CH}_2\phi$ protons as a function of temperature. An Arrhenius plot of the τ values obtained from the theoretical analysis gave a free energy of activation $\Delta G^\ddagger = 18 \pm 2$ kcal/mole, and $\Delta H^\ddagger = 10 \pm 0.5$ kcal/mole, $\Delta S^\ddagger = -26 \pm 7$ e. u.

It is difficult to speculate on why 1-phenyl-2-propylmagnesium bromide undergoes a rapid inversion at the HCMg center, whereas all secondary Grignards studied heretofore do not. The sole distinction of 1-phenyl-2-propylmagnesium bromide relative to other secondary Grignards which have been studied appears to be the phenyl group. If charge separation is important in the transition state for inversion,

Table III

Spectral Parameters for the Methylene and Methine Protons of 1-Phenyl-2-Propylmagnesium bromide.



Proton Chemical Shifts (relative to H_1) at 60 MHz.

$$\text{H}_1 \quad \delta_1 = 0.0$$

$$\text{H}_2 \quad \delta_2 = 69.83 \pm 0.2 \text{ Hz.}$$

$$\text{H}_3 \quad \delta_3 = 75.38 \pm 0.2 \text{ Hz.}$$

Proton-Proton J-Values in Hz.

$$\text{J}_{12} \quad = \quad 7.50 \pm 0.10 \text{ Hz.}$$

$$\text{J}_{13} \quad = \quad 8.40 \pm 0.10 \text{ Hz.}$$

$$\text{J}_{23} \quad = -12.51 \pm 0.15 \text{ Hz.}$$

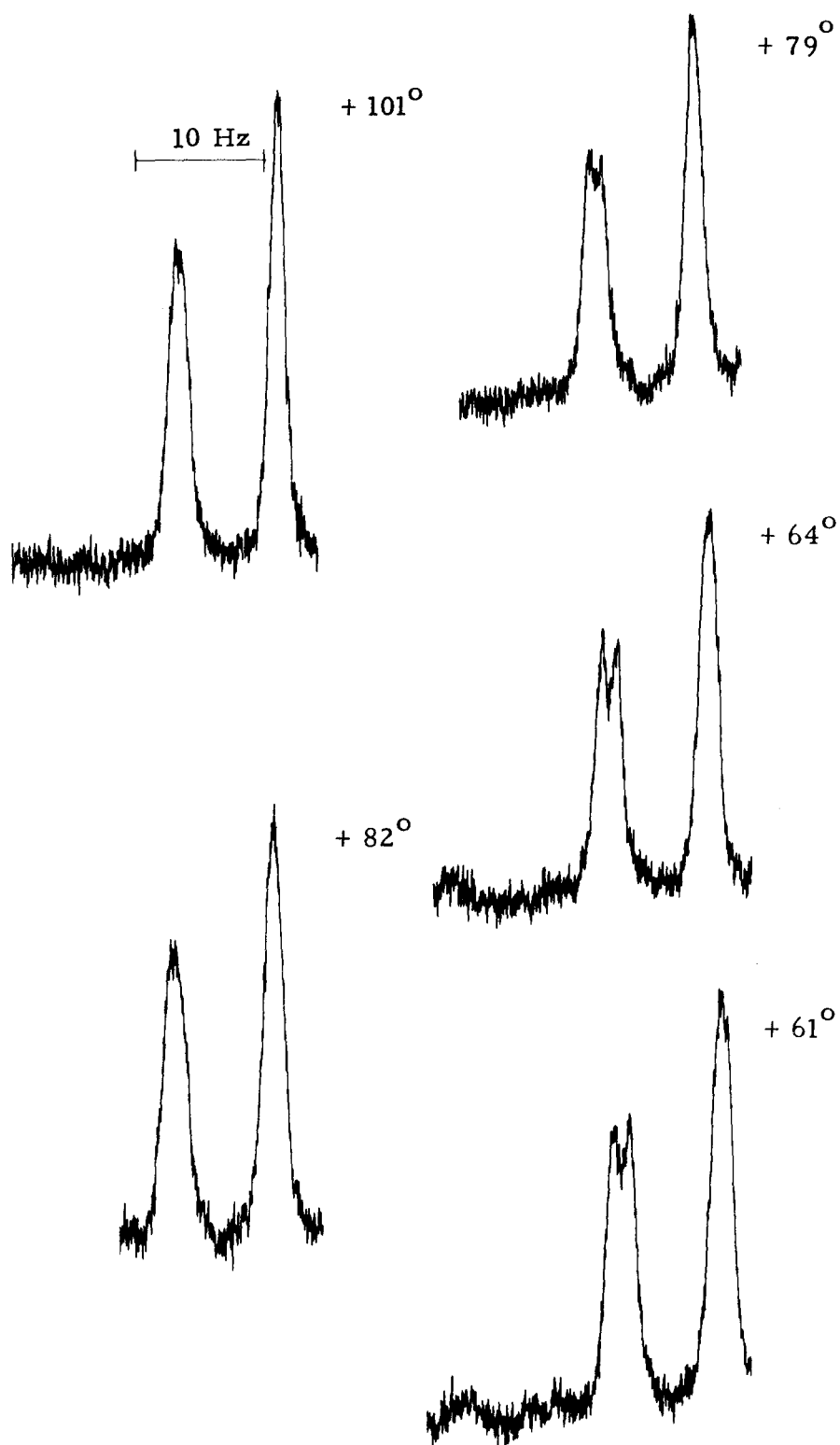


Figure 5. Nmr spectra (60 MHz) of the $\text{CH}_2\text{-}\phi$ protons of 1-phenyl-2-propylmagnesium bromide in diethyl ether as a function of temperature.

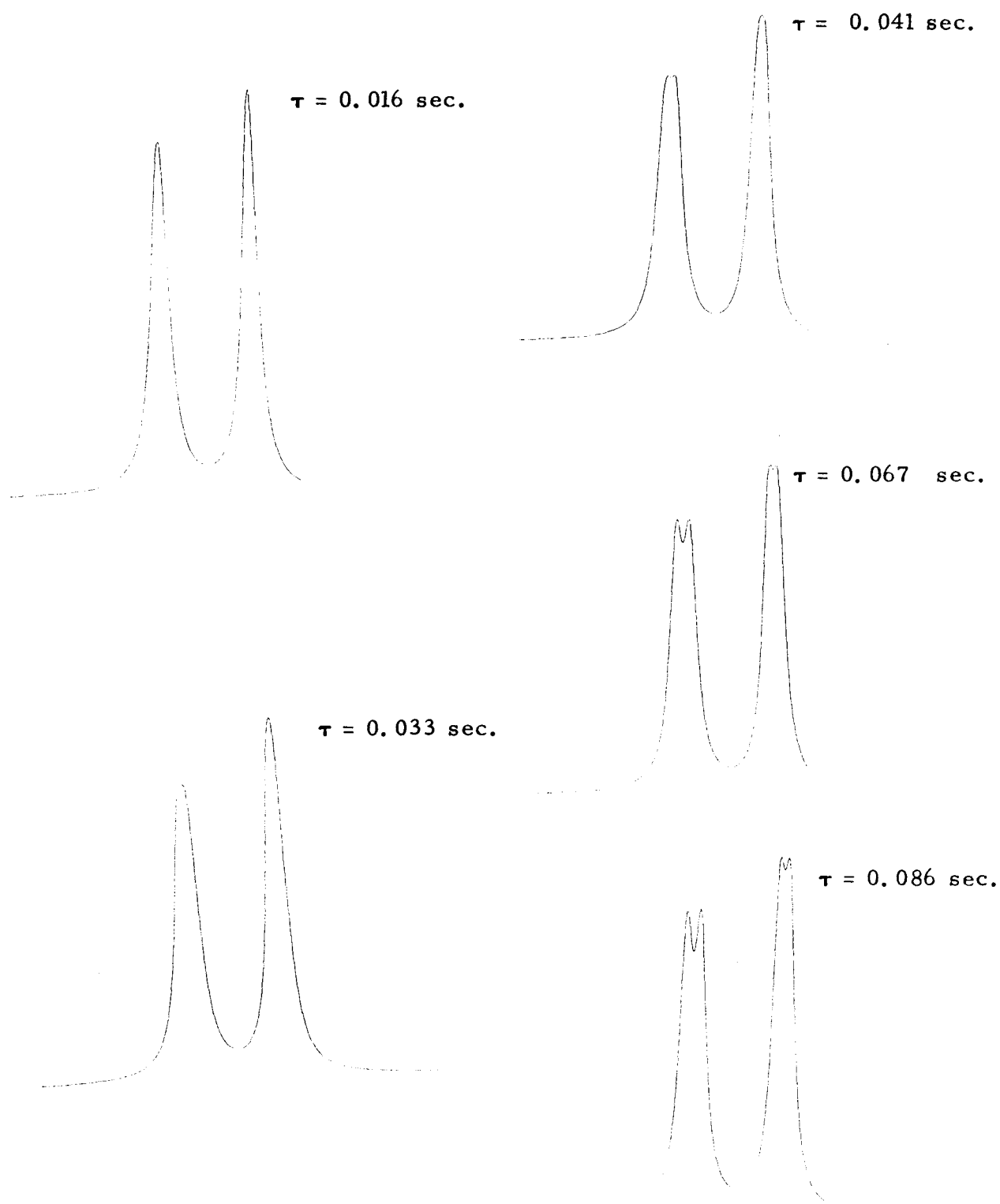


Figure 6. Calculated spectra of the $\text{CH}_2\text{-}\phi$ protons of 1-phenyl-2-propylmagnesium bromide in diethyl ether as a function of the pre-exchange lifetime τ .

then a possible explanation is that the phenyl group stabilizes the charge-separated species by bridging to the carbon bonded to the magnesium. The inductive effect of the benzyl group should also be important in stabilizing the charge separation. A more cogent explanation must await further observations of aromatically substituted secondary Grignards.

B. Unsymmetrical Dialkylmagnesium Compounds

In attempts to obtain an unsymmetrical dialkylmagnesium compound $R-Mg-R'$, mixtures of the dialkylmagnesium compounds, $R-Mg-R$ and $R'-Mg-R'$, were always prepared in three different ways:

1. Each dialkylmagnesium compound was prepared separately and subsequently the two were mixed in an nmr sample tube.
2. A mixture of the two appropriate halides were allowed to react with magnesium, and the magnesium salts were removed by the addition of dioxane.
3. The appropriate halides were allowed to react with magnesium sequentially in the same vessel, and dioxane was then added as in method 2.

The second method was consistently found to give the best yield of the dialkylmagnesium reagents. Individual compounds will now be discussed.

The nmr absorption of the methylene protons in neopentylmagnesium bromide in ether solution occurs at -26 Hz^* (Fig. 7).

* In this thesis chemical shifts will be reported in Hz from tetramethylsilane. Positive values denote shifts downfield from tetramethylsilane; negative values denote upfield shifts. Chemical shifts are reported with reference to external tetramethylsilane.

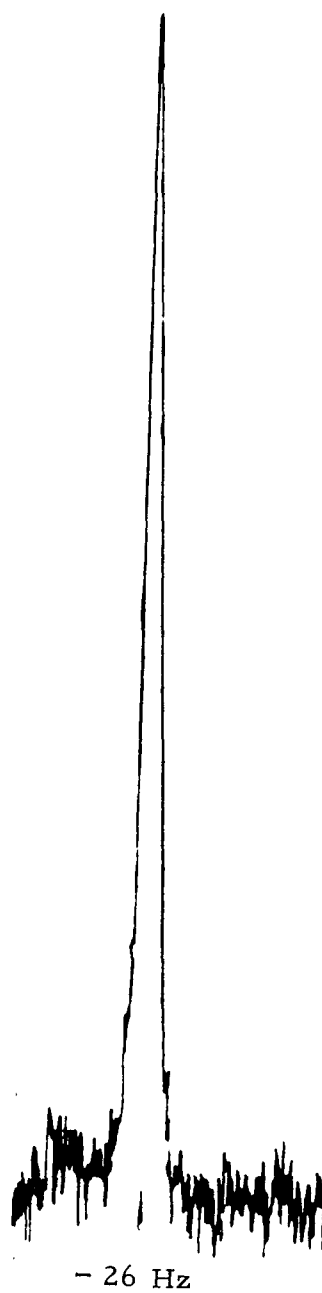


Figure 7. Spectrum (60 MHz) of the $\text{CH}_2\text{-Mg}$ protons of neopentylmagnesium bromide in diethyl ether. Sweep width is 500 Hz.

This Grignard reagent was used in an attempt to prepare an unsymmetrical dialkylmagnesium compound, because the methylene protons involved are not observably coupled to the methyl protons and hence give a very sharp singlet. Dineopentylmagnesium was prepared from neopentylmagnesium bromide using the dioxane precipitation method (3). The alpha methylene protons in dineopentylmagnesium in ether solution absorb at -31 Hz. The small difference in the chemical shift for the methylene protons of these two compounds can be attributed to differences in concentration of the organomagnesium species, as well as to more interesting factors such as differences in constitution between the two.

The simplest conceivable Grignard reagent that has an asymmetric center is the s-butyl Grignard reagent. In Figure 3 is shown the nmr spectrum of the HC-Mg proton of s-butylmagnesium bromide in ether solution. The CH-Mg proton absorbs at approximately -27 Hz. Bis-(s-butyl)-magnesium was prepared from s-butylmagnesium bromide using the dioxane precipitation method (3). The CH-Mg proton in this dialkylmagnesium compound absorbs at approximately -26 Hz.

Depending on the rate of alkyl group exchange and inversion, it may be possible to observe three species in the nmr spectrum of a mixture of dineopentylmagnesium and bis-(s-butyl)-magnesium. The three species are dineopentylmagnesium, bis-(s-butyl)-magnesium, and neopentyl-s-butylmagnesium. The unsymmetrical magnesium compound might be identifiable by the fact that the methylene protons

in the neopentyl group could now be nonequivalent and would thus show an AB pattern in the nmr spectrum.

In Figure 8 is shown the nmr spectrum of the CH_2Mg and HC-Mg protons in a mixture of dineopentylmagnesium and bis-(s-butyl)-magnesium in ether solution. Nmr spectra of this mixture were taken over a temperature range from 35° to -65°C . Although the resonance due to the $\text{H}_2\text{C-Mg}$ protons became broad at low temperatures ($\omega_{\frac{1}{2}} = 5.0 \text{ Hz}$; $\omega_{\frac{1}{2}}^{\text{ether}} = 2.5 \text{ Hz}$), there were no new absorptions that could be attributed to the formation of neopentyl-s-butylmagnesium. Based on the results for bis-(3,3-dimethylbutyl)-magnesium and bis-(2-methylbutyl)-magnesium, one would expect the inversion rate for these compounds to be slow on the nmr time scale at temperatures below 0° . The most likely reasons for not observing evidence for neopentyl-s-butylmagnesium are that intermolecular exchange of alkyl groups is rapid and/or that there is a very small chemical shift difference between the in principle nonequivalent $\text{H}_2\text{C-Mg}$ protons of neopentyl-s-butylmagnesium. The latter possibility was investigated by changing the structure of the asymmetric moiety.

The nmr spectrum of bis-(2-methylbutyl)-magnesium has been well studied over a range of temperatures (32). For this reason and because the nmr spectrum of the CH_2Mg protons is more easily observable than the CH-Mg proton in bis-(s-butyl)magnesium, it was decided to study a mixture of dineopentylmagnesium and bis-(2-methylbutyl)-magnesium.

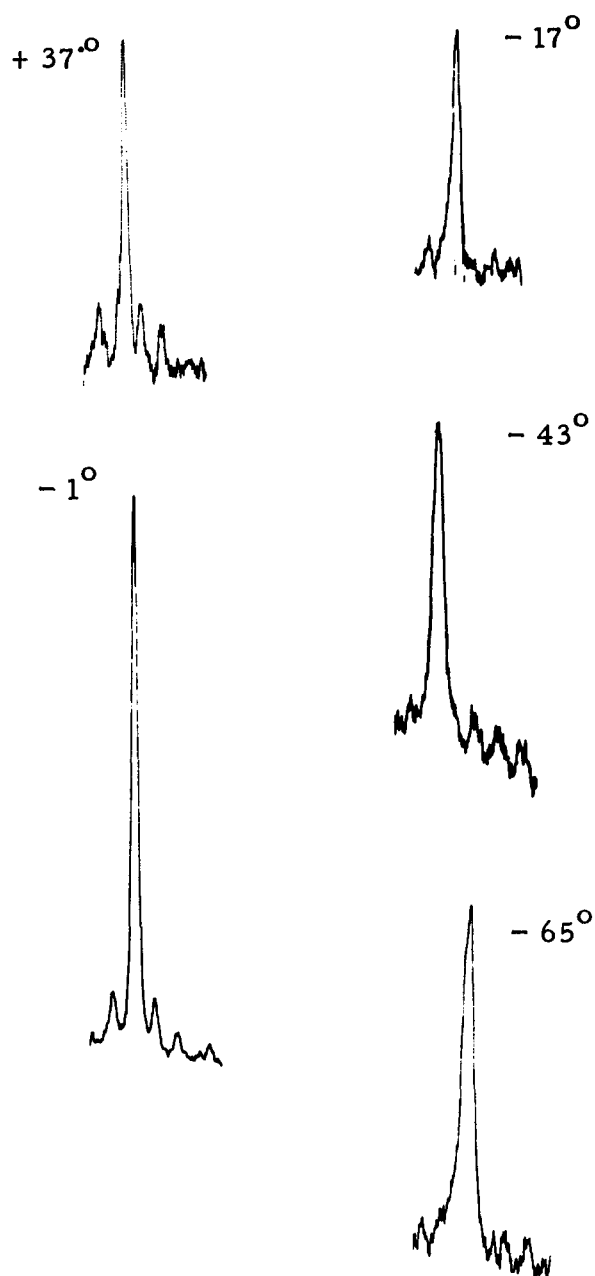
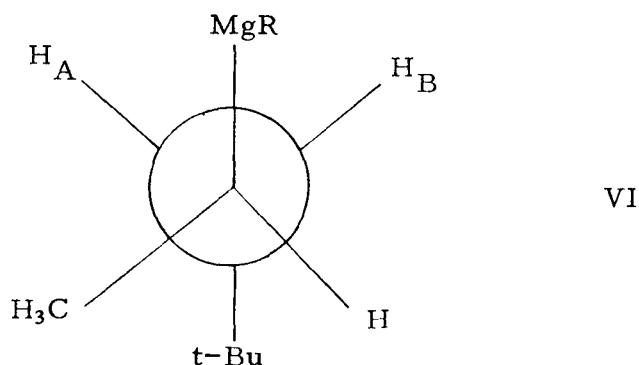


Figure 8. Spectra (60 MHz) of a mixture of di-s-butylmagnesium and dineopentylmagnesium in diethyl ether as a function of temperature. Only the CH-Mg and the CH₂-Mg protons are shown.

Figure 9 displays the nmr spectrum of the CH_2Mg protons in a mixture of dineopentylmagnesium and bis-(2-methylbutyl)-magnesium in ether solution. Nmr spectra of this mixture were taken over a temperature range from 35° to -65° . Once again the resonance due to the CH_2Mg protons of the neopentyl group became broad at low temperatures ($\omega_{\frac{1}{2}} = 6 \text{ Hz}$; $\omega_{\frac{1}{2}}^{\text{ether}} = 2 \text{ Hz}$), but there was no evidence of absorption that could be attributed to the existence of neopentyl-2-methylbutylmagnesium. The fact that the absorptions in Figure 9 due to the CH_2Mg protons of bis-(2-methylbutyl)-magnesium comprise the AB part of an ABX system unequivocally demonstrates that inversion in this compound is slow.

Because of the large size of the t-butyl group in bis-(4,4-dimethyl-2-pentyl)-magnesium, the conformation VI (sighting down the $\text{C}_2 \rightarrow \text{C}_3$ bond) should be very highly favored. This conformational restriction, coupled with the presence of an asymmetric center at $^*\text{C}_2$



necessarily produces a large nonequivalence for the methylene protons (A and B in VI) adjacent to $^*\text{C}_2$. The question now becomes, how rapid is the attenuation with distance of the magnitude of the non-

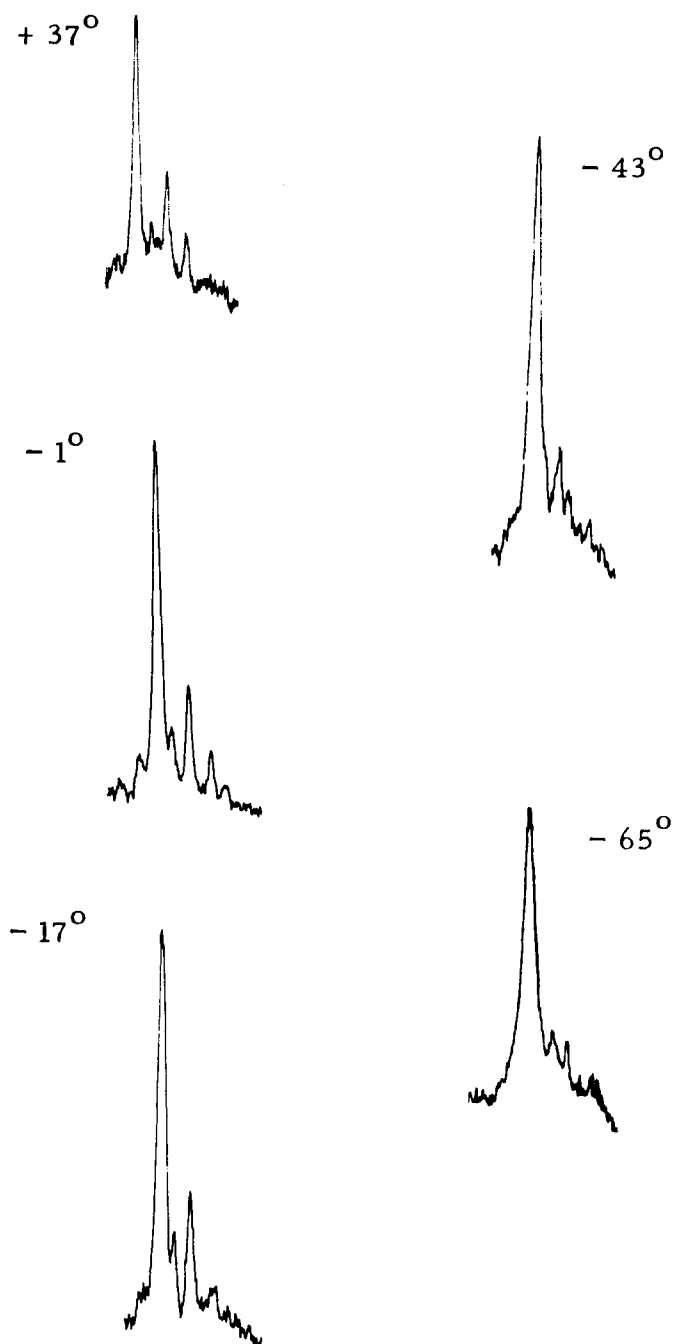
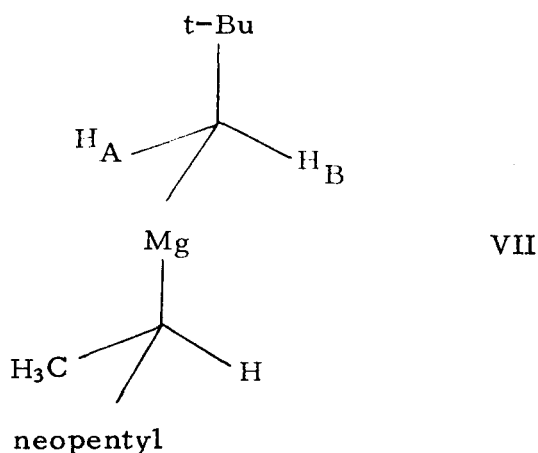


Figure 9. Spectra (60 MHz) of a mixture of bis-(2-methylbutyl)-magnesium and dineopentylmagnesium in diethyl ether as a function of temperature. Only the spectra of the CH₂-Mg protons are shown.

equivalence induced by an asymmetric center? That is, will this nonequivalence be observable in the methylene protons of the neopentyl group two bonds away in the compound neopentyl-4,4-dimethyl-2-pentylmagnesium? (VII)



In Figure 10 are shown nmr spectra of a mixture of dineopentylmagnesium and bis-(4,4-dimethyl-2-pentyl)-magnesium. These spectra were observed over a temperature range from 35° to -43°. The absorption due to the methylene protons of the neopentyl group remained a singlet over this temperature range. The important result (albeit negative) from the above three experiments is that intermolecular exchange of alkyl groups in dialkylmagnesium compounds in ether solution is probably rapid on the nmr time scale even at temperatures as low as -65°.

After these initial experiments on unsymmetrical dialkylmagnesium compounds were completed, House and coworkers (34) reported that the exchange of alkyl groups from one magnesium atom

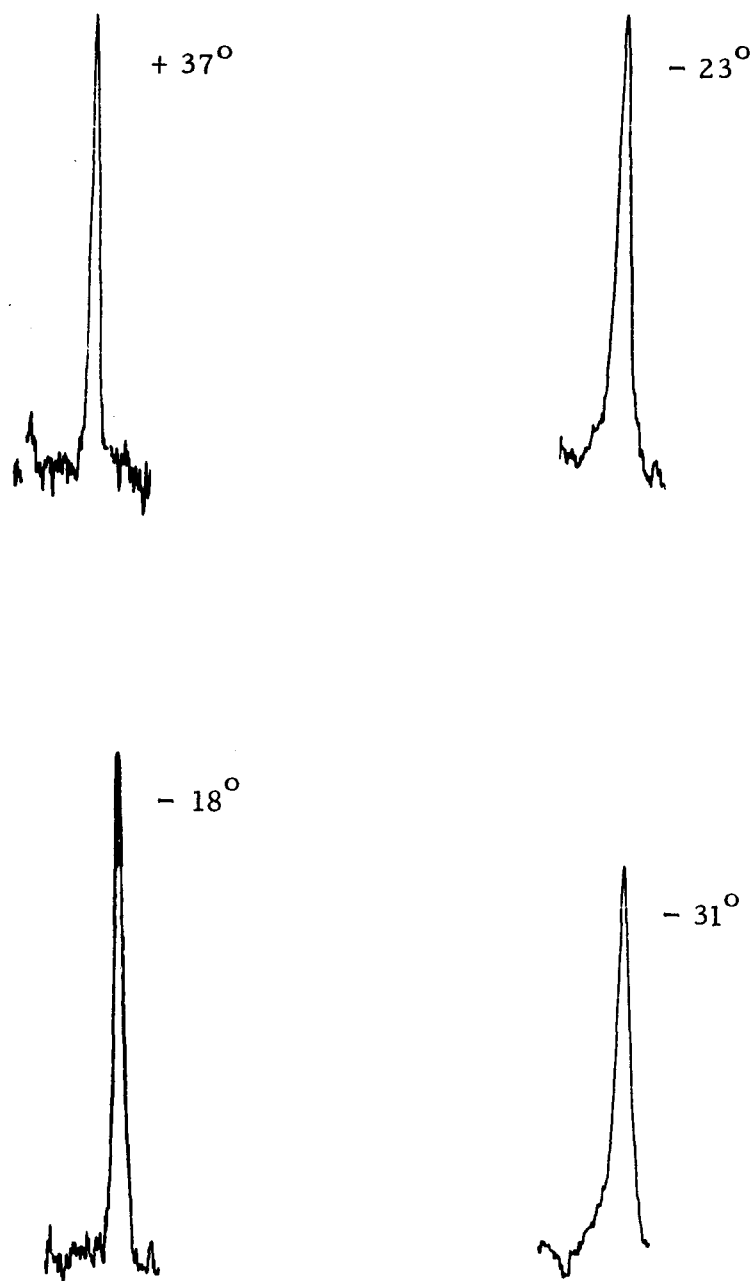
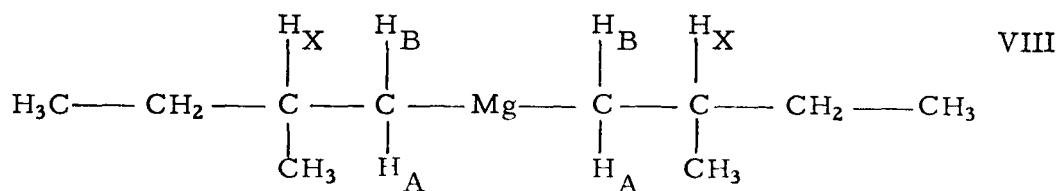
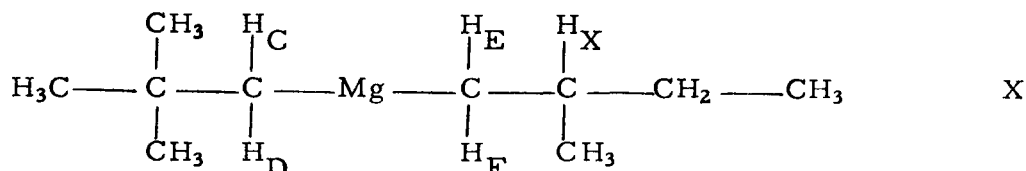
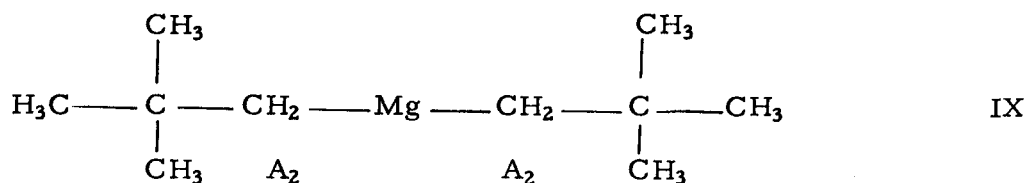


Figure 10. Spectra (60 MHz) of a mixture of bis-(4,4-dimethyl-2-pentyl)-magnesium and dineopentylmagnesium in diethyl ether as a function of temperature. Only the $\text{CH}_2\text{-Mg}$ protons of dineopentylmagnesium are shown.

to another was retarded by the presence of N, N, N', N'-tetramethylethylenediamine (henceforth called TMED). In order to determine whether the exchange of alkyl groups in the presence of TMED was slow enough to observe an unsymmetrical dialkylmagnesium compound, a mixture of dineopentylmagnesium, bis-(2-methylbutyl)-magnesium, dioxane and this diamine in ether solution was prepared. The molar ratio of ether to TMED was approximately 4:1. The concentration of organomagnesium species was not directly determined, however, it can be approximated from the nmr spectrum by comparison with the ether methyl ^{13}C satellites; this comparison suggests that the organomagnesium concentration is 4-5% by weight.

In Figure 11 is shown the 60 MHz spectrum of the CH_2Mg protons of the sample above containing TMED. This spectrum indicates the presence of a species other than the two symmetrical dialkylmagnesium compounds. As a first guess the peaks labelled 4-9 in Figure 11 can be assigned to the CH_2Mg protons of bis-(2-methylbutyl)-magnesium VIII (hereafter called protons A and B). These peaks would comprise the AB part of an ABX system. Peak 3 could be assigned to the CH_2Mg resonance in dineopentylmagnesium IX (hereafter called protons A_2), and peak 2 could be tentatively assigned to the resonances from the CH_2Mg protons of the neopentyl radical in neopentyl-2-methylbutylmagnesium X (hereafter called protons C and D).





The reasons for these particular assignments of peaks 2 and 3, and the assignment of peak 1 will be discussed later. The significance of Figure 11 lies in the fact that now there is more than one absorption from the CH_2Mg protons of the neopentyl group. However, this spectrum appears to show only one AB pattern (i. e., the AB of an ABX) arising from the CH_2Mg protons of the 2-methylbutyl group.

In Figure 12 is shown the nmr spectrum of the same sample at 100 MHz. A comparison of this spectrum with that in Figure 11 indicates that the separation between peaks 5 and 6 has greatly increased ($5-6 = 1.0$ Hz at 60 MHz; $5-6 = 11$ Hz at 100 MHz) upon changing the field strength. The distance between peaks 2 and 3 is increased in proportion to the ratio of the field strengths (100/60). The conclusion one reaches is that peaks 4-9 which at 60 MHz were the AB part of an ABX system are at 100 MHz the AM part of an AMX system. Peaks 8 and 9 are not of the same intensity as 6 and 7 because the system is not completely AMX.

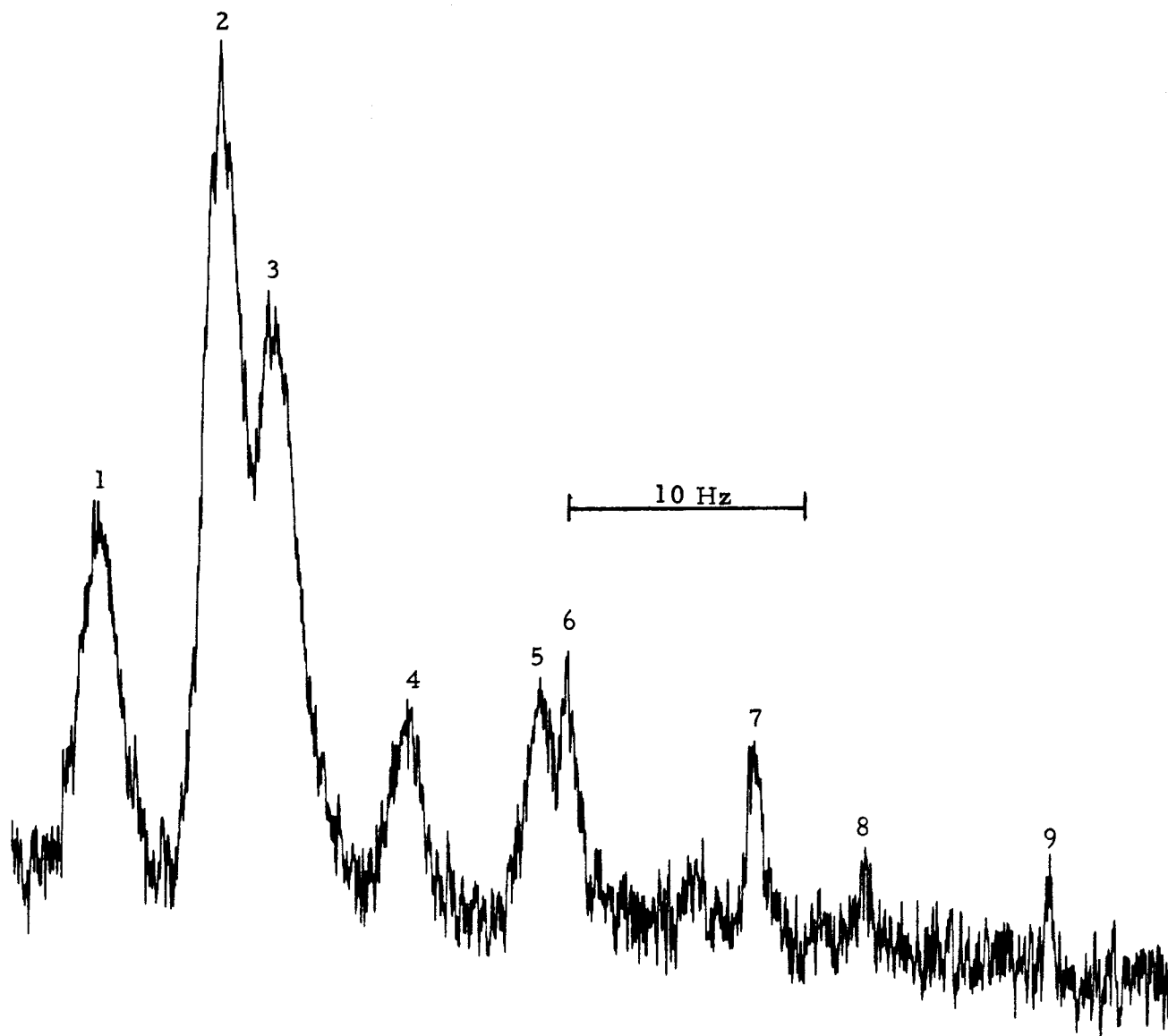


Figure 11. Spectrum (60 MHz) of a mixture of bis-(2-methylbutyl)-magnesium and dineopentylmagnesium in ether - N,N,N',N'-tetramethylethylenediamine (4:1 by mole %). Only the spectrum of the $\text{CH}_2\text{-Mg}$ protons is shown.

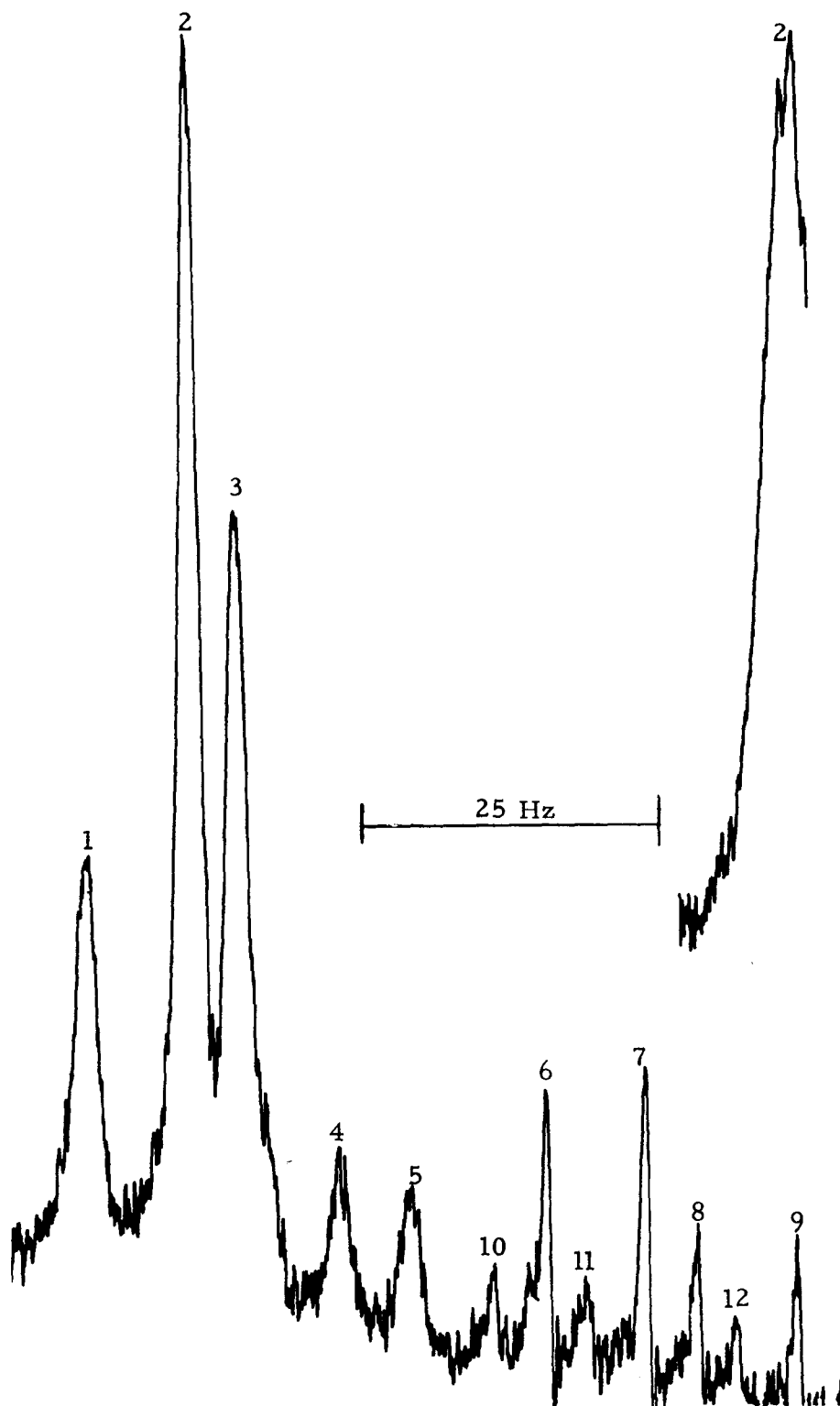


Figure 12. Spectrum (100 MHz) of a mixture of bis-(2-methylbutyl)-magnesium and dineopentylmagnesium in ether - N,N,N',N' -tetramethylethylenediamine (4:1 by mole %). Only the spectrum of the $\text{CH}_2\text{-Mg}$ protons is shown. The insert shows a spectrum of peak 2 taken on a 100 Hz sweep width.

A computer analysis of the 100 MHz spectrum of peaks 6-9 was carried out and the results appear in Table IV. The theoretical spectrum is shown in Figure 13. (It will be shown later in this discussion that, contrary to the earlier assumption, peaks 6-9 belong to species X).

The next significant point to be made about Figure 12 concerns peaks 10-12. It should be recognized that now only the A part of the AMX system is being discussed. The analogous separations between 10 and 11 and 6 and 7 and also that between 11 and 12 and 7 and 9 indicate the presence of another AMX system. In the smaller AMX the peak 13, which corresponds to 8 in the original AMX, is hidden under peak 7.

To recapitulate, what has been proposed is that there are two AMX systems slightly shifted from one another and with an intensity ratio of 3:1. The AM parts of these AMX systems can be assigned to protons A and B of bis-(2-methylbutyl)-magnesium and the CH_2Mg protons of the 2-methylbutyl group in neopentyl-2-methylbutylmagnesium (hereafter called protons E and F).

It turns out that the initial assignments of peaks 4-9 to protons A and B of bis-(2-methylbutyl)magnesium VIII must now be revised. The evident splitting of peak 2 (See magnified insert Fig. 12) indicates conclusively that it had been correctly assigned to protons C and D of neopentyl-2-methylbutylmagnesium X. (It should be noted that an AB pattern with such a small separation between the two center lines

Table IV

Spectral Parameters for the Methylene
Protons of 2-Methylbutyl-magnesium Derivatives



Solute	Solvent	δ_{ab} in ppm	J_{ab} in Hz	J_{ax} in Hz	J_{bx} in Hz
RMgBr	Ether	0.170 ± 0.003	-12.40 ± 0.02	7.65 ± 0.2	4.35 ± 0.2
R ₂ Mg	Ether	0.235 ± 0.003	-12.66 ± 0.2	7.69 ± 0.2	4.91 ± 0.2
RMg-CH ₂ C(CH ₃) ₃	Ether	0.283 ± 0.002	-12.96 ± 0.1	8.53 ± 0.1	5.63 ± 0.1

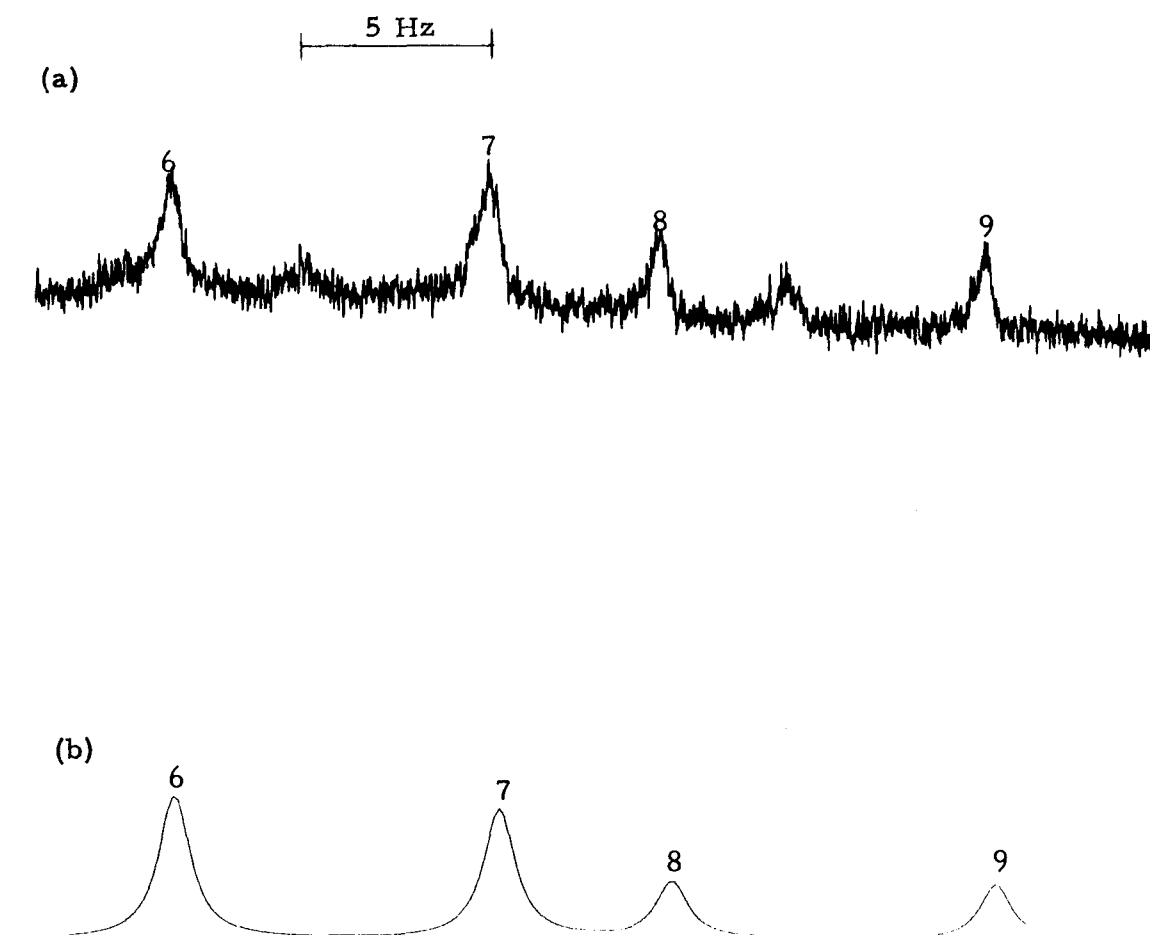


Figure 13. Spectrum (100 MHz) of peaks 6-9 as described in text:
(a) experimental spectrum (b) calculated spectrum
using the parameters given in table IV.

would not show any wings.) If peak 2 corresponds to C and D of X, then 4-9 must correspond to E and F of X on the basis of comparable intensities. Then peaks 10-12 must belong to protons A and B of VIII and 3 is the resonance due to protons A_2 of dineopentylmagnesium IX.

In Figure 14 is shown the nmr spectrum at 220 MHz (43) of the same sample shown in Figures 11 and 12. This spectrum further strengthens the argument that more than two species are being observed. Figure 14 shows the presence of new peaks 13-18. Peak 13 is the absorption from the A part of the weaker AMX that was obscured under peak 7 in Figure 12. Peaks 14 and 15 belong to the M part of the more intense AMX and 16-18 probably are the resonances from the M part of the weaker AMX. In Figure 14 the chemical-shift difference between A and M of the more intense AMX is approximately 62 Hz (0.28 ppm) as compared to 28 Hz (0.28 ppm) in the 100 MHz spectrum. (The sweep width in Figure 14 was not calibrated and hence $\delta_{AM} = 62$ Hz is only approximate.) Unfortunately the resolution in Figure 14 is too poor to show the splitting in peak 2.

If the arguments presented above are correct, then with increased exchange of alkyl groups (Exchange of alkyl groups will be more rapid at higher temperatures) lines 2 and 3 will collapse together and lines 4-18 will also collapse together. The collapsing together of two lines in an nmr spectrum indicates their interrelationship, i. e., lines 2 and 3 arise from the CH_2Mg protons in a neopentyl group and

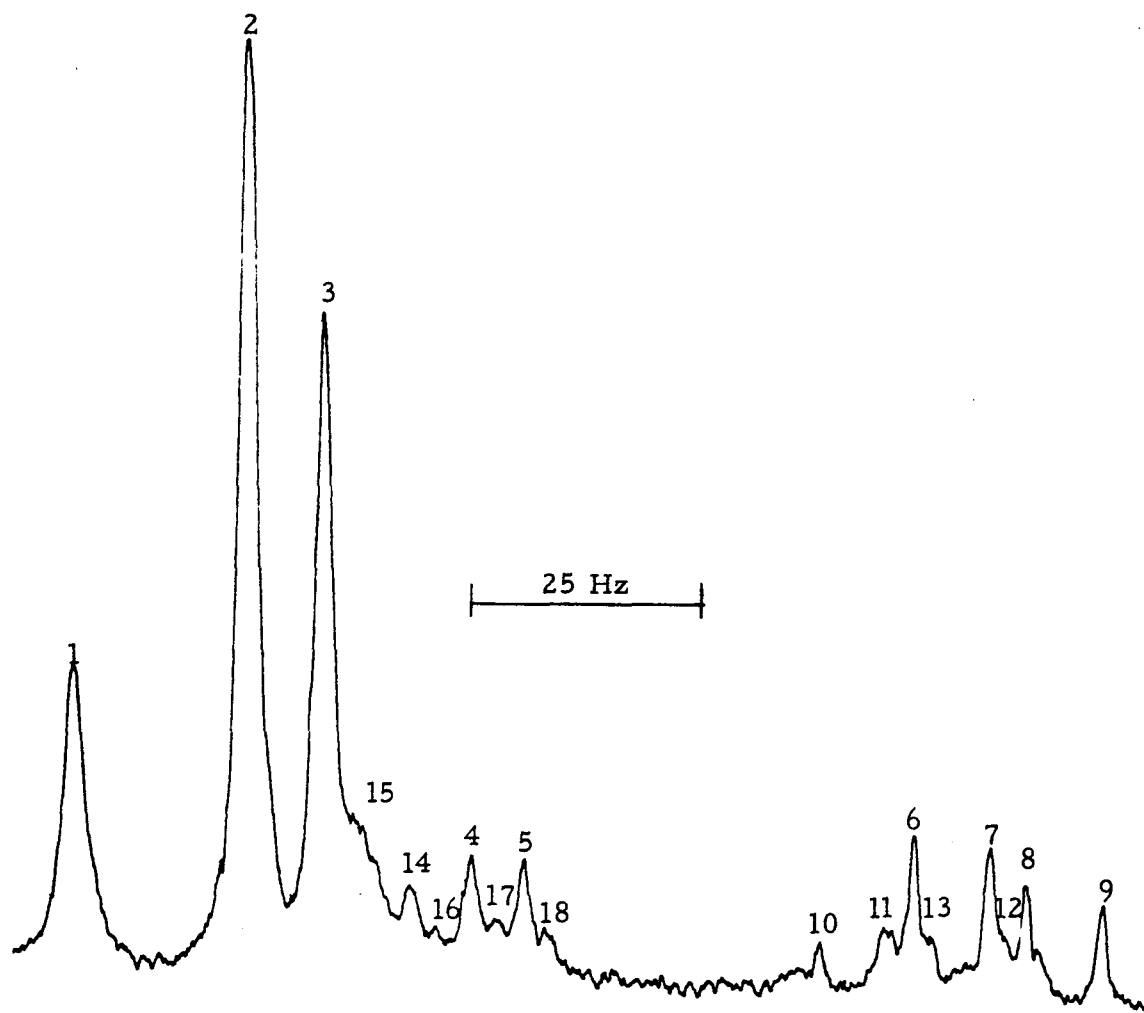


Figure 14. Spectrum (220 MHz) of a mixture of bis-(2-methylbutyl)-magnesium and dineopentylmagnesium in ether-N,N,N',N'-tetramethylethylenediamine (4:1 by mole %). Only the spectrum of the $\text{CH}_2\text{-Mg}$ protons is shown.

lines 4-18 arise from the CH_2Mg protons in a 2-methylbutyl radical. In Figure 15a is shown the nmr spectrum (60 MHz) of the above sample at 70° and figure 15b at 118° . The spectra in Figure 15 show that lines 2 and 3 do collapse together and that lines 4-18 also collapse together. Actually lines 10-18 are not visible in the 60 MHz spectrum and so all one can say is that lines 4-9 collapse together.

Figure 15 also indicates that line 1 collapses with 2 and 3. No completely satisfactory assignment for line 1 has been made as yet. It is possible, for example, that a dineopentylmagnesium-diamine complex is exchanging slowly with free dineopentylmagnesium. This would give rise to two lines for the CH_2Mg protons of the symmetrical dineopentylmagnesium. This assumption has its fault in the fact that there does not appear to be any absorption representing a slow exchange between complexed and free bis-(2-methylbutyl)-magnesium. Another possibility is that absorption 1 is due to the CH_2Mg protons of a neopentyl magnesium-alkoxide complex. Similar compounds have been reported by House et. al (34) in their study of methyl-magnesium derivatives. No absorption due to the OCH_2 protons of the alkoxide group was observed but it may be hidden under the ether resonances. A proven assignment of peak 1 will have to await further experimentation.

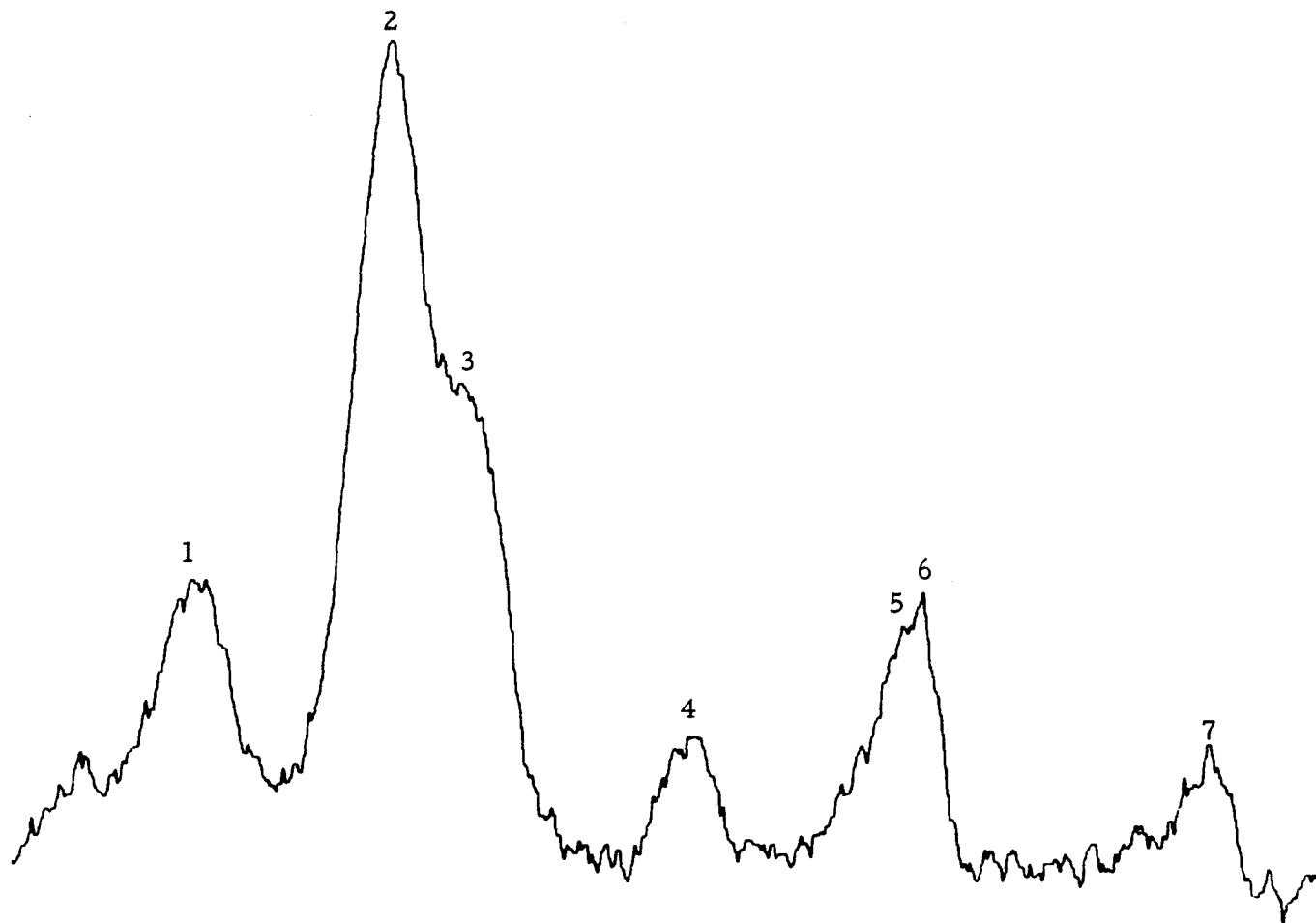


Figure 15a. Spectrum (60 MHz) of a mixture of bis-(2-methylbutyl)-magnesium and dineopentylmagnesium in ether- N,N,N',N' -tetramethylethylenediamine (4:1 by mole %) at +70°. Only the spectrum of the $\text{CH}_2\text{-Mg}$ protons is shown.

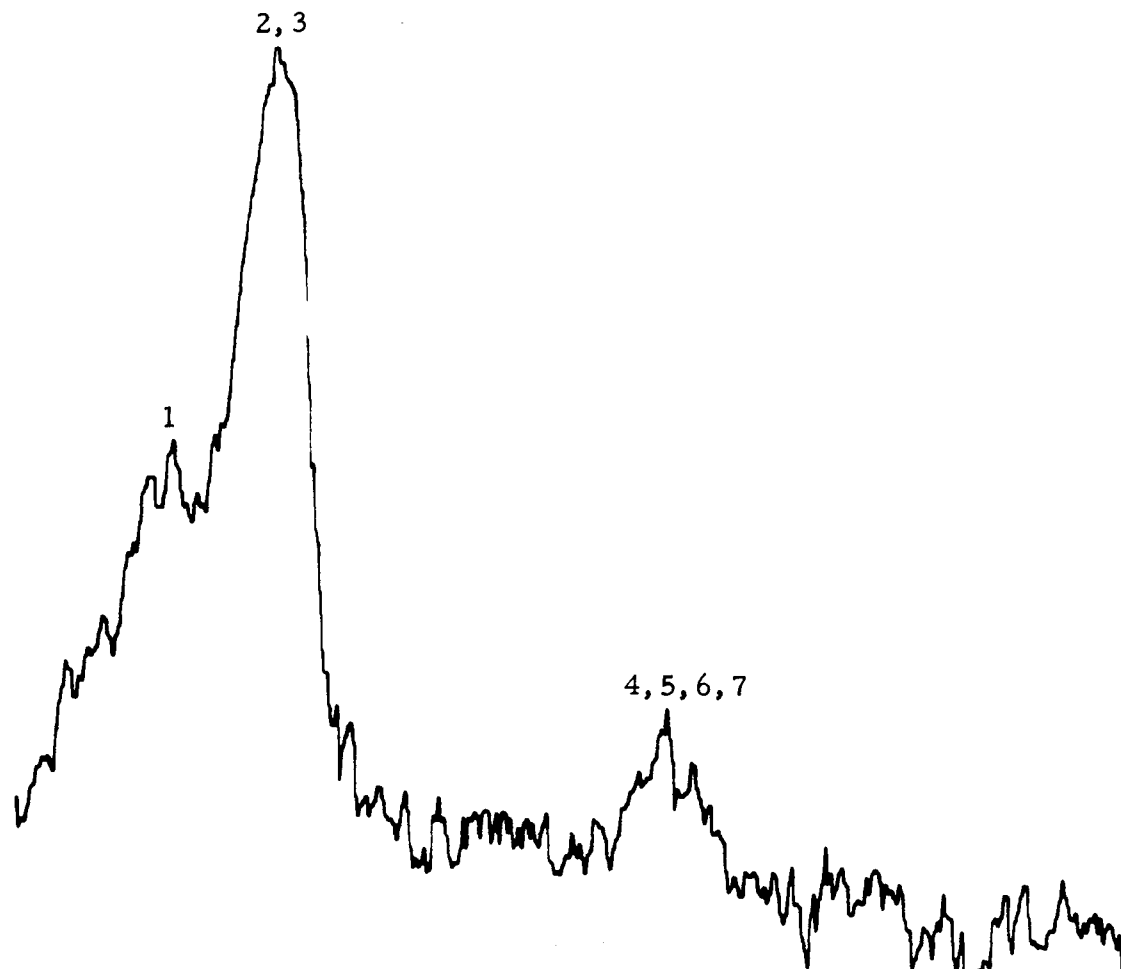


Figure 15b. Spectrum (60 MHz) of a mixture of bis-(2-methylbutyl)-magnesium and dineopentylmagnesium in ether- $\text{N}, \text{N}, -\text{N}', -\text{N}'$ -tetramethylethylenediamine (4:1 by mole %) at 118° . Only the spectrum of the $\text{CH}_2\text{-Mg}$ protons is shown.

CONCLUSIONS

A. Inversion in Organomagnesium Compounds

The result (32) that bis-(2-methylbutyl)-magnesium has a faster inversion rate in diethyl ether than in tetrahydrofuran is in agreement with a bimolecular inversion mechanism in which the electrophilicity of MgR_2 is important, because for such a mechanism the rate of inversion will be slower the more basic the ether. The more basic solvent should on the other hand promote ionization by stabilizing RMg^+ and the fact that the rate of inversion of bis-(3,3-dimethylbutyl)-magnesium is similar in diethyl ether and tetrahydrofuran may indicate that an ionization-recombination process as well as some other process, presumably bimolecular, are both at work with this compound.

When neopentylmagnesium bromide is formed in an ether solution containing 2-phenyl-3-methylbutylmagnesium chloride, the rate of inversion of the latter Grignard reagent is increased. This result supports the previous suggestion (30) that in the case of an alkyl-magnesium halide, the inversion mechanism is characterized by a molecularity higher than one.

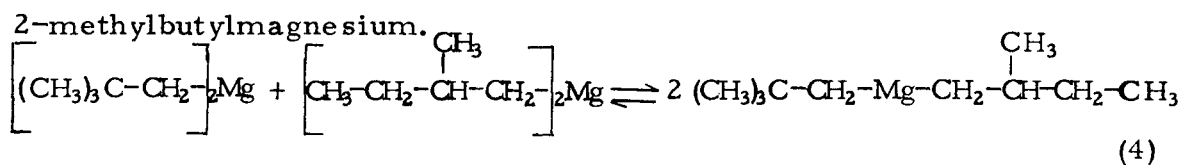
The rate of inversion at the CHMg center in 1-phenyl-2-propyl-magnesium bromide has been measured; the activation parameters were found to be $\Delta G^\ddagger = 18 \pm 2$ kcal/mole, $\Delta H^\ddagger = 10 \pm 2$ kcal/mole, and $\Delta S^\ddagger = -26 \pm 7$ eu. This is the first example of rapid inversion in a secondary Grignard reagent. Steric crowding in the transition state may preclude a bimolecular process for inversion in a secondary

Grignard reagent. If an ionization-recombination process is operative in 1-phenyl-2-propylmagnesium bromide, then a possible explanation for the unique rapid inversion in this Grignard is that the phenyl group stabilizes the charge-separated species in the transition state by bridging to the carbon bonded to the magnesium; the inductive effect of the benzyl group must also play a role in the stabilization. Future experiments on aromatically substituted secondary Grignard reagents should indicate the validity of this speculation.

B. Alkyl Group Exchange in Organomagnesium Compounds.

Mixtures in diethyl ether solutions of dineopentylmagnesium with bis-(s-butyl)-magnesium or bis-(2-methylbutyl)-magnesium, or bis-(4,4-dimethyl-2-pentyl)-magnesium showed no evidence in their nmr spectra at temperatures as low as -65° of an unsymmetrical dialkylmagnesium compound RMgR' . This is presumably due to a fast alkyl group exchange between the various organomagnesium species present.

House et al. (34) have recently reported that methyl group exchange in various methylmagnesium derivatives is retarded by N,N,N',N'-tetramethylethylenediamine. The addition of TMED to an ether solution of dineopentylmagnesium and bis-(2-methylbutyl)-magnesium sufficiently slowed the rate of alkyl group exchange, so that it was possible to observe a slow equilibrium in the nmr spectrum at 37° between the two symmetrical species and the unsymmetrical species, neopentyl-2-methylbutylmagnesium.

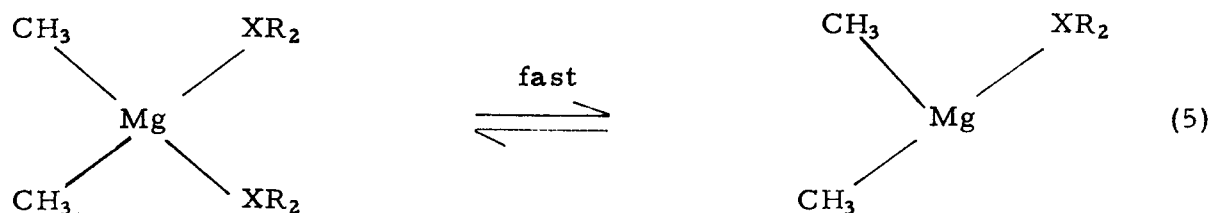


(4)

An A₂ and an AB pattern were observed in the nmr spectrum (100 Hz) for the CH₂Mg protons of the neopentyl moiety in dineopentylmagnesium and neopentyl-2-methylbutylmagnesium respectively. Two AMX patterns were observed for the CH₂Mg protons in the 2-methylbutyl group of bis-(2-methylbutyl)-magnesium and neopentyl-2-methylbutylmagnesium.

It is interesting to note that although methyl group exchange in methylphenylmagnesium (34) was rapid until -50°, exchange in the system reported here is slow at 37°. The neopentyl and 2-methylbutyl radicals are bulkier groups than either methyl or phenyl and consequently steric crowding in the transition state (cf. 34) will be more important in the exchange herein studied. This steric crowding will lead to a higher energy barrier and hence to a slower rate of exchange. The slow rate of exchange reported in this study may also reflect the greater stability of an unsymmetrical dialkylmagnesium compound containing similar R groups. In this connection it is perhaps significant that the exchange of cyclopentadienyl groups in a mixture of phenylcyclopentadienylmagnesium and dicyclopentadienylmagnesium is much slower than the exchange of methyl groups in a mixture of methylphenylmagnesium and dimethylmagnesium in the same solvent (34).

The retardation of the exchange rate observed in the presence of TMED may arise from a rapid equilibrium, prior to the metal-metal exchange step, involving dissociation of one or more solvent molecules from one of the organomagnesium compounds (34):



This rapid equilibrium is followed by a rate-limiting process involving the species on the right in equation 5.

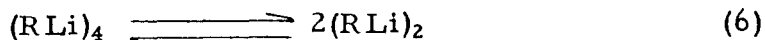
A very crude approximation of the equilibrium constant in equation 4 was obtained by cutting out the peaks in Figure 14 and weighing them. This led to $K = 23$. Hence the unsymmetrical compound appears to be more stable than the two symmetrical compounds.

Part II

REDISTRIBUTION EQUILIBRIA
IN
ORGANOCADMIUM COMPOUNDS

INTRODUCTION

Nuclear magnetic resonance spectroscopy has been very helpful in yielding information concerning exchange processes in organometallic compounds. Of course, exchange in organomagnesium compounds has been widely studied by nmr and continues to be investigated as witnessed by recent reports (34, 37, 47). Brown (44-46) has observed that alkyl exchange in organolithium compounds in ether is rapid and he has interpreted this exchange in terms of the process:



The temperature dependence of the proton nmr spectrum of $[Al(CH_3)_3]_2$ in cyclohexane has yielded information on three-centered bonding in organoaluminum compounds (48-49). Gallium trialkyls undergo rapid self-exchange of alkyl groups in solution (50-51). Exchanges of methyl, phenyl, and vinyl groups have been studied in organothallium compounds (52-53) by observing the collapse of the Tl-H spin-spin multiplets as the temperature was increased from -100° .

In 1962 McCoy and Allred reported proton nmr studies on mixtures of zinc, cadmium, mercury, and aluminum organometallic compounds (54). These authors reported that a mixture of dimethylcadmium and dimethylzinc in benzene gave a single, rather broad signal in the nmr spectrum. The chemical shift varied with the relative composition of the two organometallics. Moderately dilute,

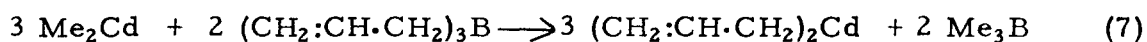
~ 0.1 M, solutions of dimethylzinc and dimethylcadmium exhibited two methyl absorption peaks in their nmr spectra, thus indicating that exchange can be slow in dilute solutions. The same authors also studied the intermolecular exchange of methyl groups in a mixture of trimethylaluminum and dimethylcadmium in benzene. McCoy and Allred carried out their nmr studies at a single temperature and hence they were able to assign only upper and lower limits to the rate of exchange.

Dessy and coworkers (55) investigated the exchange between dimethylmagnesium and dimethylcadmium or dimethylzinc, respectively. The average lifetime was found to be < 0.009 second in both cases.

The research in Part II of this thesis was carried out in an effort to obtain a more quantitative understanding of the rates of exchange of alkyl groups in dialkylcadmium compounds. Another aim of the present study was to provide physical evidence for the existence of alkylcadmium halides and study the equilibrium of such an organometallic with the dialkylcadmium compounds. An equilibrium between a dialkylcadmium compound and an alkylcadmium halide would be the cadmium analog of the Schlenk equilibrium for organomagnesium compounds discussed in Part I of this dissertation. Alkylcadmium halides have reportedly been prepared by Kocheshkov and coworkers, but no physical evidence for their existence has been provided (56).

Organocadmium compounds are usually prepared by the addition of an anhydrous cadmium halide to a Grignard reagent or to

an organolithium compound. An alternate general synthetic route might now be available as the result of the recent report of Thiele and coworkers (57) on the preparation of diallylcadmium from triallylboron.



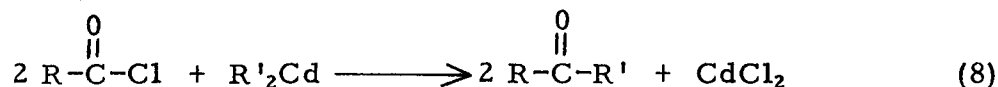
The dialkylcadmiums are liquids which may be distilled at reduced pressure. Thermal decomposition occurs above 150° and may become explosive in compounds other than dimethylcadmium.

There are very few reports in the literature on physicochemical studies of organocadmium compounds. The energy of dissociation of the C-Cd bond has been determined in dimethylcadmium (58-59) and diethylcadmium (60). Infrared spectra of dimethylcadmium (61) and diethylcadmium (62-63) and the Raman spectrum of the former (64) have also been measured. Studies on the electrical conductivity (65-66) and also on the photochemical (67), electrochemical, and thermochemical decomposition of dimethylcadmium have been published (68-70).

McCoy and Allred (54) determined the molecular weight of dimethylcadmium in benzene. These cryoscopic measurements in dilute benzene indicated a molecular weight of approximately 141 compared with the calculated value of 142.5 for the monomeric species. This measurement, of course, cannot rule out the existence of a very small amount of associated species.

The most important synthetic utility of organocadmium com-

pounds is in the preparation of ketones from acid chlorides:



Although the reaction of Grignard reagents with ketones is rapid, organocadmium compounds react with ketones sufficiently slowly to allow the isolation of the desired product ketone in Equation 8.

The reactivity of organocadmium compounds is greatly affected by the presence of magnesium (and other) halides (71). The relatively low reactivity of dialkylcadmiums compared with mixtures presumed to contain some kind of alkylcadmium halide species stands in marked contrast to the relative reactivities of R_2Mg and RMgX which do not differ to any significant degree (72).

Dimethylcadmium has been shown to form complexes with chelating diamines and diethers. However, a mixture of dimethylcadmium and dioxane (1:1 molar ratio) has been shown to be largely dissociated into its components, whereas the corresponding dimethylzinc-dioxane mixture was found to be only slightly dissociated (73).

After the present research began, Ham, Mole, and coworkers (74) reported a study of methyl group exchange in dimethylcadmium in toluene and pyridine. These workers reported that the exchange of methyl groups was catalyzed by the presence of oxygen. In Table V is shown the effect of methanol on the pre-exchange of dimethylcadmium. Activation energies of 16 and 13 kcal/mole were observed for the catalyzed exchange in toluene and pyridine respectively.

TABLE V

Effect of Methanol on the Pre-Exchange
Lifetime of Dimethylcadmium

$[\text{Me Cd}]$ moles/l.	$[\text{MeOH}]$ moles/l.	$\tau(\text{sec})$ (a)	Solvent
0.45	0.0	0.23 ± 0.07	Toluene
0.58	0.0049	0.014 ± 0.001	Toluene
0.56	0.010	0.011 ± 0.001	Toluene
0.48	0.020	0.0072 ± 0.0006	Toluene
0.57	0.0	0.030 ± 0.002	Pyridine
0.50	0.0065	0.0082 ± 0.0007	Pyridine
0.48	0.012	0.0025 ± 0.0002	Pyridine
0.50	0.030	0.0012 ± 0.0001	Pyridine

(a) The tau values in toluene solution are at 120° and in pyridine at 40°.

RESULTS AND DISCUSSION

A. Methyl Group Exchange in Neat Dimethylcadmium.

In Figure 16 is shown the nmr spectrum (60 MHz) of a neat sample of dimethylcadmium at -5° . The magnified peaks are the cadmium-proton satellites. The isotopes ^{111}Cd (natural abundance = 12.9%) and ^{113}Cd (12.3%) each have spin $\frac{1}{2}$ while the several other naturally abundant isotopes with even mass numbers have spin zero. Therefore the spectrum of dimethylcadmium in the slow-exchange limit shows five lines. The center line (line 5) arises from dimethylcadmium molecules having zero spin. The assignment of lines 1-4 to the appropriate Cd species is simplified by the fact that the magnetic moments of ^{111}Cd ($\mu = -0.5922$) and ^{113}Cd ($\mu = -0.6195$) are different and hence their respective couplings will not be equal. Because the distances between lines 1 and 2 and 3 and 4 are equal, the only possible assignment of lines in accord with the difference in magnetic moments is to assign lines 1 and 4 to $J_{^{113}\text{Cd}-\text{C}-\text{H}}$ and 2 and 3 to $J_{^{111}\text{Cd}-\text{C}-\text{H}}$. The magnitudes of the coupling constants are given in Table VI.

Figure 17 shows the nmr spectra, as a function of temperature, of a neat sample of dimethylcadmium. This sample was distilled and thoroughly degassed on a vacuum line before use. At 20° lines 1 and 2 collapse together as do lines 3 and 4. At 50° the satellites peaks

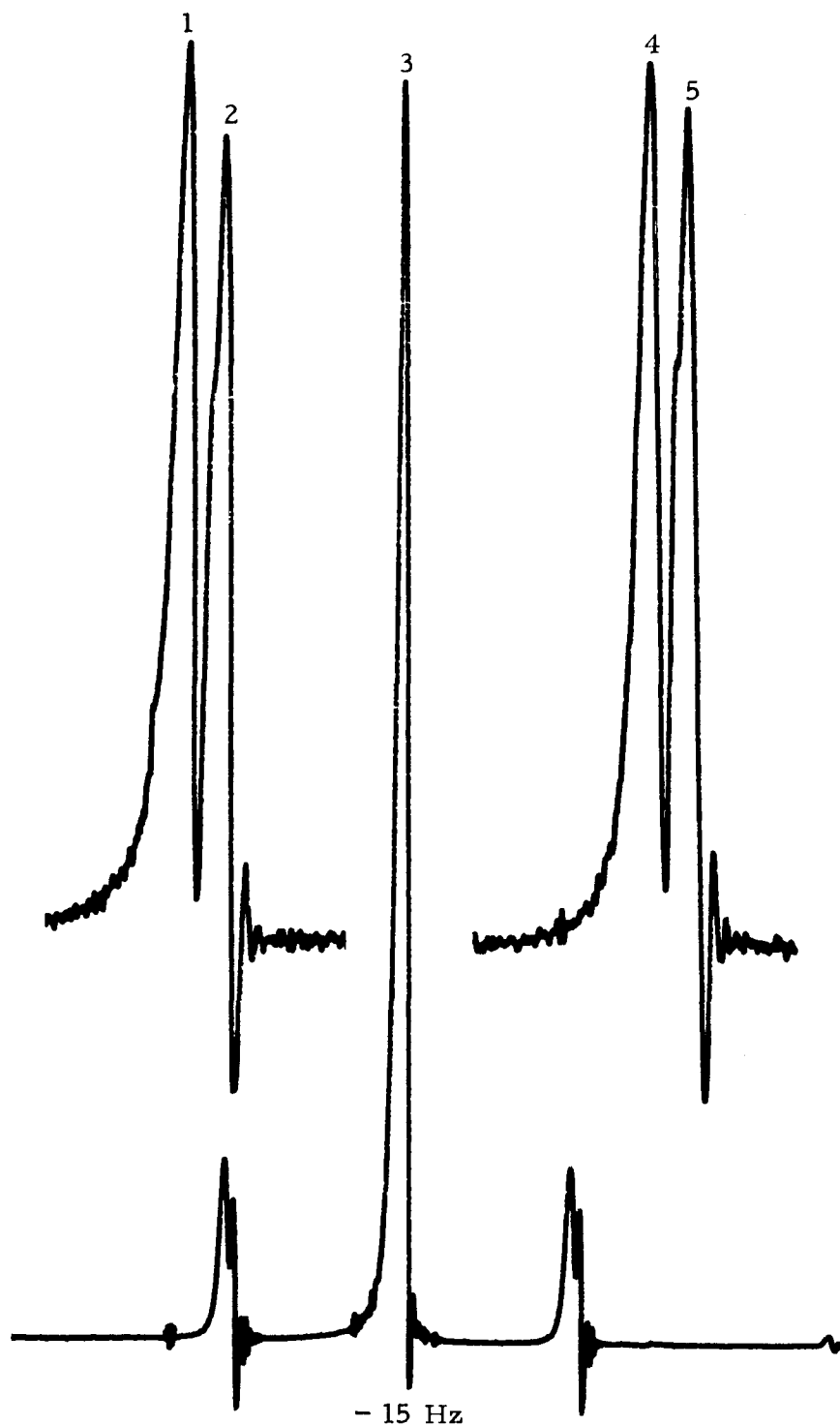


Figure 16. Nmr spectrum (60 MHz) of a neat sample of dimethylcadmium at -5° . The sweep width is 500 Hz. The inserts show a blowup of the cadmium-proton spin-spin satellites taken at a sweep width of 100 Hz.

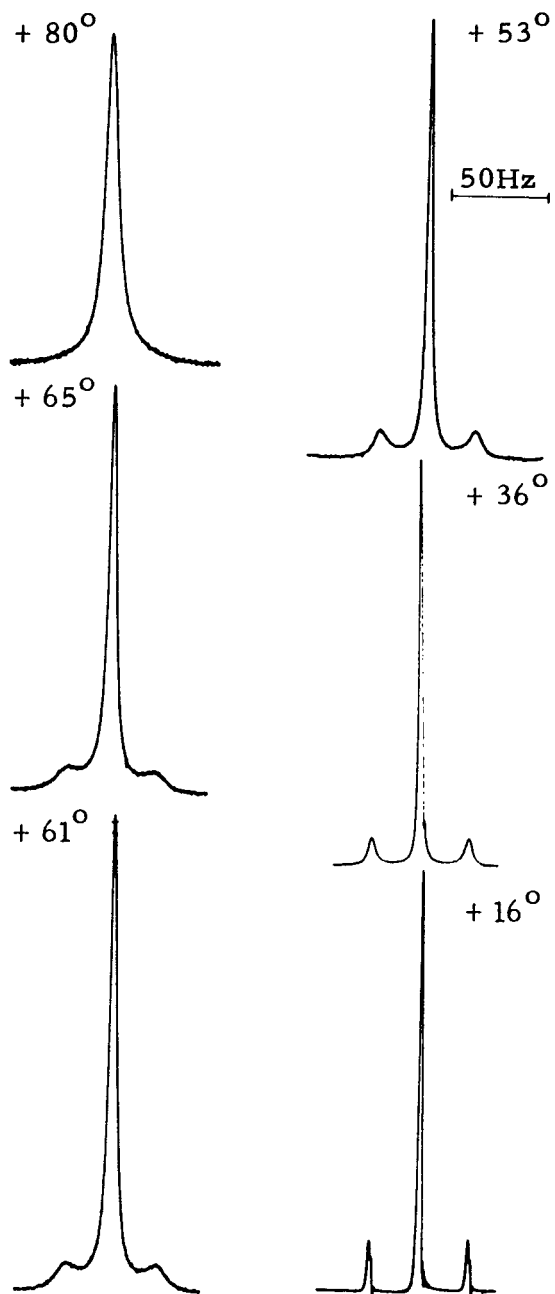


Figure 17. Nmr spectra (60 MHz) of a neat sample of dimethylcadmium as a function of temperature.

TABLE VINmr Parameters for Dimethylcadmium

	Chemical Shift in ppm	$J_{111}\text{Cd-CH}$ in Hz	$J_{113}\text{Cd-C-H}$ in Hz
Neat $(\text{CH}_3)_2\text{Cd}$	0.25	49.6	51.7
$(\text{CH}_3)_2\text{Cd}$ 10% by volume in tetrahydrofuran	0.50	50.2	52.6
$(\text{CH}_3)_2\text{Cd}$ 10% by volume in cyclohexane	0.33	50 ^a	50 ^a
$(\text{CH}_3)_2\text{Cd}$ 10% by volume in benzene	0.37	48 ^a	48 ^a

(a) This number is an average of $J_{111}\text{Cd-C-H}$ and $J_{113}\text{Cd-C-H}$.

begin to visibly merge into the center line. The disappearance of $J_{\text{Cd-C-H}}$ at the high-temperature limit requires that the exchange be intermolecular (75) in nature.

In Figure 18 are shown theoretical spectra as a function of τ for neat dimethylcadmium. Figure 19 shows an Arrhenius plot of $\ln \left(\frac{1}{\tau} \right)$ against $\frac{1}{T}$. The activation parameters for the exchange in neat dimethylcadmium are shown in Table VII. Tau (τ) is a measure of the pre-exchange lifetime of a carbon-cadmium bond. It is related to the first order rate constant (k_1) by $\tau = 2/k_1$. The factor of 2 is involved because there are two methyl groups, either one of which may exchange at any time.

The rate constants for exchange were obtained by computing line shapes as a function of rate constants taken at close intervals over an appropriate range, and matching the line shapes so obtained to the observed spectra. The method of computation described below is that originally formulated by Kubo (76) and Sack (77). The computations were carried out on an IBM 7094 digital computer using a program (78) the output of which is a trace of the spectrum drawn on a Calcomp plotter. To briefly summarize, $I(\omega)$, that is, the intensity I as a function of frequency ω is expressed as the product of three matrices shown in equation 9.

$$I(\omega) = (\text{Population}) \cdot \begin{pmatrix} \text{Exchange} \\ \text{Matrix} \end{pmatrix}^{-1} \cdot \begin{pmatrix} \text{Transition} \\ \text{Probabilities} \end{pmatrix} \quad (9)$$

Population is a row matrix the n components of which are proportional to the occupation probabilities of the n available sites. The exchange

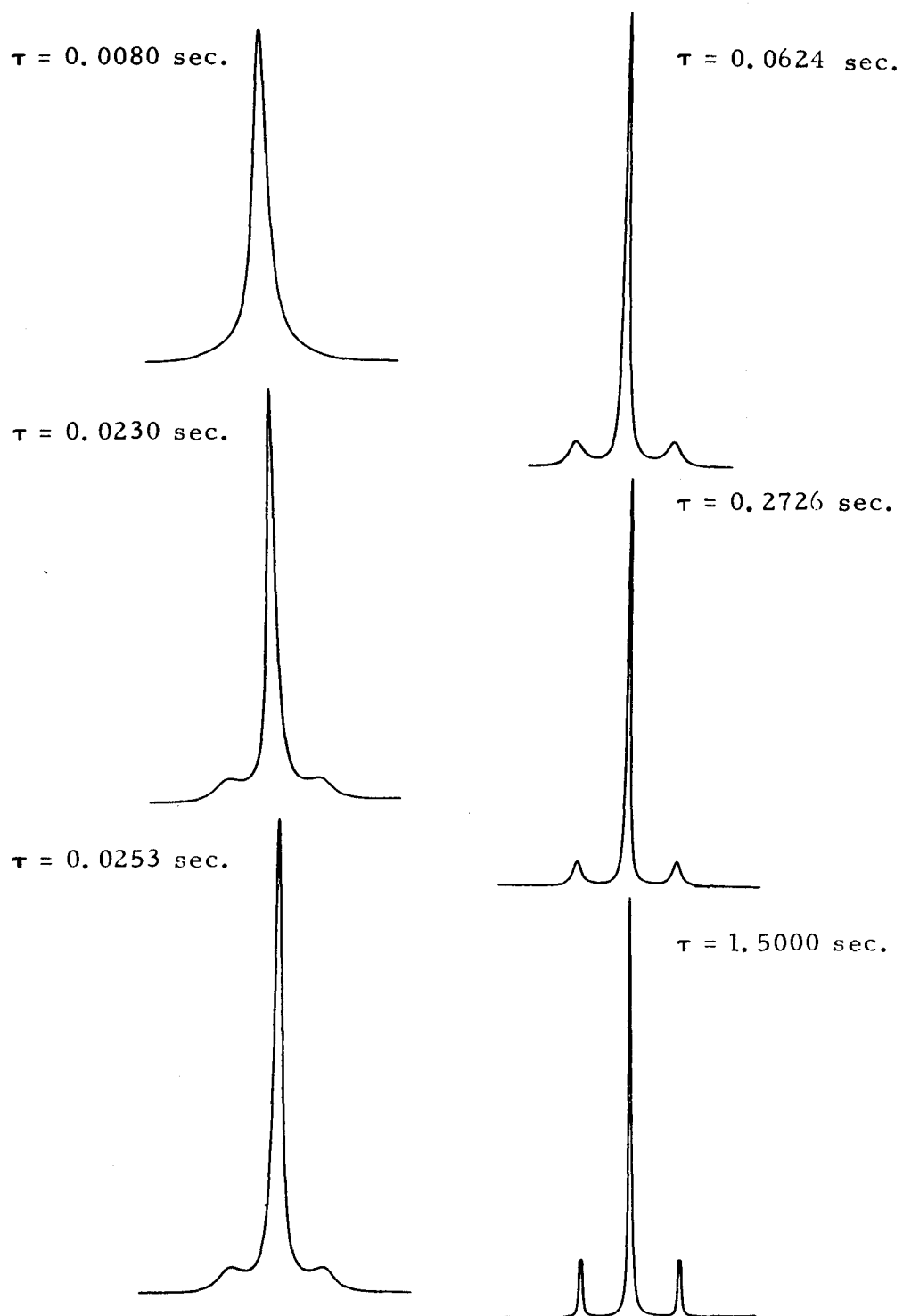


Figure 18. Calculated spectra for a neat sample of dimethylcadmium as a function of the pre-exchange lifetime τ .

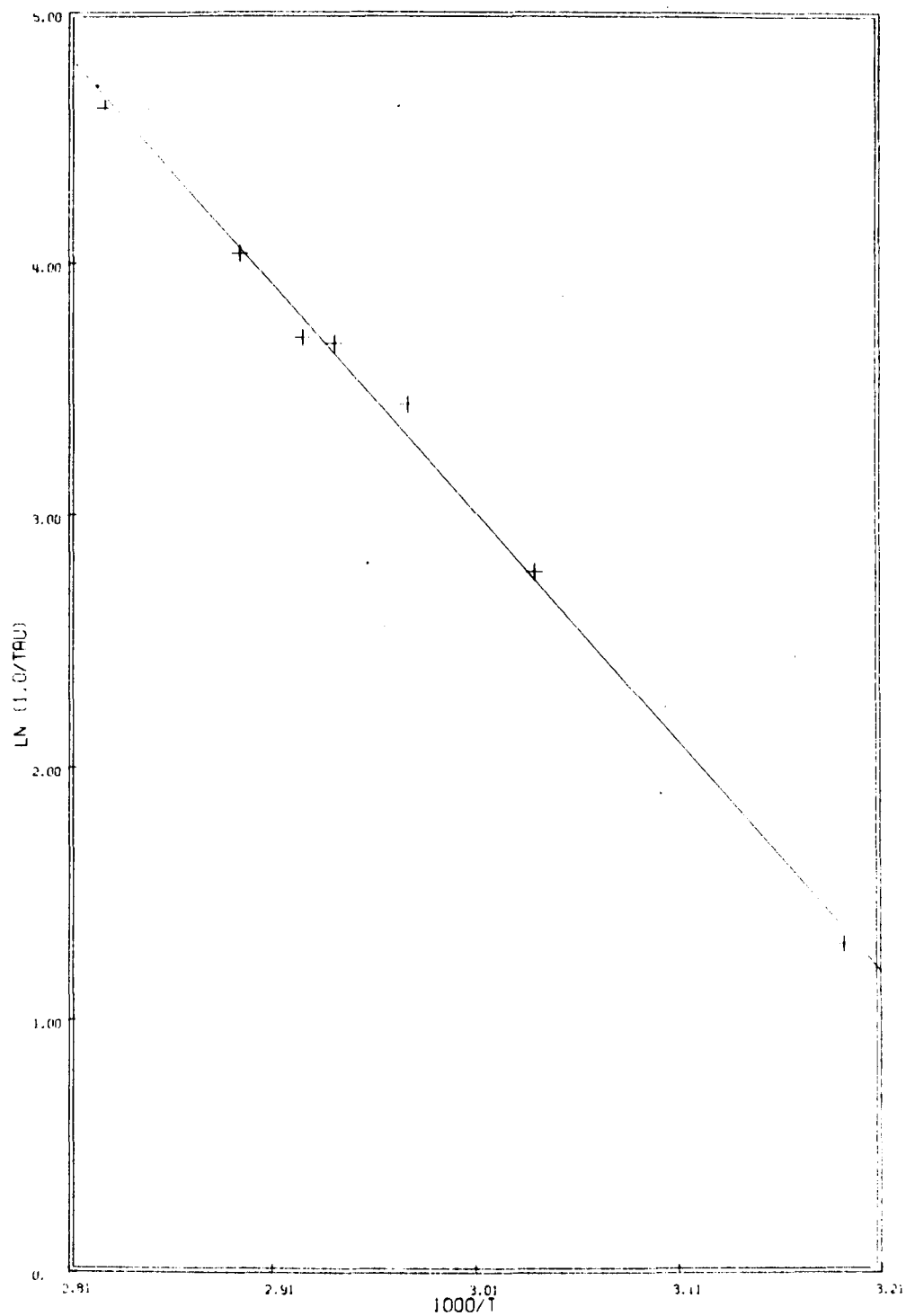


Figure 19. Plot of $\text{Ln } (l\tau)$ as a function of $1/T$ for a neat sample of dimethylcadmium.

matrix can be considered as composed of two other matrices. The first of these has diagonal elements describing the line frequencies and line widths comprising the spectrum in the absence of exchange, and off-diagonal elements equal to zero. The second matrix of these has been called a π matrix by Whitesides (78) and it describes the effect of the exchange on the spectrum. The elements of the π matrix are defined as

$$\left. \begin{aligned} \pi_{jk} &= p_{jk} \\ \pi_{jj} &= -\sum_k p_{jk} \end{aligned} \right\} j \neq k$$

where j and k are indices over the sites from 1 to n . p_{jk} is the probability that an exchange will take place from site j to site k . Each p_{jk} is multiplied by the rate constant which is expressed as $\frac{1}{\tau}$, τ having the definition given above. The transition probabilities matrix is a column matrix which in the case of intermolecular exchange (the case of interest here) is simply a unit column matrix.

Ham, et al. (74) have reported that for dimethylcadmium in toluene τ at 120° is 0.23. (It will be assumed for the moment that the rate of exchange in toluene is the same as a neat sample of dimethylcadmium; this assumption is approximately correct as will be shown at a later point in this thesis.) In contrast the tau values in Figure 18 show that here the exchange being observed is proceeding at a much faster rate. That is, for example, at 80° we already observe $\tau = 0.008$ sec. One possibility to explain this contradiction is that

advanced by the authors above (74) that oxygen acts as a catalyst in the exchange of methyl groups in dimethylcadmium, and that the present sample is oxygen contaminated. The mechanism of oxygen catalysis is thought to be such that oxygen reacts with dimethylcadmium to give methyl(methylperoxy)cadmium and finally methylcadmium methoxide (79). This metal alkoxide is thought (74) to be the reactive species in the catalysis of methyl group exchange in dimethylcadmium by oxygen. However, the exact mechanism of the catalysis is not known.

In the study presented in this thesis, attempts have been made to assure the absence of methylcadmium methoxide by careful bulb-to-bulb vacuum distillation of dimethylcadmium. The donor character of oxygen in alkoxides is greater than that of oxygen in ether and hence it is quite understandable that methylcadmium methoxide has been found to exist as a tetramer (80). This tetrameric nature probably indicates that the species has a very high boiling point, and thus should not distill over with the dimethylcadmium. (Methylzinc methoxide does not melt until 190°!!) Ham, et al. (74) report that their solutions were prepared by vacuum-line techniques, but these workers do not elaborate on the experimental details and hence it is difficult to tell if any special very high vacuums (10^{-3} mm) were needed to observe the lower rates of exchange. The pressures used in the present study were on the order of 0.02 mm.

Thus it is concluded that the disagreement between the tau values presented in Figure 18 and those of Ham, et al. is puzzling. No

completely satisfactory explanation for this disagreement has been found. Such an explanation will probably have to await a full report from the laboratories of Ham and Mole on their experimental techniques and method of calculation of the methyl group exchange rate in dimethylcadmium. The present author's work on the effect of added methanol on the exchange rate in dimethylcadmium will be discussed at a later point in this dissertation.

B. Methyl Group Exchange in Hydrocarbon Solutions of Dimethylcadmium.

Attention will now be turned to the study of methyl group exchange in dimethylcadmium in hydrocarbon solvents such as cyclohexane and benzene. These solvents, especially cyclohexane, should be relatively inert toward dimethylcadmium and thus should not produce any noticeable effects on the exchange rate. Figure 20 displays the nmr spectra of 10 and 50% (by volume) solutions of dimethylcadmium in cyclohexane at an ambient probe temperature of 37°.

There are two important points to be made about these spectra:

- 1) A comparison of the two indicates that their respective rates of exchange are essentially identical.
- 2) A comparison of the spectra in Figure 20 with the spectrum in Figure 17, which is the spectrum of neat dimethylcadmium observed at 36°, shows that the exchange rate is only slightly increased in cyclohexane.

The fact that solutions of 10 and 50% dimethylcadmium in cyclohexane show identical spectra demonstrates that the exchange is

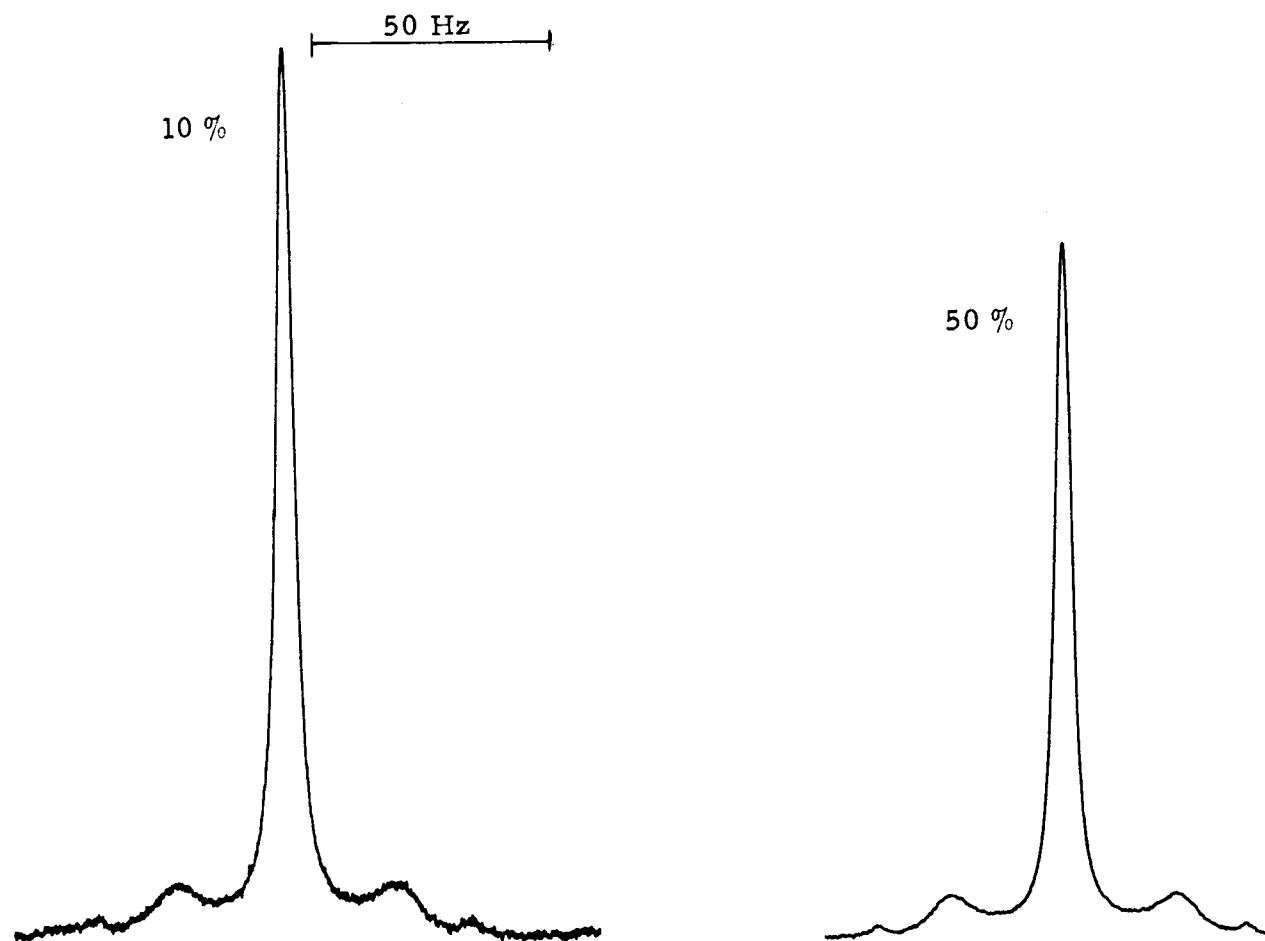


Figure 20. Spectra (60 MHz) of 10 and 50% solutions of dimethylcadmium in cyclohexane.

TABLE VII

Activation Parameters for the Exchange
of Methyl Groups in Dimethylcadmium

	$\Delta E_a,$ kcal/mole	$\Delta S,^\ddagger$ e. u.	$\frac{2}{T}$ at 25°
Neat $(CH_3)_2Cd$	16.3 ± 0.5	-5.0 ± 1.6	2.2
$(CH_3)_2Cd$, 10% by volume in tetrahydrofuran	6.8 ± 0.1	-28.3 ± 0.4	250

concentration independent in this solvent. A 50% solution of dimethylcadmium in benzene gave essentially the same spectrum as the 10 and 50% solutions in cyclohexane. The absorption of the center line of dimethylcadmium in benzene occurs at -22 Hz, whereas the same line in cyclohexane falls at -20 Hz. The combination of the two facts that the exchange rate and the chemical shift of dimethylcadmium is essentially the same in benzene and cyclohexane indicates that these two solvents probably interact in a similar manner with the organometallic. That is, it does not appear that the π -cloud of the benzene ring coordinates in any significant way with dimethylcadmium. If the π -cloud of benzene did interact with the cadmium compound, then the properties of the organometallic should differ in benzene and cyclohexane.

In order to determine if a monomer-dimer type equilibrium was responsible for the methyl exchange in dimethylcadmium, the molecular weight of the organocadmium compound was determined in benzene. Cryoscopic measurements in dilute benzene showed a molecular weight of approximately 140 compared with the actual value of 142.5 for the monomeric species. Of course, the existence of a small amount of dimer cannot be entirely discounted and it should be recognized that, in principle, a small amount of dimer in rapid equilibrium with the monomer could account for the methyl group exchange. However, the presence of such a monomer-dimer equilibrium would be much less probable in donor solvents.

C. Exchange of Methyl Groups of Dimethylcadmium in Donor Solvents.

It then seemed appropriate to study solutions of dimethylcadmium in more highly basic solvents. Tetrahydrofuran was the solvent of choice because its resonance signals are conveniently separated from those of dimethylcadmium and because it offered a greater temperature range over which spectra could be taken. In Figure 21 are shown the nmr spectra of 10, 30, and 50% solutions of dimethylcadmium in tetrahydrofuran. These spectra show a decreasing rate of exchange with increasing dimethylcadmium concentration. The question of the linearity of the decrease in exchange with increasing organometallic concentration was not investigated. The effect of increasing the dimethylcadmium concentration above 50% also has not been studied. The resonance due to the center line in dimethylcadmium appeared at $\delta = -33$, -25 , and -23 Hz in 10, 30, and 50% tetrahydrofuran solutions respectively. It is interesting to note that it is the peak in the 10% solution that is the farthest upfield and that this solution also shows the fastest exchange rate. An explanation in agreement with the above results is that tetrahydrofuran effectively coordinates with the organocadmium compound, thereby stabilizing the charge polarization which is present in the organometallic.

A study was undertaken to determine the activation parameters for the methyl group exchange of dimethylcadmium in tetrahydrofuran. It should be recognized that the mechanism of the exchange may be different in this donor solvent than in the neat sample. Figure 22 displays the nmr spectra (60 MHz) of a 10% (by volume) solution of

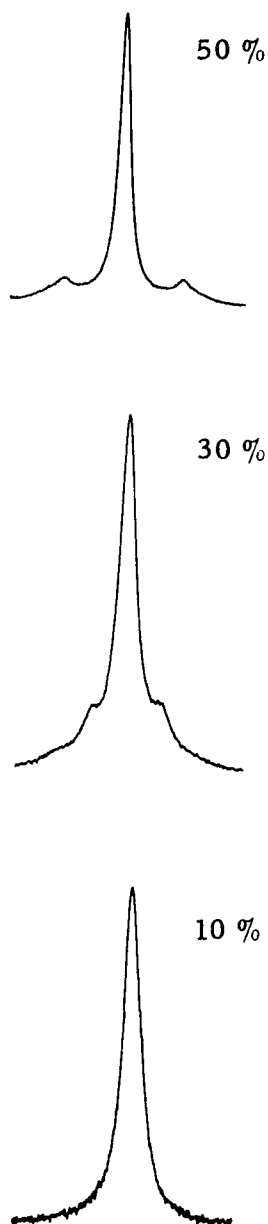


Figure 21. Spectra (60 MHz) of 10, 30, and 50% solutions of dimethylcadmium in tetrahydrofuran.

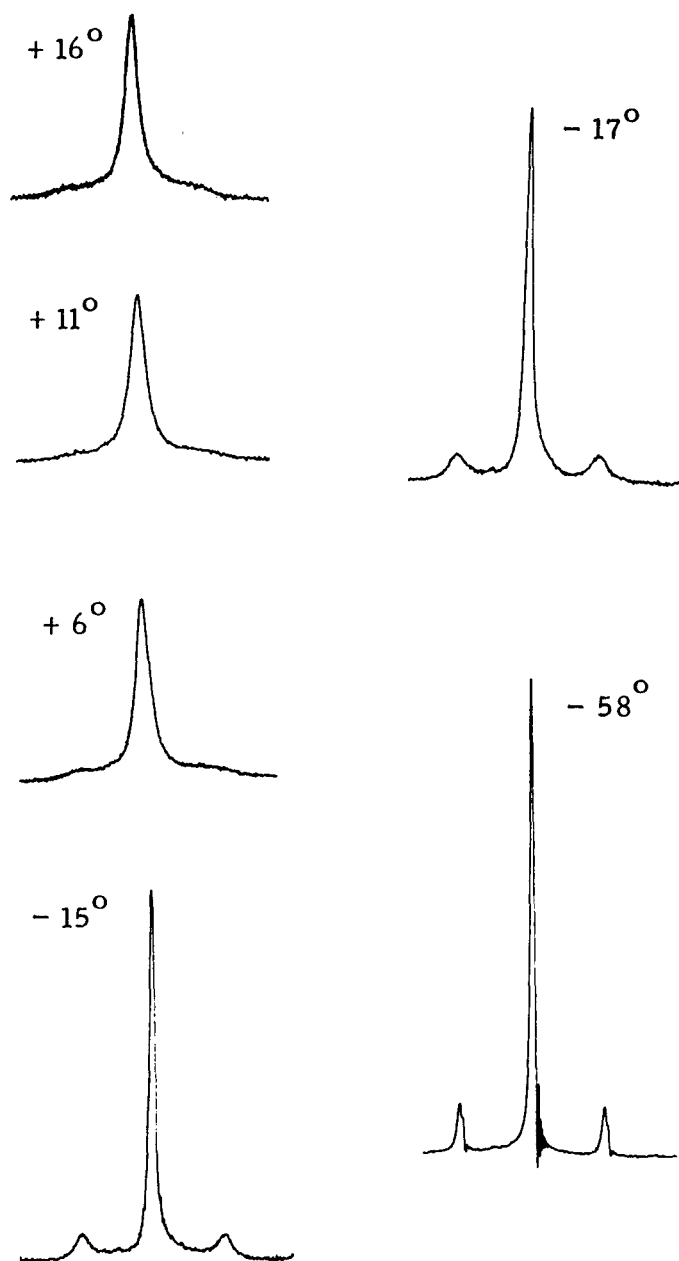


Figure 22. Spectra of dimethylcadmium in tetrahydrofuran solution (10% by volume) as a function of temperature. Spectra were taken on a 500 Hz sweep width.

dimethylcadmium in tetrahydrofuran. The spectra were taken over a temperature range from -58° to $+16^{\circ}$. One immediately observes that the exchange is much faster here than in either the neat sample or the cyclohexane and benzene solutions. A comparison of Figure 17 and 22 shows that the line shape realized in the neat sample at 53° is not obtained in the tetrahydrofuran sample until approximately -17° . In Figure 23 are shown theoretical nmr spectra which relate to the spectra in Figure 22. These spectra were computed as a function of tau and were obtained using the program described earlier. Figure 24 shows an Arrhenius plot of the tau values obtained from Figure 23 and the temperatures observed in Figure 22. The activation parameters for the exchange of the organocadmium compound in tetrahydrofuran are given in Table VII.

Table VII shows that the rate of exchange of methyl groups in dimethylcadmium is greatly increased in tetrahydrofuran. Perhaps even more important is the large decrease in entropy in going from the neat sample to the tetrahydrofuran sample. This large negative entropy in tetrahydrofuran could result from an orientation of the solvent molecules which arises to stabilize the large charge separation in the transition state of the exchange. This leads to the suspicion that an ionization-recombination process might be the mechanism of exchange. However, a cyclic transition state, similar to the four-centered transition state proposed to account for electrophilic substitution reactions of organomercury compounds, would also lead to a large negative entropy. But if a cyclic four-centered species is

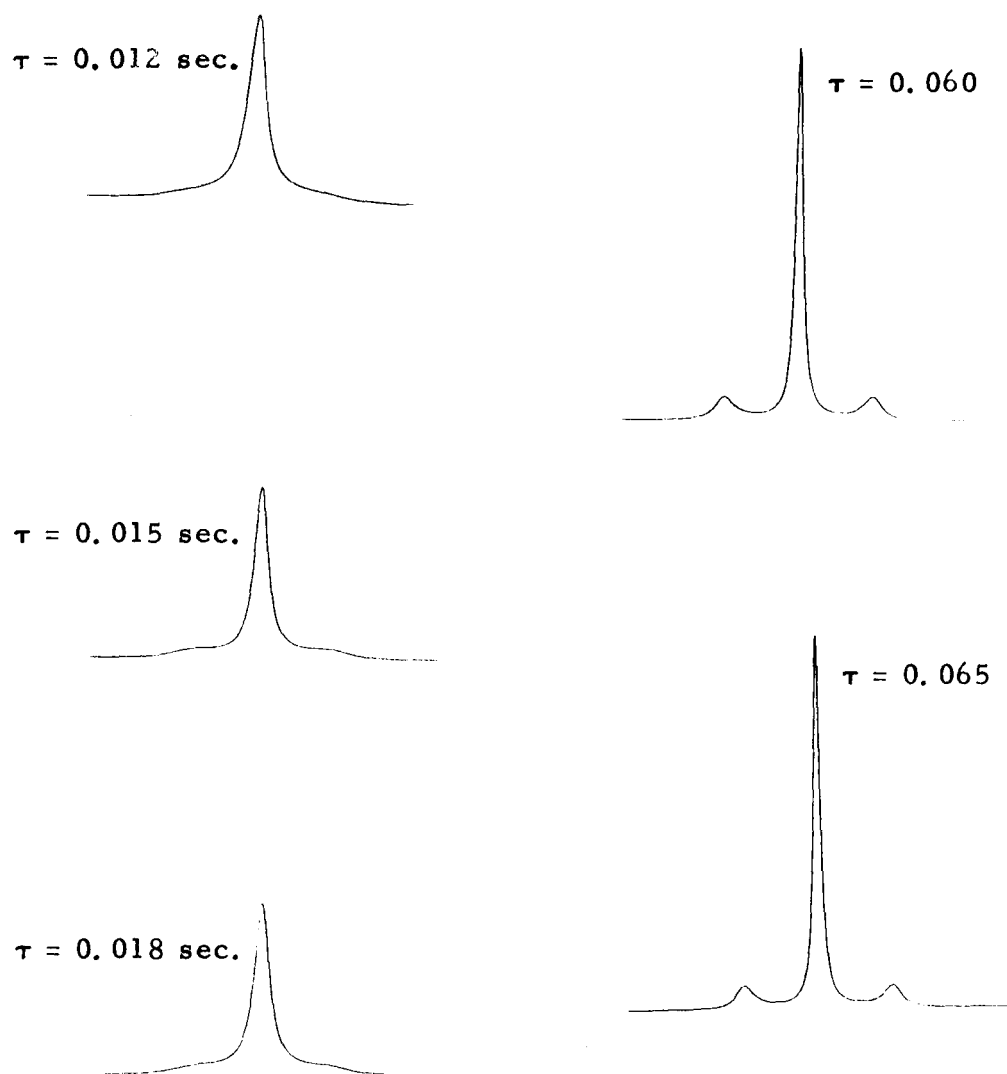


Figure 23. Calculated spectra for a sample of dimethylcadmium in tetrahydrofuran (10% by volume) as a function of the pre-exchange lifetime τ .

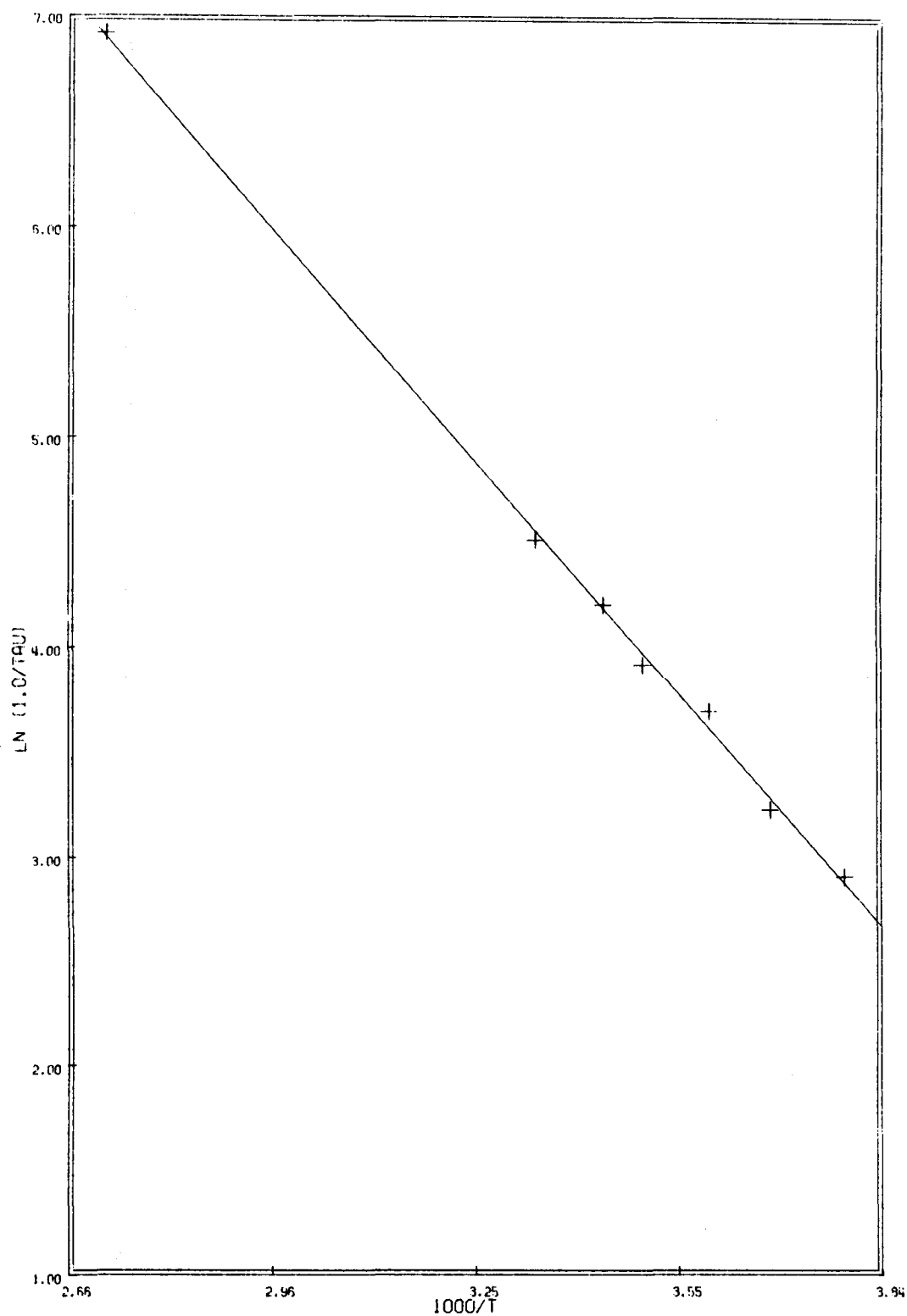


Figure 24. Plot of $\ln(1/\tau)$ as a function of $1/T$ for a solution of dimethylcadmium in tetrahydrofuran (10% by volume).

an intermediate in the exchange, then it should be possible at low temperature to observe an absorption for a bridging methyl group similar to the bridging observed in trimethylaluminum (81). No evidence for a bridging methyl group was found in the nmr spectrum of dimethylcadmium at the lowest temperature investigated (-70°). Further studies, such as the dependence of the exchange rate on the concentration of the organometallic (that is, over a range of dilute tetrahydrofuran solutions of dimethylcadmium), are needed to elucidate the exchange mechanism.

In order to determine the concentration dependence of the exchange rate in tetrahydrofuran, nmr spectra of 10, 5, and 3.3% solutions of dimethylcadmium in tetrahydrofuran have been obtained. These spectra were taken at a fixed temperature (39°) near the coalescence point where the line shapes are expected to be very sensitive to τ . Figure 25 shows these spectra. The important result from Figure 25 is that the exchange rate in tetrahydrofuran is independent of the concentration of the organocadmium compound. It should be recognized that this discussion is restricted to dilute solutions in which tetrahydrofuran can completely solvate the organometallic without any significant change in solvent concentration. Very concentrated 30 and 50% solutions of dimethylcadmium in tetrahydrofuran do not meet this criterion and hence are not discussed here. The fact that the exchange is concentration independent implies that this is a first-order reaction and any attempt at devising a mechanism for the exchange process must account for this fact.

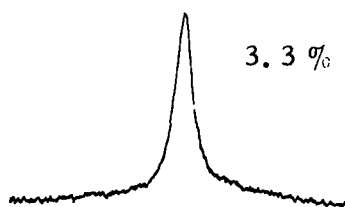
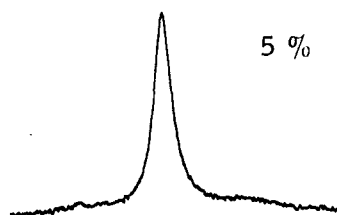
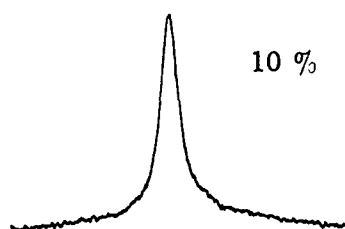
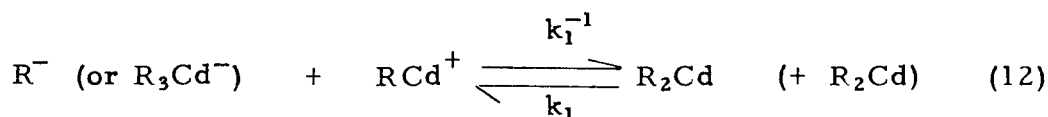
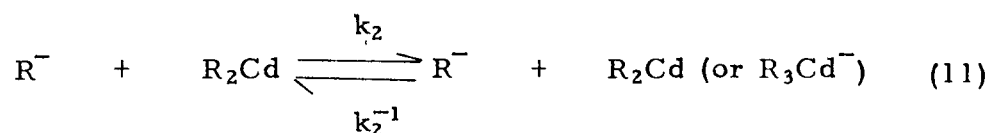
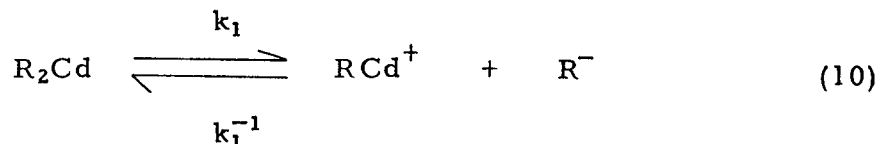


Figure 25. Spectra (60 MHz) of 10, 5, and 3.3% solutions (by volume) of dimethylcadmium in tetrahydrofuran.

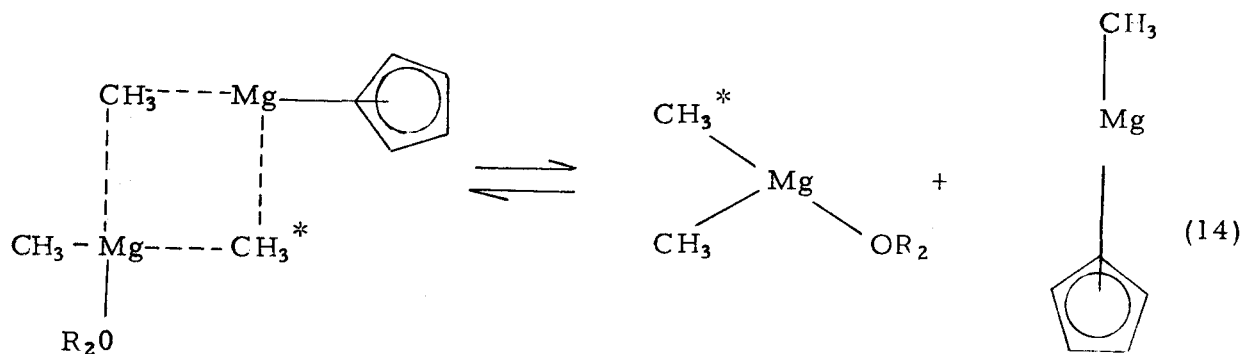
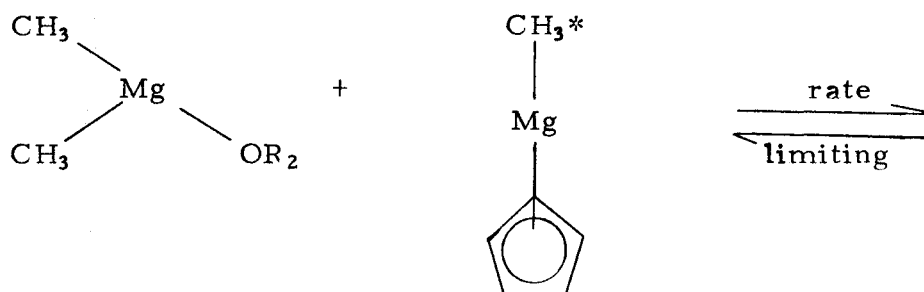
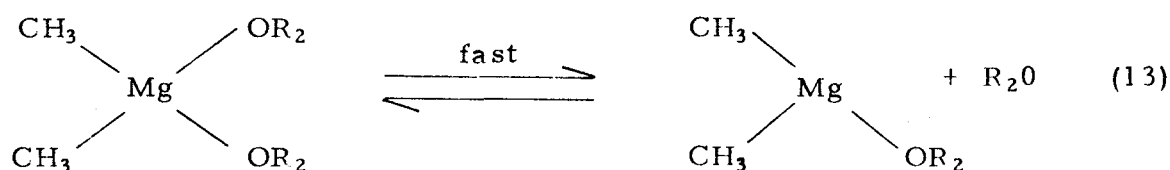
In tetrahydrofuran the simplest mechanism which accords with the data, presented to this point, appears to be an ionization-recombination process:



It should be understood that all species shown are solvated. Here step 1 is taken to be slow and rate determining with $k_1 \ll k_1^{-1}$. The activation energy for step 1 is expected to be greatly solvent dependent and this is observed. The entropy change in going to the transition state for methyl exchange in tetrahydrofuran is reasonable for an ionization process in a relatively non-polar solvent. It is possible that exchange in the neat liquid and in hydrocarbon solvents also involves an ionization-recombination mechanism, but no real evidence for this has as yet been adduced.

It appears to be a general result that alkyl group exchange in organomagnesium solutions is retarded by the presence of N,N,N',N',-tetramethylethylenediamine (TMED) (34, 37, 82). In order to explain the rate depression observed upon adding the

chelating ligand TMED, House, et al. (34) have proposed an equilibrium (equation 13), prior to the rate limiting step for methyl exchange (equation 14), involving dissociation of one or more solvent molecules from the organomagnesium compound.



However, in the case of dimethylcadmium if the mechanism proposed above (equations 10-12) is correct, then one would expect that the rate of methyl exchange should be increased with the addition of TMED to a solution of this organocadmium compound in tetrahydrofuran. The reason for this is the same as that given for the increase in exchange rate upon going from a neat sample of dimethylcadmium to a solution of the organometallic in tetrahydrofuran. The pK_b of tetrahydrofuran is 16.1 whereas the pK_b of TMED is 9.0 (83).

Figure 26 displays the nmr spectra of a tetrahydrofuran solution of dimethylcadmium (2 Molar) and TMED (5 Molar). The spectra in Figure 26 are to be compared with those in Figure 22, which depict a tetrahydrofuran solution of dimethylcadmium with no diamine added. This comparison shows that the rate of exchange is slower in the solution containing the diamine. A spectrum at -17° of the sample without TMED added (Fig. 22) has approximately the same exchange rate as a solution of dimethylcadmium plus TMED in tetrahydrofuran at 11° (Fig. 26). This observation is in serious disagreement with a simple ionization recombination process (equations 10-12) for the exchange. The exchange rate was still independent of the concentration of the organometallic in the tetrahydrofuran solution containing TMED. Unfortunately the exchange rate was not measured as a function of diamine concentration.

D. Stereochemistry of the Exchange Process.

To obtain information about the stereochemistry of the exchange the nmr spectra of bis-(3,3-dimethylbutyl)-cadmium and bis-(2-methyl-

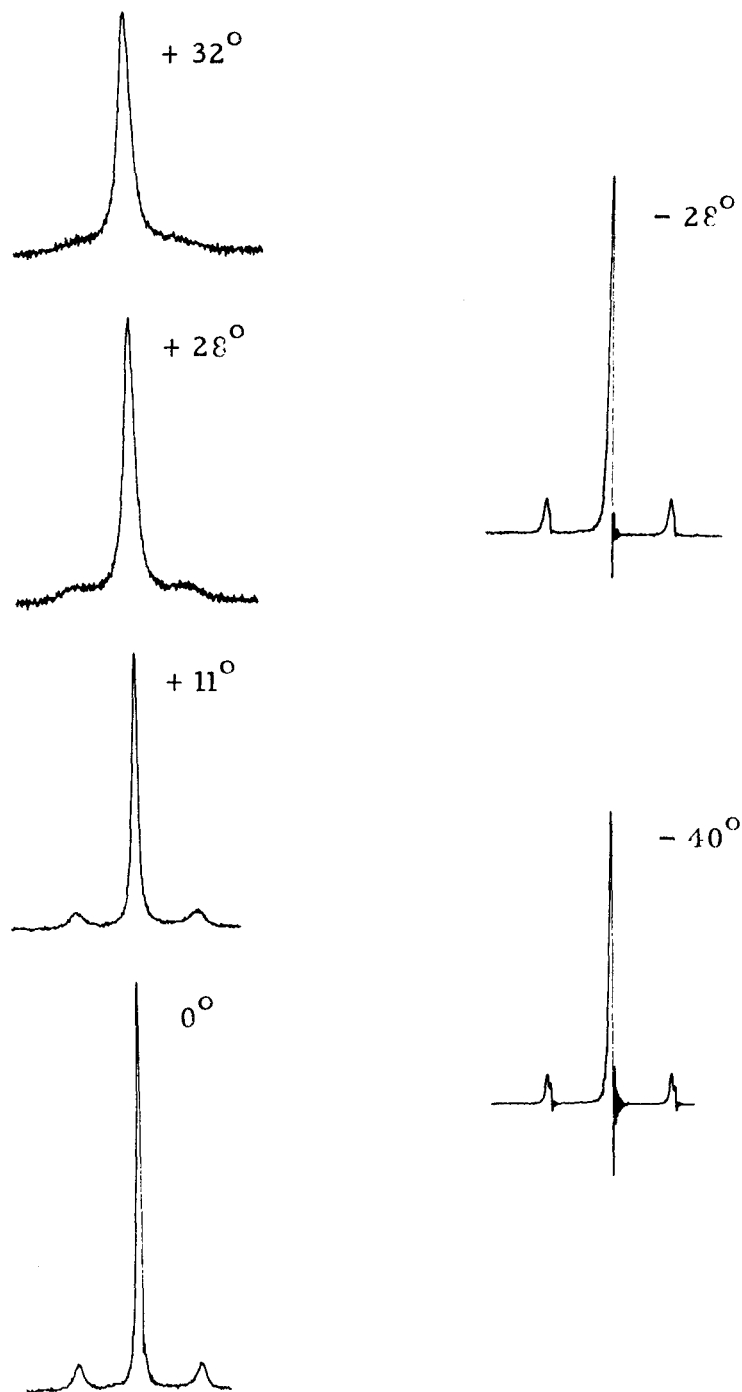


Figure 26. Spectra (60 MHz) of a solution of dimethylcadmium in tetrahydrofuran containing N,N,N',N'-tetramethylethylenediamine (THF-TMED, 4:1 by mole %) as a function of temperature. Sweep width is 500 Hz.

butyl)-cadmium in ether have been examined. In ether solution both compounds undergo a relatively slow inversion of configuration at the carbon atom adjacent to cadmium. This is in agreement with the results of Roberts and Witanowski (84) for other neohexyl derivatives of Group II metals. The question then is whether the rate of exchange of dimethylbutyl- groups from one cadmium atom to another is faster than the rate of configurational inversion or whether the two rates are equal.

Figure 27 shows the nmr spectrum (at 37°) of bis-(2-methylbutyl)-cadmium. Although inversion is slow as evidenced by the complex spectrum for the CH_2Cd protons, there is no evidence of the cadmium satellites, which indicates that the exchange rate is fast. Spectra were obtained at temperatures as high as 80°, but even at this temperature no simplification of the spectrum for the CH_2Cd protons was observed indicating that inversion is still slow at 80°. Hence it appears that the exchange process proceeds with retention. This finding is similar to that of House, et al. (34) for organomagnesium compounds. So once again we have arrived at a conclusion that is in agreement with an exchange mechanism proceeding through a four-center transition state but that is not in accord with the mechanism presented in equations 10-12.

A mechanism analogous to that of House, et al. (34) can account for all the present results except for the fact that the exchange appears to obey first-order kinetics. Incorporating the fact

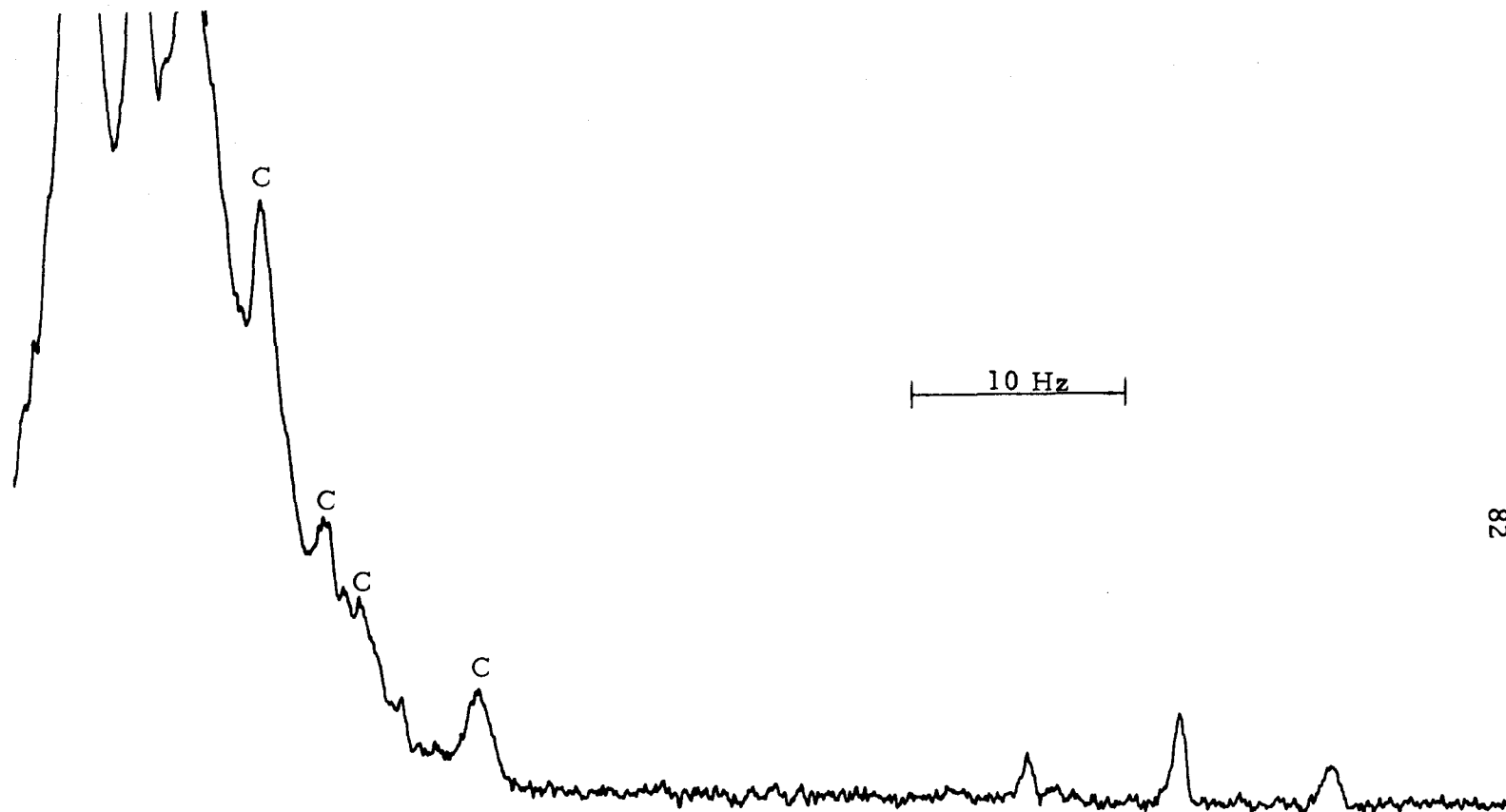
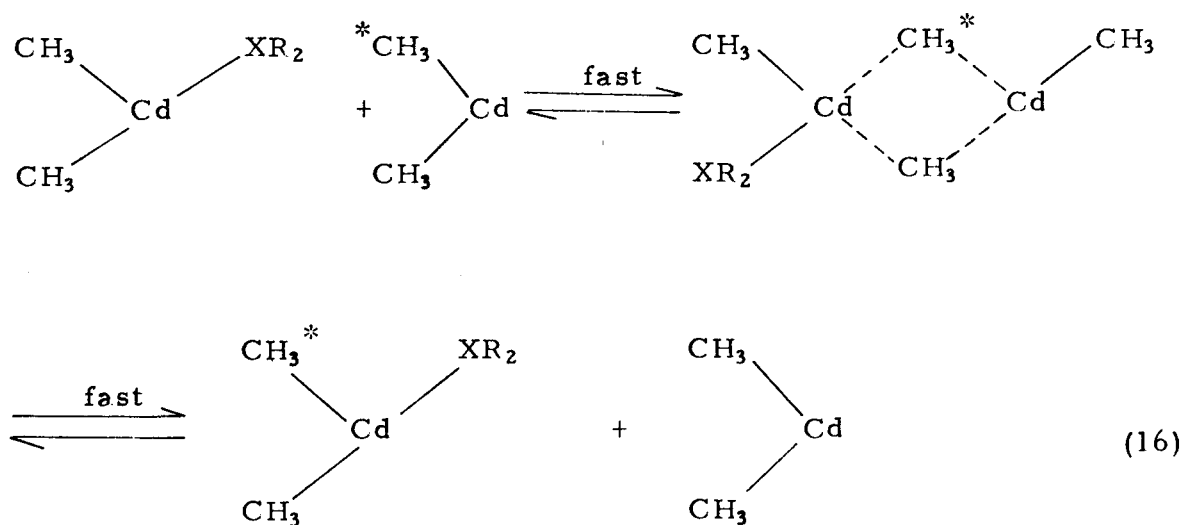
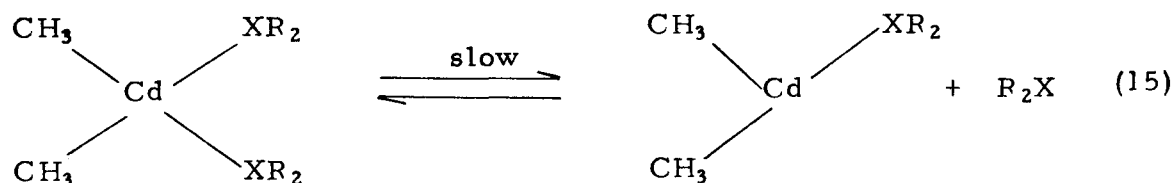


Figure 27. Spectrum (60 MHz) of bis-(2-methylbutyl)-cadmium in diethyl ether. The peaks labelled C belong to the $\text{CH}_2\text{-Cd}$ protons and comprise the AB part of an ABX system. The off-scale peaks belong to the methyl protons of the organocadmium compound. The three small peaks on the right belong to the ^{13}C satellites of ether. The cadmium-proton satellites are not visible in this spectrum at the gain shown and with the gain increased by a factor of ten.

of first-order kinetics into a mechanism similar to that of House leads to the proposal of the following mechanism:



XR_2 = Solvent Molecule

This mechanism accounts for the observed first-order kinetics and retention of stereochemistry. The rate-determining step becomes slower in a solution of the organometallic in tetrahydrofuran containing TMED as compared to a solution of dimethylcadmium in tetrahydrofuran alone, because XR_2 may now be the better coordinating

ligand TMED.

Seitz (85) has recently reported that methyl group exchange for dimethylcadmium is faster in diethyl ether than in tetrahydrofuran. This result is in agreement with the mechanism proposed in equations 15 and 16.

E. Effect of Methanol on the Methyl Exchange in Dimethylcadmium

Attention will now be turned toward the effects of oxygen and halide ion upon the rate of exchange of methyl groups in solutions of dimethylcadmium. It has been observed that the addition of methanol to a solution of dimethylcadmium in tetrahydrofuran, which leads to the formation of methylcadmium methoxide, has very little effect on the rate of methyl group exchange. In Figure 28 are shown the nmr spectra of a solution (10% by volume) of dimethylcadmium in tetrahydrofuran before and after the addition of methanol (molar ratio of dimethylcadmium to methanol = 5:1). The absorption of the methyl group of methylcadmium methoxide is readily apparent at approximately 10 Hz downfield from the methyl resonance for dimethylcadmium. The spectra in Figure 28 were taken at the same temperature (ambient probe temperature of 37°) and they illustrate the important point that the exchange of dimethylcadmium in tetrahydrofuran is not significantly affected by the presence of methylcadmium methoxide.

To further elaborate on the above result nmr spectra for the same "before and after" experiment were observed at -10° and are

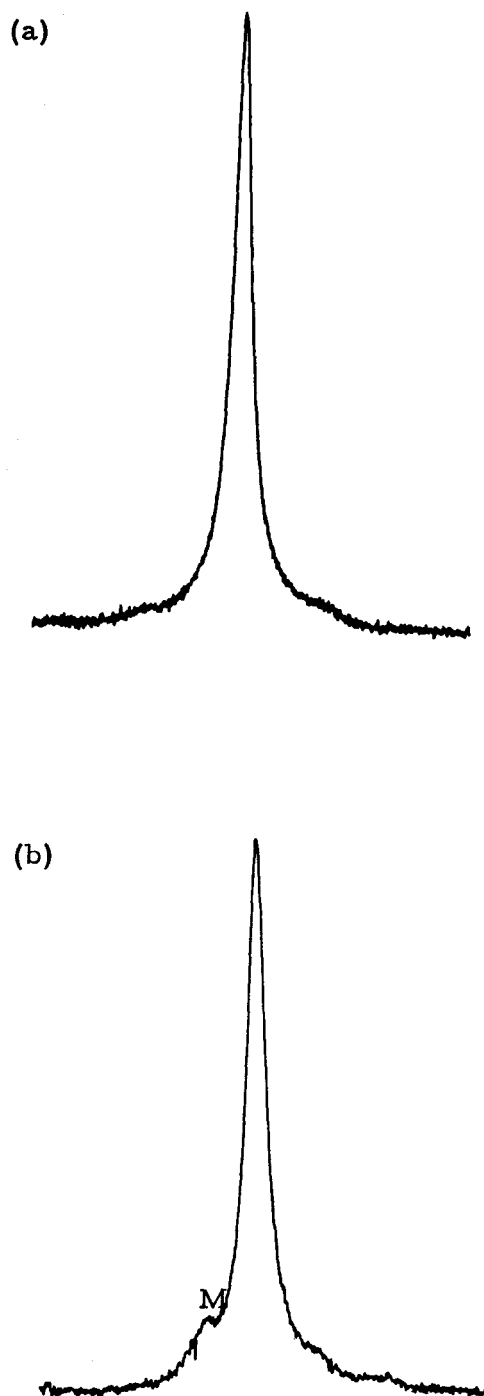


Figure 28. Spectra (60 MHz) of a solution of dimethylcadmium in tetrahydrofuran: (a) without methanol (b) with methanol (molar ratio of dimethylcadmium to methanol = 5:1). The peak labelled M belongs to the methyl resonance of methylcadmium methoxide. The sweep width is 500 Hz.

shown in Figure 29. Again it can be concluded that the exchange rate is unaffected by the presence of methylcadmium methoxide. It should be recognized that this is in contradiction to the findings of Ham, et.al. (74) in toluene and pyridine solution. However, since Ham et. al. (74) have not reported any studies in tetrahydrofuran solution, direct comparison of the tau values reported in the present research is not possible.

F. Effect of Cadmium Bromide on the Methyl Exchange in Dimethylcadmium.

Much recent work in Grignard chemistry has centered on the influence of the Schlenk equilibrium in solutions of such organometallics (86). The reactivity of organocadmium compounds toward ketones is greatly affected by the presence of metal halides (87), and it is thus of considerable interest to investigate the role of a Schlenk-type equilibrium in solutions of organocadmium compounds.

Figure 30 displays the nmr spectrum, at an ambient probe temperature of 37°, of dimethylcadmium (10% by volume) in a solution of tetrahydrofuran saturated with cadmium bromide. As is immediately obvious from a comparison of Figures 30 and 28, the addition of either cadmium bromide or cadmium chloride to a solution of dimethylcadmium in tetrahydrofuran substantially enhances the rate of methyl group exchange. In this connection it is significant that neither cadmium bromide nor cadmium chloride dissolves appreciably in tetrahydrofuran unless dimethylcadmium is present.

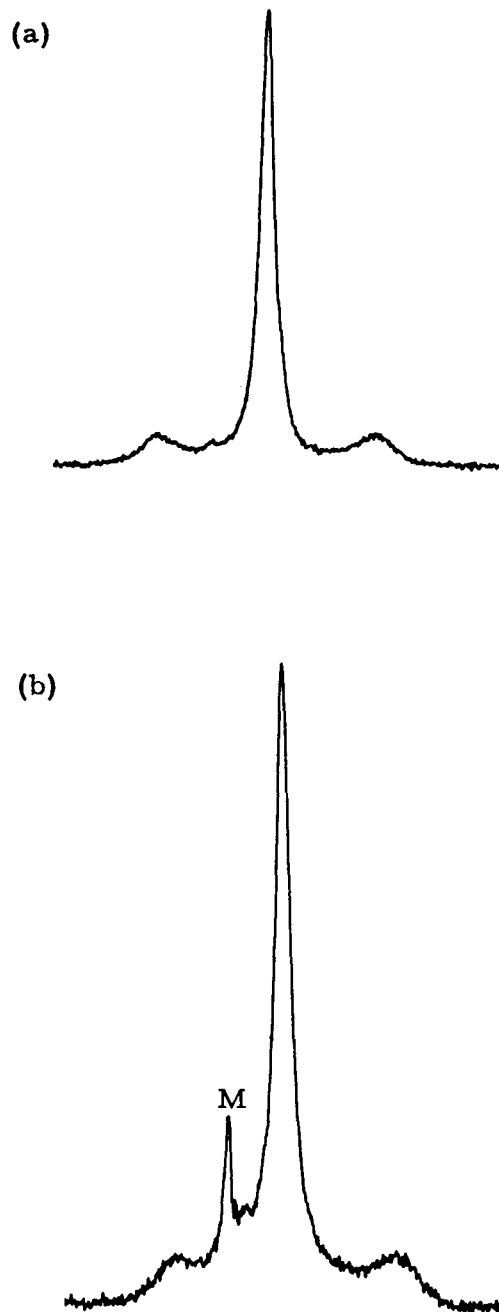


Figure 29. Spectra (60 MHz) of a solution of dimethylcadmium in tetrahydrofuran at -10° : (a) without methanol (b) with methanol (molar ratio of dimethylcadmium to methanol = 5:1). The peak labelled M belongs to the methyl resonance of methylcadmium methoxide. The sweep width is 500 Hz.

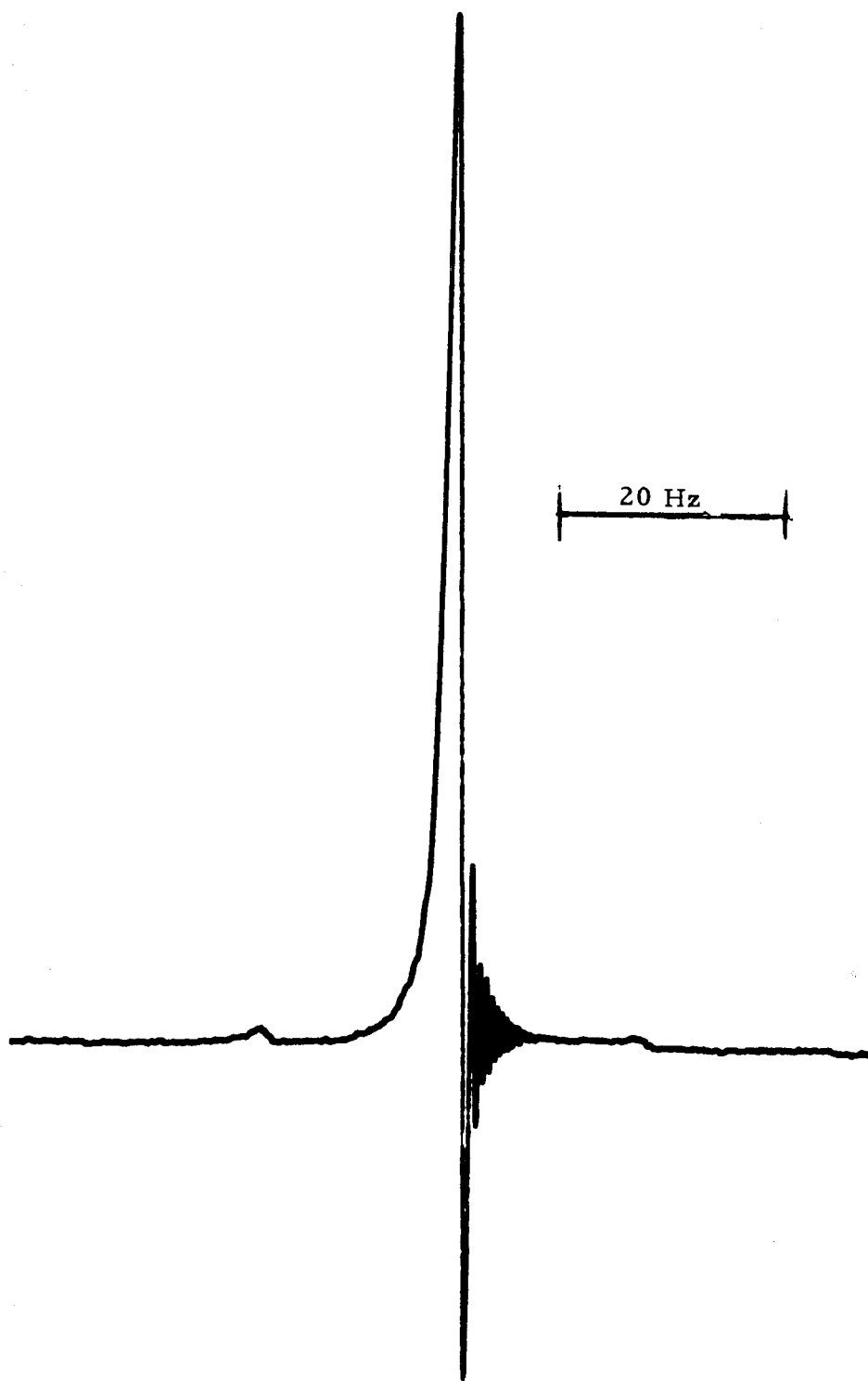
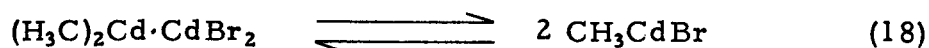
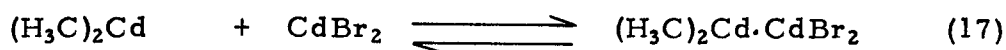


Figure 30. Nmr spectrum (60 MHz) of a solution of dimethylcadmium in tetrahydrofuran saturated with cadmium bromide.

In Figure 31 spectra are shown at low temperature of the sample described above. Although 10% solutions of dimethylcadmium in tetrahydrofuran were shown (Fig. 22) to have a slow methyl group exchange rate at -50° , a similar solution of the organometallic in tetrahydrofuran saturated with cadmium bromide does not show any evidence of the Cd-C-H splitting satellites at this temperature. However, a complicated pattern of peaks is observed at -100° . These spectra indicate both the presence of and the equilibration of methyl groups between dimethylcadmium and methylcadmium bromide. Although the present data are at variance with the lack of exchange reported from radioisotopic labelling experiments for diethylcadmium and cadmium bromide (88), similar conflicts between nmr studies and isotope labelling studies of exchange of alkyl groups in magnesium compounds appear to have been resolved in favor of the nmr method (34, 37).

Simple association between dimethylcadmium and cadmium bromide as in Equation 17 is not expected to lead to methyl exchange and cannot account for the fact that Cd-C-H splitting does not appear in tetrahydrofuran solutions of dimethylcadmium and cadmium bromide until -100° . Therefore the equilibrium in equation 18 must be very fast at ordinary temperatures.



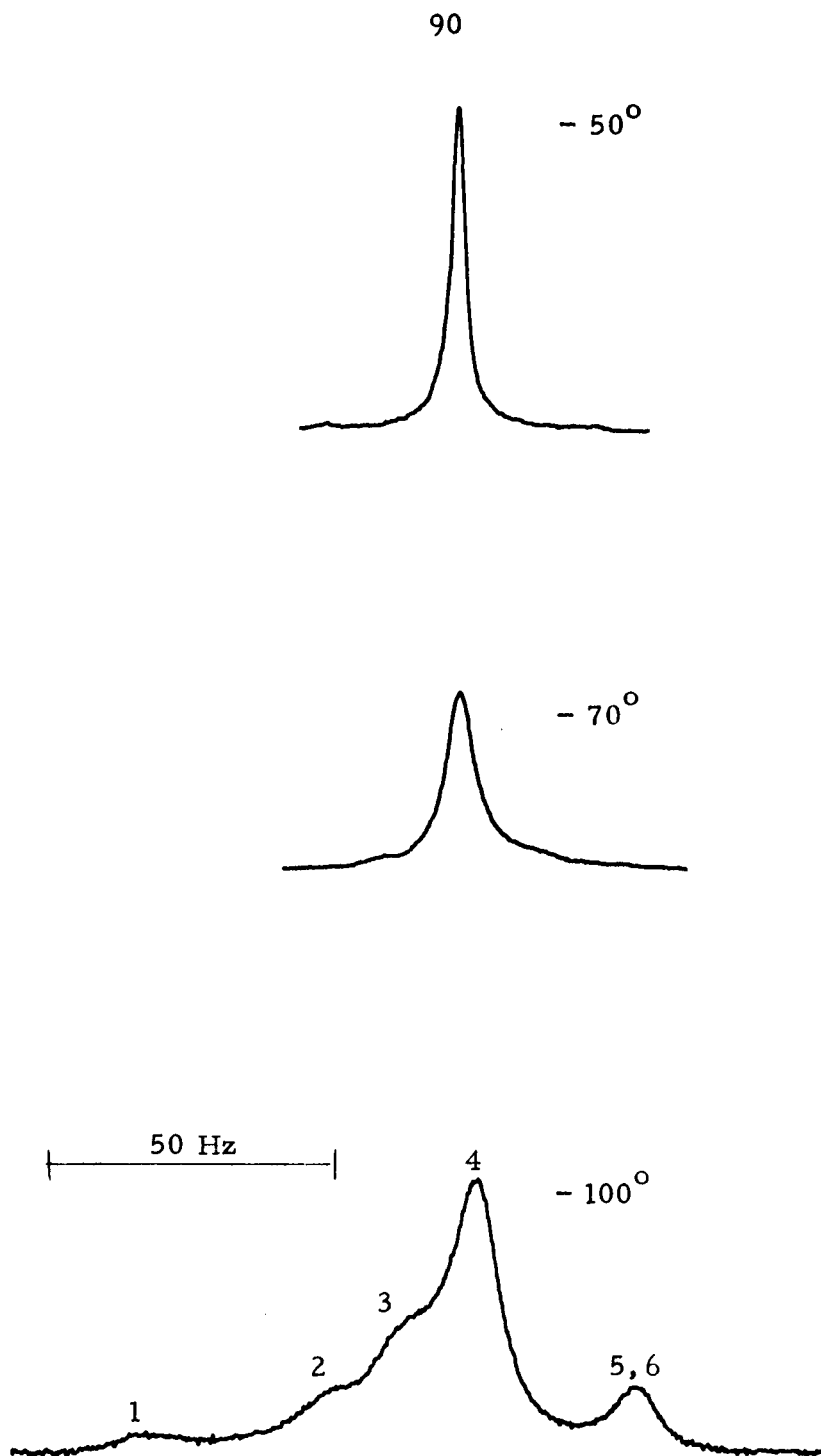


Figure 31. Spectra (60 MHz) of a solution of dimethylcadmium in tetrahydrofuran saturated with cadmium bromide as a function of temperature.

The resonance lines in the spectrum at -100° shown in Figure 31 have been assigned by the following arguments. First, the areas under peaks 4 and 5 are of the approximate ratio of 7:1 which makes it reasonable (natural abundance $^{111}\text{Cd} = 12.86\%$, $^{113}\text{Cd} = 12.34\%$) to assign 4 as the main peak of dimethylcadmium and 5 as a satellite. Thus 2 must be the other satellite. Peak 3 then must be the central absorption for methylcadmium bromide and 1 and 6 are the satellite lines for this species. Peak 6 falls under 5 and this was taken into account in determining the ratio of peaks 4 and 5. This assignment for methylcadmium bromide leads to $J_{^{111},^{113}\text{Cd}-\text{C}-\text{H}} \cong 80$ Hz as compared to $J_{^{111},^{113}\text{Cd}-\text{C}-\text{H}} = 51.4$ Hz for dimethylcadmium. This difference corresponds to a larger value for $J_{\text{Hg}-\text{C}-\text{H}}$ in the alkylmercuric salts as compared to the organomercury compounds (89). Thus for the first time the organic components and the rate of a Schlenk-type equilibrium in organocadmium compounds has been observed, and the first physical evidence for the existence of an alkylcadmium halide has been provided.

Unsymmetrical dialkylcadmium compounds were in a similar stage of investigation as the alkylcadmium halides at the outset of the present study. That is, though their preparation had been claimed, no physical evidence had been provided for their existence. In principle, if ethylmethylcadmium can exist, a mixture of dimethylcadmium and diethylcadmium should show two CH_3Cd absorptions in the nmr spectrum. In Figure 32 is shown the nmr spectrum at -50° of a mixture of dimethylcadmium and diethylcadmium in heptane. This

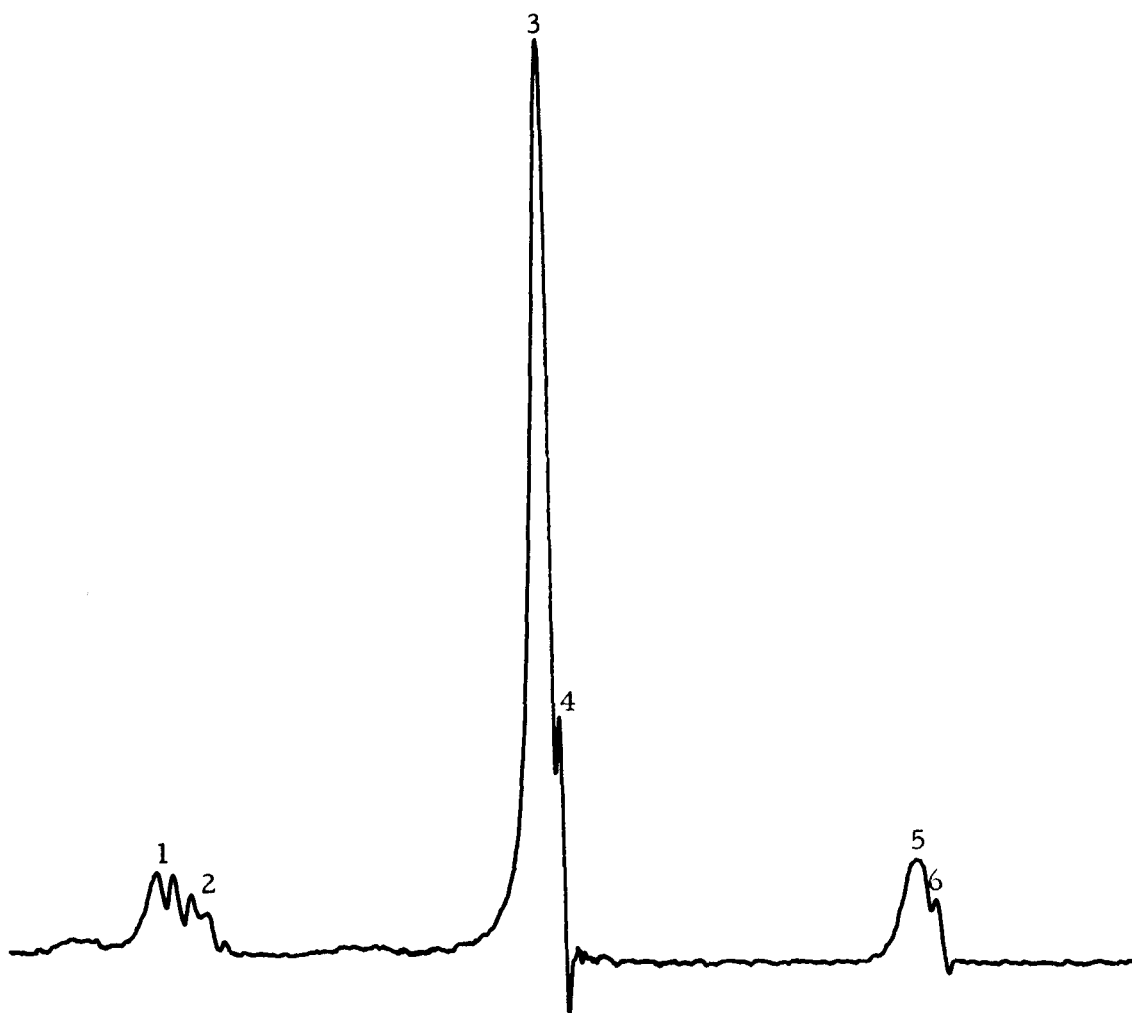
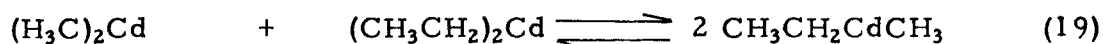


Figure 32. Spectrum (60 MHz) of a mixture of dimethylcadmium and diethylcadmium in heptane at -50° . The sweep width is 250 Hz.

spectrum shows two methyl signals and two sets of Cd-C-H couplings. This spectrum can only be rationalized in terms of a slow equilibrium (equation 19). Thus, as in the case of the alkylcadmium



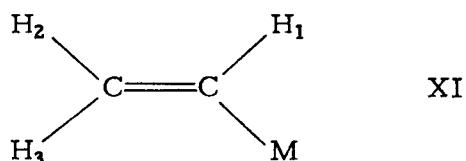
halides, unique nmr evidence has been provided for the existence of an unsymmetrical dialkylcadmium compound. By the addition of a large excess of dimethylcadmium to the solution in Figure 32 it was possible to assign line 3 to dimethylcadmium, and 4 to methylethylcadmium. Unsymmetrical dialkylcadmium compounds should become useful "probes" in the further study of the equilibria involved in organocadmium solutions.

Very few studies concerning vinyl group exchange in organometallic systems have been reported. It appears such an exchange has been studied only in the Group III organometallics. Vinyl groups in mixed methylvinylthallium compounds undergo rapid exchange (90). Vinyl group exchange has also been found to be rapid in trivinylgallium (91). Using techniques analogous to those employed in the study of dimethylcadmium, an investigation of vinyl group exchange in divinylcadmium was begun.

Although divinylzinc (92) and divinylmercury (93) are known compounds, the preparation of divinylcadmium has never been reported. Attempts at metal-metal exchanges with divinylmercury and cadmium and di-n-butyl-divinyltin and cadmium gave only starting material. The direct vinylation of cadmium bromide and vinylmagnesium

chloride failed to give divinylcadmium. However, a convenient method of preparation was found in the reaction of vinyl lithium with cadmium bromide. The initial indication of the formation of the desired cadmium compound was the color change in the reaction mixture from the deep-red tetrahydrofuran solution of vinyl lithium to a colorless tetrahydrofuran solution. Further, this colorless solution gave a negative Gilman color test and showed an nmr spectrum in the vinyl region which was distinct from that of vinyl lithium.

Figure 33 displays the nmr spectrum at 100 MHz (ambient probe temperature of 37°) of a dilute solution of divinylcadmium in tetrahydrofuran. A small amount of benzene and ethylene are present as impurities. No evidence of the cadmium-proton spin-spin multiplets is present in the spectrum. This indicates that exchange of vinyl groups must be fast on the nmr time scale. The spectrum in Figure 33 was analyzed at both 100 MHz and 60 MHz and the parameters are reported in Table VIII. The values for divinylmercury and vinyl lithium are given for comparison purposes. The numbering in Table VIII follows:



The assignment of lines for the spectrum of divinylcadmium was based upon the presumed relationship between proton-proton

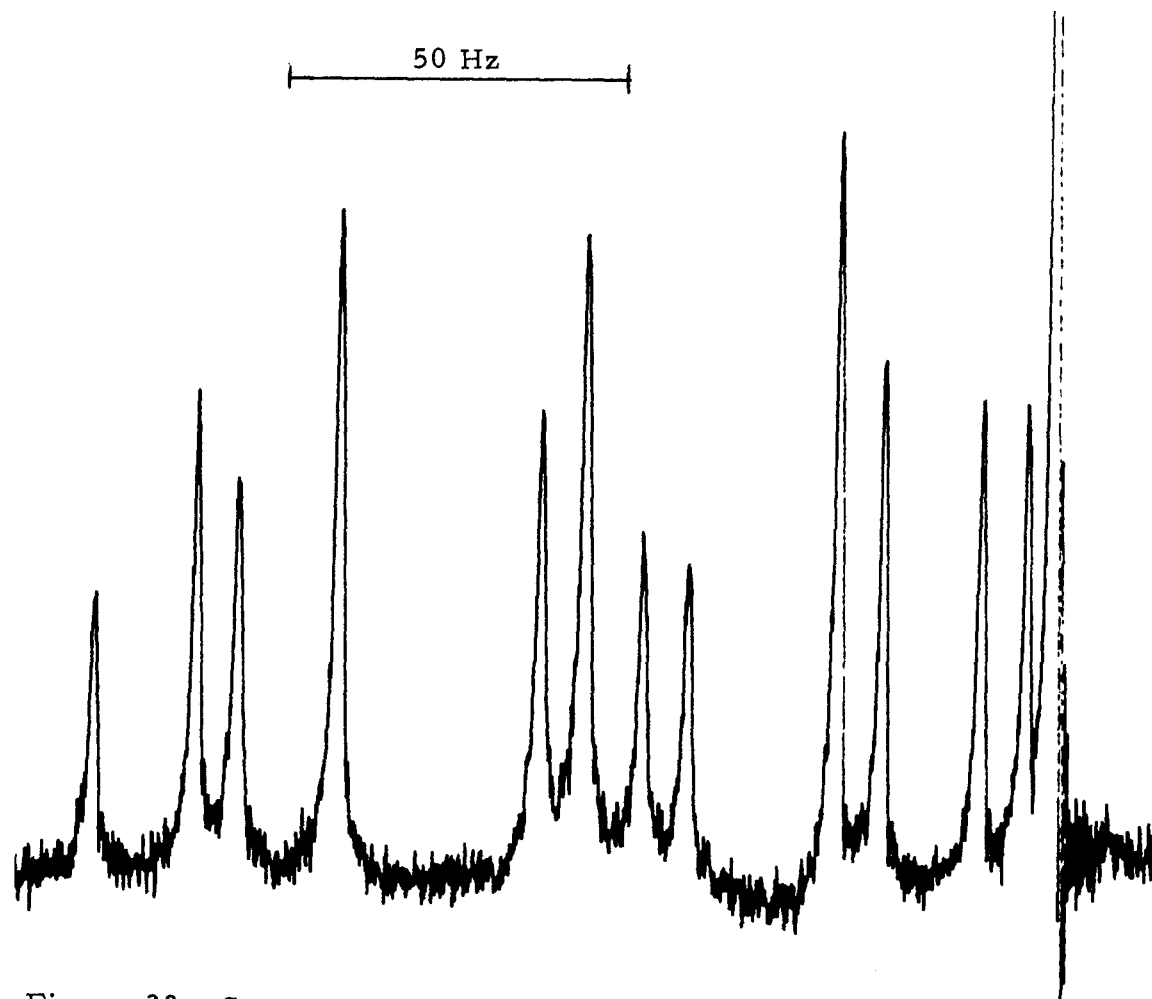


Figure 33. Spectrum (100 MHz) of a solution of divinylcadmium in tetrahydrofuran. The off-scale peak belongs to ethylene which is present as an impurity.

TABLE VIII

Nmr Parameters for the Vinyl
Protons of Vinyl Organometallics

	H_1^a	H_2	H_3	J_{12} in Hz	J_{13} in Hz	J_{23} in Hz
Divinylcadmium in tetrahydrofuran	0.0	0.57 ± 0.05	1.01 ± 0.05	15.4 ± 0.4	22.1 ± 0.5	6.3 ± 0.5
Vinyl lithium in ether (b)	0.0	0.511 ± 0.005	1.190 ± 0.005	19.3 ± 0.5	23.9 ± 0.5	7.1 ± 0.5
Divinylmercury (c)	0.0	0.80	1.34	13.1	21.0	3.5
Vinylmagnesium chloride in tetrahydrofuran (d)	0.0	0.48	1.10	17.6	23.0	7.5
Vinylmagnesium bromide in tetrahydrofuran (e)	0.0	0.50	0.82	17.2	22.1	7.4

(a) All shifts are reported in ppm upfield from H_1 . (b) C. S. Johnson, M. A. Weiner, J. S. Waugh and D. Seyferth, J. Am. Chem. Soc., **83**, 1306 (1961). (c) D. W. Moore and J. A. Hoppe, J. Phys. Chem., **65**, 224 (1961). (d) R. T. Hobgood Jr. and J. H. Goldstein, Spectrochimica Acta, **18**, 1280 (1962). (e) G. Fraenkel, D. G. Adams and J. Williams, Tetrahedron Letters, 767 (1963).

spin coupling constants in vinyl groups: $J_{\text{trans}} \rangle J_{\text{cis}} \rangle J_{\text{gem}}$.

Schaefer (94) has observed a relationship between the sum of the three coupling constants in a vinyl system and the electronegativity of the substituent. Using the coupling constants for divinylcadmium in Table VIII, Schaefer's relationship gives an electronegativity value of 1.3-1.6 for cadmium. The Pauling electronegativity for cadmium is 1.7, whereas the electrostatic model gives 1.46 (95).

The off-scale line in Figure 33 belongs to ethylene. The reader should recognize that all three vinyl protons of divinylcadmium fall downfield of ethylene. This downfield shift in metal-vinyl systems is quite general and is contrary to the assignment one would make solely on the electron-donating characteristics of the metal atom. A possible explanation is the withdrawal of π -electrons from the vinyl group into vacant p-orbitals of cadmium. Similar π -electron transfer has previously been proposed to account for the nmr spectra of certain vinylsilanes (96). Although it is not shown in Table VIII, the vinyl protons in vinyl lithium fall downfield from their respective counterparts in divinylcadmium. Perhaps this indicates that π -electron transfer from the vinyl group to the empty p-orbitals of the lithium metal is greater than π -electron transfer to the p-orbitals of cadmium.

The lines in Figure 33 became broad at low temperatures, but at -100° there was no evidence of the cadmium-proton spin-spin multiplets. The question arises as to whether the exchange of vinyl groups is fast because of the presence of cadmium bromide. In an effort to answer this question a sample of divinylcadmium was

prepared in tetrahydrofuran, the solvent was removed by distillation and replaced with benzene. After two days the benzene solution had precipitated a large amount of solid residue. An nmr spectrum was taken of the mother liquor of this sample. It is difficult to say just how much salt, if any, was still present in the benzene solution. The nmr spectrum (at an ambient probe temperature of 37°) of divinyl-cadmium in benzene showed that the vinyl protons were shifted downfield relative to their position in tetrahydrofuran. This downfield shift could arise from a change in the bonding between the vinyl group and the metal resulting from a slowing of the vinyl group exchange rate, or it could be due to a specific interaction of benzene with the π -electrons of the vinyl group. Some indication of the presence of new peaks, which could possibly be attributed to the cadmium-proton splitting satellites, was observed. However, the spectrum was much too noisy (even after 300 scans on the CAT) to allow this evidence to be positive proof for a slow vinyl group exchange. There is definitely a need for further work on salt-free hydrocarbon solutions of divinyl-cadmium.

CONCLUSIONS

The rate of methyl group exchange in a neat sample of dimethylcadmium was quantitatively studied. The tau values reported in this study are in disagreement with those observed by Ham, et al. (74).

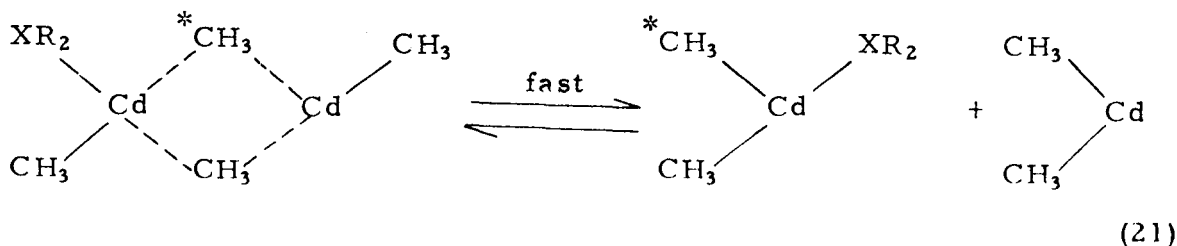
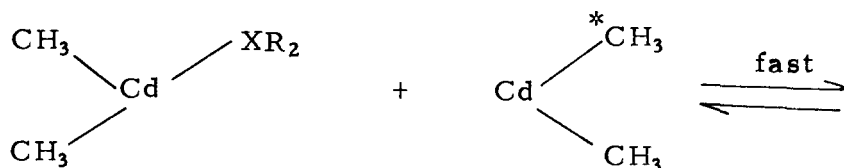
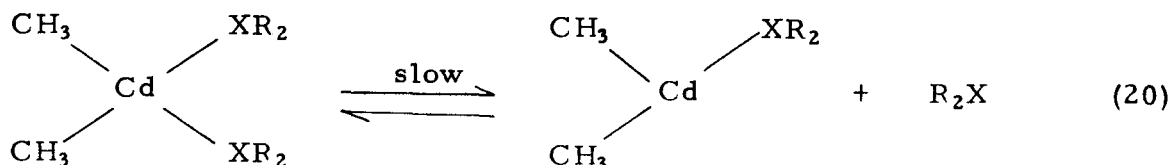
Solutions of dimethylcadmium in benzene and cyclohexane show only slightly increased exchange rates over that of the neat sample. However, the same exchange rate was observed in cyclohexane and benzene solutions. The exchange was found to be concentration independent in cyclohexane. Dimethylcadmium was found to be predominantly monomeric in benzene solution.

The exchange of methyl groups in tetrahydrofuran is much faster than in either the neat sample of the cyclohexane or benzene solutions. The exchange in the tetrahydrofuran solution was found to be concentration independent. This implies that the exchange obeys first-order kinetics. Addition of N,N,N',N'-tetramethylethylenediamine to a solution of dimethylcadmium in tetrahydrofuran results in retarding the rate of methyl exchange relative to a similar solution without diamine. First-order kinetics was also observed in the solution with diamine. It should be noted that the diamine is a much more effective coordinating agent than tetrahydrofuran, as evidenced by the fact that several dialkylmagnesium compounds have been found (97) to yield isolable monomeric complexes with the diamine, whereas no complexes with tetrahydrofuran have been isolated. The pK_b of tetrahydrofuran is 16.1 whereas the pK_b of TMED is 9.0. A simple

ionization-recombination process is not in agreement with this result, i. e., that the diamine retards the rate of exchange of methyl exchange in a solution of dimethylcadmium in tetrahydrofuran.

Studies on the stereochemistry of the exchange process in bis-(2-methylbutyl)-cadmium and bis-(3, 3-dimethylbutyl)-cadmium have demonstrated that the exchange proceeds with retention. House and coworkers (34) arrived at a similar conclusion for the exchange in organomagnesium compounds.

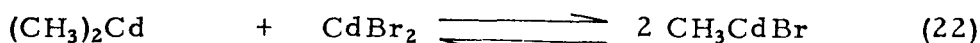
The first-order kinetics, the retardation of the exchange rate caused by the addition of diamine, and the retention of stereochemistry can all be accounted for by the following mechanism, which relates to a solution of dimethylcadmium in tetrahydrofuran.



This mechanism is in agreement with the recent finding (85) that methyl group exchange for dimethylcadmium is faster in diethyl ether than in tetrahydrofuran.

It has been observed that the addition of methanol to a solution of dimethylcadmium in tetrahydrofuran, which leads to the formation of methylcadmium methoxide, has very little effect on the rate of methyl group exchange.

Addition of cadmium bromide to a solution of dimethylcadmium in tetrahydrofuran greatly increases the rate of exchange. At -100° , a slow equilibration between dimethylcadmium, cadmium bromide and methylcadmium bromide was observed. This is the first direct observation of the organic components of, and the rate of, a Schlenk-type equilibrium with organocadmium compounds. It is difficult to ascertain an accurate value for the equilibrium constant of this Schlenk-type equilibrium because of the overlapping of the peaks in the spectrum which prevents an accurate measurement of the exact amount of each species. However, a crude estimate indicates that 50% of the methyl groups are in the dimethylcadmium form and 50% are in the methylcadmium bromide form. Thus the equilibrium constant for equation 20 would be approximately 4.



Evidence has been presented for the existence of an unsymmetrical dialkylcadmium compound, methylethylcadmium.

Vinyl group exchange in a solution of divinylcadmium in tetra-

hydrofuran is fast. The divinylcadmium was prepared by the reaction of cadmium bromide with vinyl lithium in a tetrahydrofuran solution. Unfortunately the preparation may not preclude the presence of cadmium bromide in the final divinylcadmium solution.

An nmr investigation of a salt-free solution of divinylcadmium in benzene at an ambient probe temperature of 37° indicated the presence of new peaks which did not appear in the spectrum of the above solution in tetrahydrofuran. These new peaks may be the cadmium-proton satellites. Unfortunately the solution of divinylcadmium in benzene was very dilute and even after 500 scans on the CAT the noise level in the spectrum of this sample was so high that an unambiguous assignment of the new peaks as real absorptions was difficult.

The small chemical shift difference between the vinyl protons precluded the use of otherwise valuable decoupling experiments. If the cadmium-proton satellites are present in a salt-free solution of divinylcadmium in benzene, then the vinyl group exchange rate must be slow on the nmr time scale.

Part I. Configurational Stability and Redistribution Equilibria in
Organomagnesium Compounds.

EXPERIMENTAL

All boiling points are uncorrected. Vapor chromatograms were obtained using an F & M Prepmaster Model 750 and a Perkin-Elmer Vapor Fractometer Model 800. Microanalyses were performed by Elek Microanalytical Laboratories, Torrance, California.

Proton magnetic resonance spectra were obtained with the following different spectrometers:

- 1) Varian Associates Model A-60A for room-temperature spectra.
- 2) Varian Associates Model A-56/60A operated at 60 MHz and equipped with a Varian C-1024 time averaging computer and a V-6040 variable temperature probe and controller.
- 3) Varian Associates Model HA-100.
- 4) Varian Associates Model HA-60il, converted from a Varian V-4300B spectrometer.
- 5) Varian Associates Model HR-220.

Sweep widths were calibrated using a Hewlett-Packard Model 4204A oscillator. The frequency output of this oscillator was periodically checked using a Hewlett-Packard Model 5245-L electronic counter. Probe temperatures were determined by measuring peak separations in methanol or ethylene glycol samples. The sweep width was always calibrated before making a measurement of the

temperature. Most temperatures reported in this thesis are estimated to be accurate to $\pm 2^\circ$.

Concentrations of the organometallic species were directly measured in ether solution by a comparison of the intensity of the ^{13}C satellites of the methyl group in ether with the intensity of the organometallic peak. The concentration of naturally abundant $^{13}\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ in diethyl ether is known to be 2.2%.

Diethyl ether. - Mallinckrodt anhydrous ether, from a newly-opened can, was used without further purification.

Tetrahydrofuran was distilled from sodium wire immediately prior to use.

Dioxane. - Mathieson, Coleman, and Bell chromatography grade dioxane was distilled from lithium aluminum hydride and stored over sodium or Linde 5A Molecular Sieves until use.

N,N,N',N' - Tetramethylethylenediamine from Mathieson, Coleman, and Bell was distilled from sodium before use and stored over Linde 13X Molecular Sieves.

Magnesium was in the form of shavings turned from blocks of triply sublimed magnesium (98). No broad resonances characteristic of Grignard reagents prepared from Grignard-grade magnesium were observed using this special sample of triply sublimed magnesium.

Alkyl halides were used as received from the manufacturer with the exception of those specifically mentioned below. These halides were better than 98% pure as shown by vapor phase chromatography, and thus were used without further purification.

Preparation of Organomagnesium Compounds. - To a 5-mm nmr tube, precision ground by the Wilmad Glass Company to a wall thickness of 0.30 mm, was added 50 mg of magnesium turnings, 0.1 ml of solvent, and 0.1 ml of halide. The solvent and halide were added by means of a 0.5 ml gas-tight Hamilton syringe equipped with a Teflon plunger. If the reaction did not begin immediately, two drops of ethylenedibromide were added to the solution to initiate the reaction. As soon as the reaction had visibly begun, 0.4 ml more solvent was added and the tube was cooled in a dry ice-acetone bath and sealed. If the sealing was done well, either end of the nmr tube could be placed downward in the probe.

After sealing the tube, the reaction was initiated again by rubbing and shaking the tube and/or by warming it in a steam bath. The tube was then heated in a steam bath for 1-3 hours. After heating was complete, the tube was centrifuged so that the solid residue was lodged in one end of the tube. Careful decantation of the liquid to the other end of the tube provided a clear sample.

Dialkylmagnesium Compounds. - Solutions of the dialkylmagnesium compounds were prepared from the corresponding Grignard reagents by cooling the nmr tube of above in dry ice-acetone, cutting off approximately 1 cm from the top, and adding 0.15 ml of dry dioxane. The mixture was stirred as well as possible, the neck of the tube cleaned with a pipe cleaner, and the tube was sealed as before. The large amount of precipitate sometimes formed resulted in the sample becoming almost solid.

If the dialkylmagnesium compound was prepared from two Grignard reagents in separate tubes, the individual Grignard reagents were added to a third tube by means of a gas-tight Hamilton syringe equipped with Teflon plunger. The syringe had previously been carefully cleaned and dried in an oven at 150° for one hour. The decomposition of the Grignard reagents in the transfer usually totalled approximately 25%.

The preparation of a mixture of dialkylmagnesium compounds from two different Grignard reagents was found to give the best yields when both Grignard reagents were prepared in the same tube. In the preparation of a mixture of a secondary Grignard reagent and a primary Grignard reagent, the secondary species always was more difficult to prepare and required more heating. It was possible to follow the preparation of each Grignard reagent in the mixture by observing the nmr spectrum.

The characterization of both primary and secondary Grignard reagents was carried out in the nmr spectrum by identification of the unique resonances due to protons bonded to a carbon alpha to magnesium.

Yields of Grignard reagents (based on starting halide) were estimated to be 60-95% by comparison with the ¹³C satellites of the solvent. Secondary Grignard reagents usually gave yields in the lower range.

2-Phenyl-3-methyl-butan-1-ol was prepared by Dr. George M. Whitesides and this preparation is described in his dissertation (99).

2-Phenyl-3-methylbutyl chloride. - To a three-necked round-bottomed flask equipped with condenser, mechanical stirrer, and addition funnel was added 20 ml of 2-phenyl-3-methylbutan-1-ol dissolved in 50 ml of reagent grade DMF. Thionyl chloride (20 ml) was slowly added to this solution with cooling after each addition. The solution was stirred for 7 hours and slowly poured over 250 g of an ice-water mixture. This mixture was extracted with three 50 ml portions of ether. The ether layers were combined, dried over calcium chloride and the ether stripped off on a rotary evaporator. The remaining liquid was distilled at reduced pressure. Infrared and nmr spectra showed that fraction two, which boiled at 80-82° at 1.0 mm, was the purest. This fraction was carefully distilled through a 15-cm wire-spiral packed column and collected in a cow. The final product boiled over a range 73-75° at 0.7-0.8 mm. The yield was 7.3 g (60%).

Anal. Calcd for $C_{11}H_{15}Cl$: C, 72.32; H, 8.28; Cl, 19.41.
Found: C, 72.20; H, 8.35; Cl, 19.25.

4,4-Dimethylpentan-2-ol. - To a 500-ml three-necked round-bottomed flask equipped with condenser, nitrogen inlet and outlet, mechanical stirrer, and addition funnel was added a slurry of 3.25 g of lithium aluminum hydride in 200 ml of ethyl ether. To this was added dropwise 13.0 g of 4,4-dimethylpentan-2-one dissolved in 200 ml of ether. After this addition was complete, the solution was allowed to stir overnight and the reaction mixture was slowly neutralized by the addition of 14 ml of a 5% aqueous sodium hydroxide

solution. The reaction mixture was filtered, the ether layer dried, and evaporated. Infrared spectra and vapor phase chromatography showed the residual liquid to be better than 95% alcohol. The yield was 9.5 g (75%).

2-Bromo-4,4-dimethylpentane. - In a 300-ml three-necked round-bottomed flask equipped with condenser and addition funnel, 9.5 g of crude 4,4-dimethylpentan-2-ol was dissolved in 50 ml of methylene chloride and cooled in an ice-salt bath. To this was added slowly 11.1 g of phosphorus tribromide dissolved in 10 ml of methylene chloride. This mixture was added at such a rate as to keep the temperature at 0°. After the addition was complete, the solution was allowed to stand at room temperature overnight. The methylene chloride was distilled as was the remaining liquid at atmospheric pressure. The purest fraction (98%) as determined by vapor phase chromatography boiled at 131-133° (755 mm) and was characterized by its nmr spectrum.

Anal. Calcd for $C_7H_{15}Cl$: C, 46.93; H, 8.37; Cl, 44.69.
Found: C, 46.60; H, 8.50; Cl, 44.20.

Part II. Redistribution Equilibria in Organocadmium Compounds.

EXPERIMENTAL

Benzene and cyclohexane were obtained from commercial sources and were used without further purification.

Cadmium bromide was dried by heating in an oven for 5 hours at 150°. Immediately before use it was cooled in a nitrogen atmosphere.

Dimethylcadmium was purchased from the Orgmet Chemical Company. It was carefully distilled by bulb-to-bulb distillation (0.02 mm) directly into nmr tubes which were then sealed on the vacuum line with the usual freeze-thaw technique.

Molecular Weight Determination of Dimethylcadmium. - The procedure used was that of Shoemaker and Garland (100). Benzene (15.84 g) was placed in a three-necked flask equipped with mechanical stirrer and Beckman thermometer. The constantly stirred benzene solution was cooled by an ice-salt mixture. Temperature readings were taken on the stirred solution at intervals of 30 seconds. The solution at first supercooled, but then returned to the freezing point. Dimethylcadmium (3.960 g; 0.877 molal) was added to the benzene and the freezing point was again determined. Three similar runs gave an average depression of 4.218°. The theoretical depression for a 0.877 molal solution is 4.490 and hence the solute is predominantly monomeric.

Bis-(2-methylbutyl)-cadmium. - To a three-necked flask equipped with mechanical stirrer, condenser, and nitrogen inlet and outlet, and containing 1.6 g of magnesium metal turnings was added slowly 8.0 ml of 2-methylbutyl bromide dissolved in 50 ml of ethyl ether. A few drops of 1,2-dibromoethane were added to initiate the reaction. The reaction mixture was allowed to reflux for several hours. Cadmium bromide (8.2 g) was added and the mixture refluxed for two more hours. A Gilman test for the presence of Grignard reagent gave a negative response. Dioxane (8 ml) was added to the mixture resulting in immediate production of a voluminous white precipitate. The mixture was suction-filtered and about half the solvent was stripped off on a rotary evaporator. The product was stored in the refrigerator in an evacuated ampoule and was characterized by its nmr spectrum.

Bis-(3,3-dimethylbutyl)-cadmium was prepared in a similar manner as described above for bis-(2-methylbutyl)-cadmium.

Vinyl lithium was obtained from Alfa Inorganics and was used without further purification.

Divinylcadmium. -To a slurry of 0.544 g of cadmium bromide (0.001 mole) in tetrahydrofuran in a three-necked round-bottomed flask equipped with addition funnel, mechanical stirrer, and nitrogen inlet and outlet was added dropwise at 0° 2 ml of vinyl lithium (0.002 mole) in tetrahydrofuran. The reaction mixture was stirred for 30 minutes at 0° and then brought to room temperature. The mixture gave a negative Gilman test and the product was character-

ized by its nmr spectrum. If the reaction was carried out at temperatures higher than 0° , the mixture blackened and gave no evidence in the nmr spectrum of divinylcadmium.

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PROPOSITIONS

Proposition I

An experiment is proposed to determine whether the allyl rearrangement in diallylmagnesium is an inter- or intramolecular process.

Nmr has been a useful probe in studying the allylic rearrangements which occur in allyl or diallyl organometallic compounds such as allyllithium, diallylmagnesium, diallylzinc, and diallylcadmium (1, 2, 3, 4). The allyl groups of these organometallics all show AX_4 type nmr spectra at room temperature indicating that the rearrangement is fast on the nmr time scale.

One of the fundamental questions in the study of the allyl rearrangements in the above systems is whether rearrangement takes place by an inter- or intramolecular process.

The allylic rearrangement in diallylmagnesium has been studied over the temperature range from $+40$ to -80° (2, 5) and an AX_4 type spectrum was observed at the lowest temperature. Intermolecular exchange of alkyl groups has been shown to be a slow process at low temperature in solutions of dialkylmagnesium compounds containing N,N,N',N'-tetramethylethylenediamine (6, 7). The question is whether intermolecular exchange of allyl groups in allylmagnesium

derivatives is a slow process at low temperatures. If intermolecular exchange is slow and the allyl rearrangement is fast, then rearrangement must be proceeding by an intramolecular process.

Methylcyclopentadienylmagnesium and phenylcyclopentadienylmagnesium have been prepared (6) from dimethyl- and dicyclopentadienylmagnesium and diphenyl- and dicyclopentadienylmagnesium, respectively. Based on these findings it should be possible to prepare allylcyclopentadienylmagnesium from diallylmagnesium and dicyclopentadienylmagnesium. Because of the magnetic anisotropy of the cyclopentadienyl ring a high field shift should be observed for the resonances due to the allyl group in allylcyclopentadienylmagnesium relative to the absorptions in diallylmagnesium. A shift of approximately 20 Hz was observed (6) between the nmr methyl signals of methylcyclopentadienylmagnesium and dimethylmagnesium. Hence, two AX_4 type spectra (or two more complicated nmr patterns, if the allyl rearrangement is slow) will be observed for the allyl groups in a mixture of allylcyclopentadienylmagnesium and diallylmagnesium when intermolecular exchange of allyl groups between these species is slow, and one average AX_4 spectrum will be observed when the exchange is rapid. Thus we have a method for determining the rate of intermolecular exchange of allyl groups and the activation parameters for this exchange. The rate of intramolecular exchange can be monitored

by observing the type of spectrum obtained. An AX_4 spectrum would indicate fast intramolecular exchange while a more complicated pattern, such as an $ABCD_2$, would indicate slow intramolecular exchange.

In the presence of N,N,N',N'-tetramethylethylenediamine slow intermolecular exchange of phenyl-, cyclopentadienyl-, and alkyl-groups between various organomagnesium species has been observed. Based on these results it should be possible to observe a slow intermolecular exchange of allyl groups, thus leading to a conclusive result for this proposition.

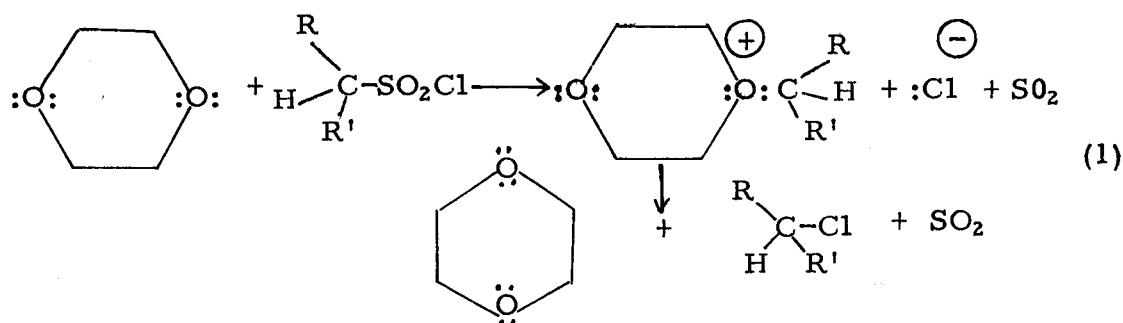
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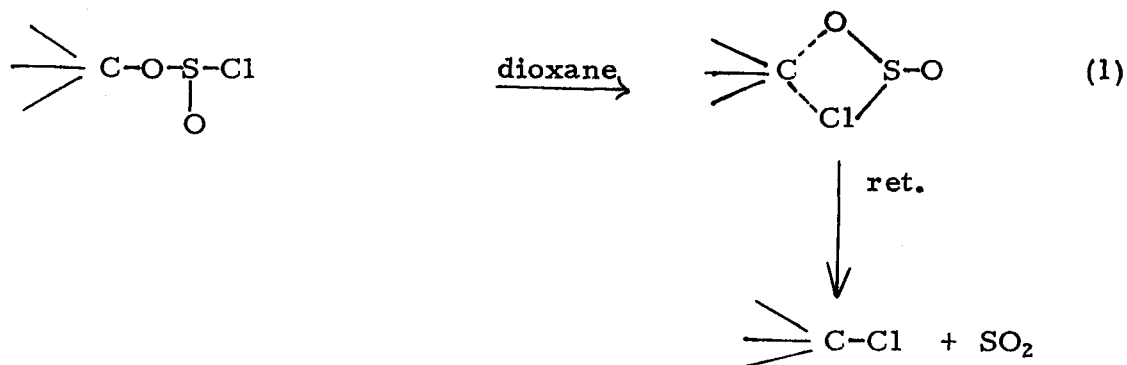
Proposition II

A method is given that will allow a distinction to be made between the possible mechanisms in the decomposition of the mixed carbonate ester formed from β -hydroxyethyl benzoate and diphenyl carbonate.

Lewis and Boozer (1) decomposed secondary alkyl chlorosulfites and in dilute dioxane solution found the reactions to be first order. The chloride obtained as a product was found to have the same configuration as the alcohol from which it was derived. A double inversion mechanism was proposed for the decomposition in dioxane.



Optically active α -phenylethyl alcohol reacts with thionyl chloride in the presence of pyridine to give (2) α -phenylethyl chloride of opposite rotation and configuration. In the absence of pyridine the product is α -phenylethyl chloride of the same configuration as the starting material (3). Hughes, Ingold and co-workers (4) have rationalized this finding in terms of an $\text{S}_{\text{N}}1$ mechanism.



In the presence of a base such as pyridine, the HCl formed in the initial condensation of alcohol and SOCl_2 is converted to the nucleophilic Cl^- ion which may react with the alkyl chlorosulfite present as an intermediate by way of an ordinary displacement reaction resulting in inversion. In the absence of base the reaction probably proceeds through a cyclic intermediate as above in equation 1. However, Cram (5) has pointed out that the reaction may begin like a $\text{S}_{\text{N}}1$ reaction with the formation of an ion pair. In the case of a chlorosulfite the anion formed is SO_2Cl^- which may rapidly decompose to sulfur dioxide and a chloride ion. Recombination of the ion pair thus gives the chloride, with the same configuration as the original alcohol.

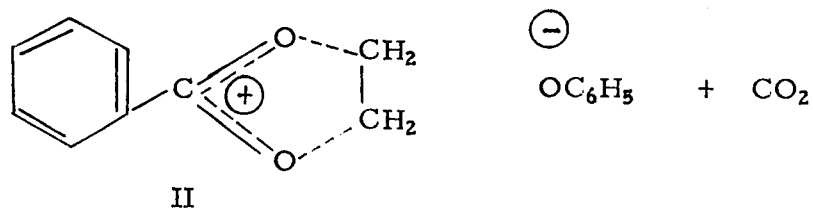
$\text{S}_{\text{N}}2$ displacements on allylic systems sometimes lead to rearrangement and hence it is not surprising that we find that $\text{S}_{\text{N}}1$ substitutions on allylic alcohols may also lead to rearranged products. α -Methylallyl alcohol reacts with dry HCl in ether to form only α -methylallyl chloride (6). Under the same conditions α -methylallyl

alcohol is converted to α -methylallyl chloride.

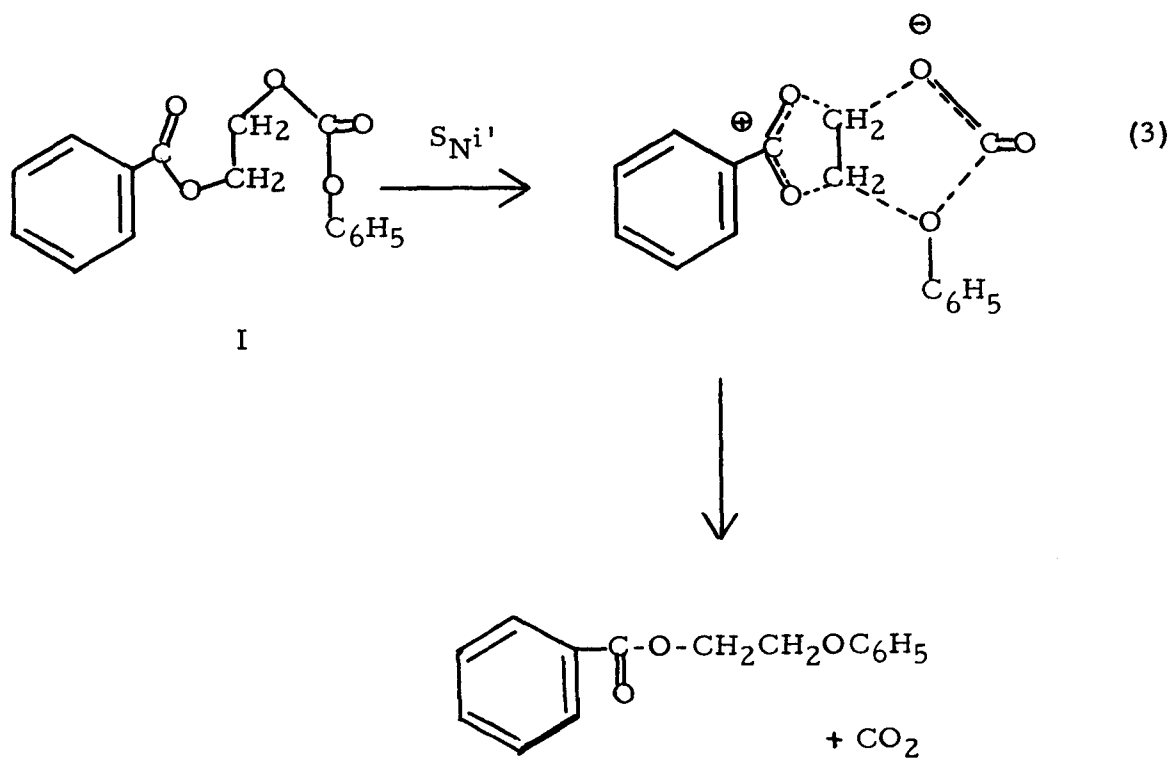
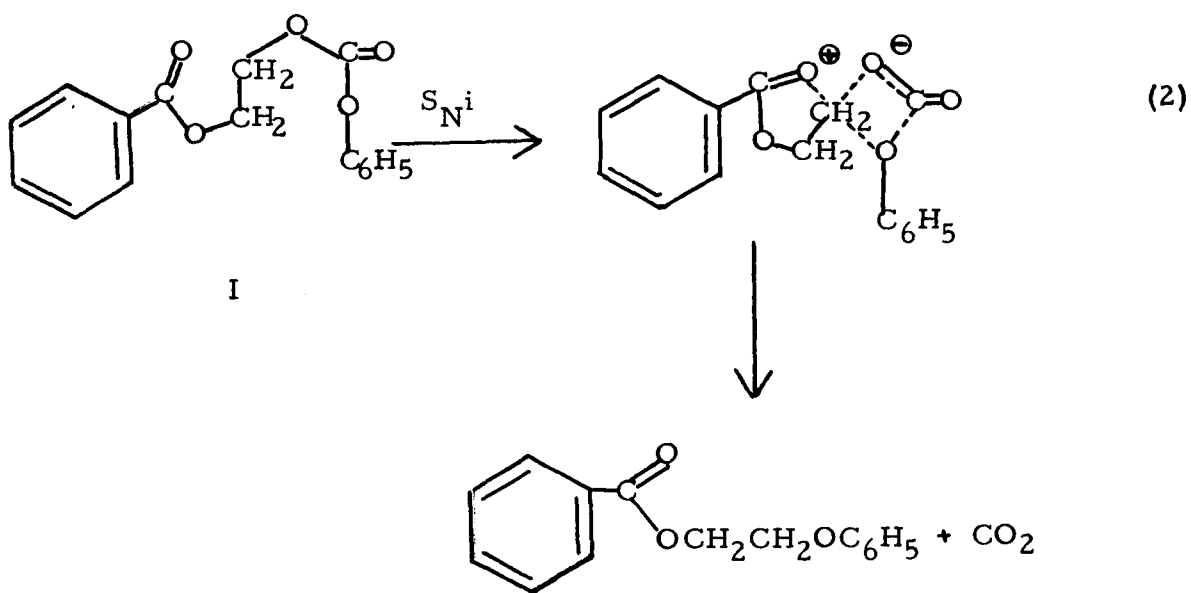
Recently (7) it has been found that thiocarbonates decompose to carbon dioxide and the corresponding sulfides on being heated at elevated temperatures in inert solvents.

This reaction is clearly analogous to the decomposition of chlorocarbonates, the mechanism of which is thought to be S_Ni ; hence it is believed that the decomposition of thiocarbonates proceeds through an S_Ni mechanism. The thiocarbonate decomposition adds the mercaptide linkage to the list of groups that can act as nucleophiles in the S_Ni reaction.

McDonough (8) has now found what appears to be a new example of an internal nucleophilic substitution reaction. Heating β -hydroxyethyl benzoate with an equimolar amount of diphenyl carbonate for four hours at 210–230° gave phenol (96%), carbon dioxide (92%), and β -phenoxyethyl benzoate. The most plausible reaction pathway seems to be initial displacement of phenol to give compound (I) which then decomposes to give β -phenoxyethylbenzoate and carbon dioxide. This decomposition is interesting in that it may proceed through an S_Ni pathway as in equation 2 or through an S_{N^i} pathway as in equation 3, or through a symmetric intermediate such as the ion pair (II). The phenoxy anion can, of course, attack at either methylene group



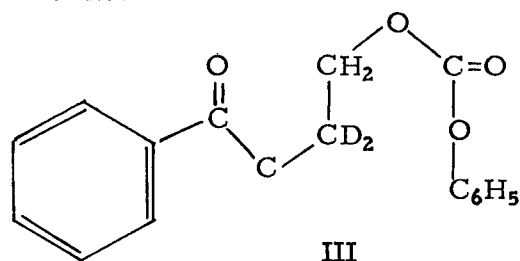
to give the final product. The term S_{N^i} is used to describe equa-



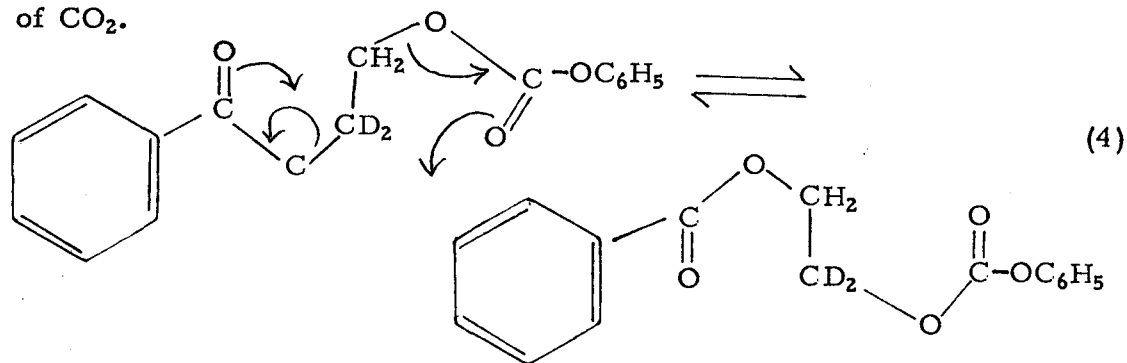
tion (3) because in essence one has an internal nucleophilic attack which leads to rearrangement.

The S_N1 reaction of alkyl chlorocarbonates is facilitated by the ability of the alkyl group to form stable carbonium ions (1). In the present example a stable carbonium ion intermediate could be formed by the neighboring group participation of benzoate. A carbonium ion similar to the one postulated in the mechanism below has been isolated as the fluoroborate salt (9).

It is proposed that the decomposition of compound (III) will allow a distinction to be made between the two mechanistic possibilities.



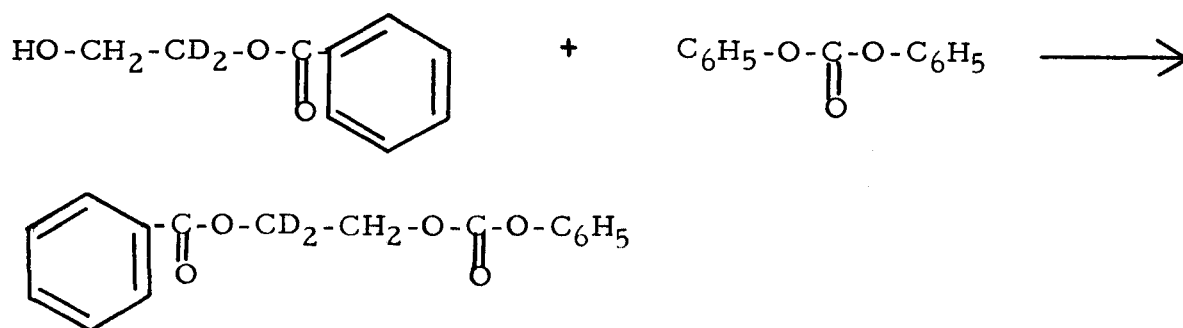
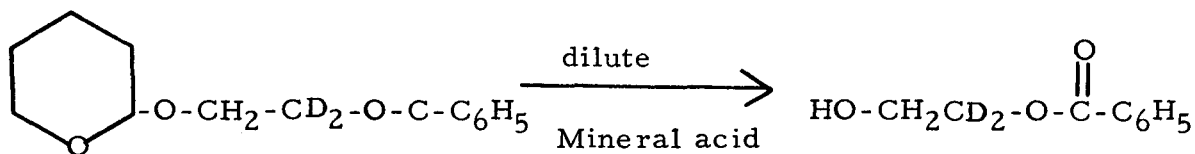
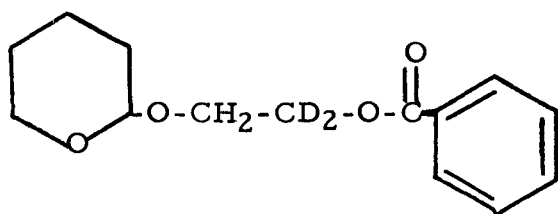
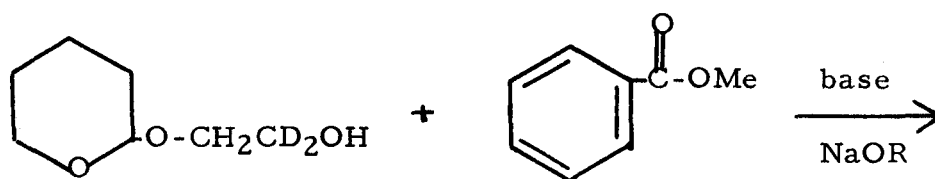
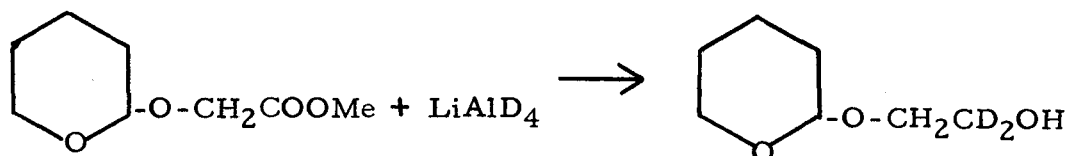
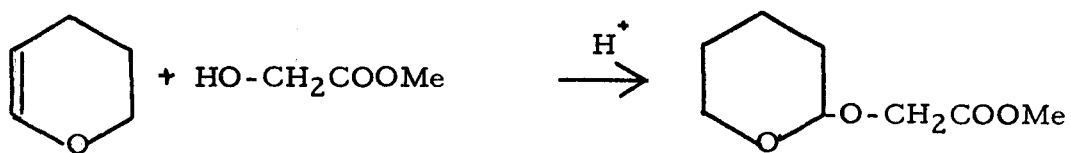
However, before we can proceed further we must first take into account a possible rearrangement of the starting material (III) by way of a reaction such as (4) or internal return involving (II), which would lead to a scrambling of the deuteriums before the loss of CO_2 .



Whether reaction (4) occurs or not can be determined by stopping the reaction after 2 hours and determining if rearrangement of the deuteriums in (III) has occurred. If rearrangement of the deuterium in (II) has occurred, then the proposition can not lead to a conclusive result, but if rearrangement does not occur in (III) then a determination of the deuterium positions in the final product will allow a conclusion to be drawn concerning the mechanism of decomposition of (III).

If the decomposition of (III) proceeds through the S_N^i pathway, then the methylene group alpha to the ester linkage in (III) will remain in that position in the final product. If the decomposition proceeds through the S_N^i pathway, the methylene group alpha to the ester linkage in the starting material will then be beta to the methylene group in the product. If the decomposition proceeds through the symmetric ion pair intermediate (II) then the deuteriums in the final product will be equally displaced between the two methylene positions. However, the proposition cannot distinguish between decomposition through (II) and a rather unlikely decomposition involving just equal amounts of (2) and (3). A comparison of the nmr spectrum of β -phenoxyethyl benzoate obtained from deuterated and undeuterated starting material should allow a distinction to be made as to which mechanism is proceeding. Jackman (10) reports that methylene protons alpha to a hydroxy group absorb at $\delta = 6.44$, while protons alpha to the benzoyl group absorb at $\delta = 5.77$.

The synthesis of compound (II) can be carried out in the following manner:



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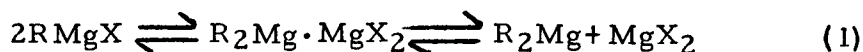
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Proposition III

An exchange experiment is proposed to determine if the Schlenk equilibrium proceeds in the case of an optically active Grignard reagent.

It is well known (1) that a pair of electrons in a tetrahedrally hybridized carbon orbital (sp^3) does not maintain its spatial configuration very readily, but rather the pair of electrons inverts its configuration very rapidly. In contrast to the above, an electron pair in a trigonally hybridized orbital (sp^2) seems to be able to maintain its spatial configuration to a greater extent. The exo-orbitals of cyclopropane are believed (2) to have a hybridization of $sp^{2.3}$ and hence one might infer that an electron pair in an exo-orbital of a three membered ring system should maintain its spatial configuration as well as a trigonally hybridized system. This conclusion was borne out in the work of Walborsky (3) and ultimately led to his synthesis of the only known optically active Grignard reagent. The compound 1-methyl-2,2-diphenylcyclopropylmagnesium bromide can be formed with complete retention of optical activity from optically pure 1-methyl-2,2-diphenylcyclopropyllithium and magnesium bromide.

The Schlenk equilibrium (equation 1) was proposed by Schlenk and Schlenk (4) when they found that a magnesium halide-dioxane



complex can be precipitated from ethereal Grignard solutions by the addition of dioxane. The question of whether this equilibrium actually proceeds has only recently been successfully investigated. Two groups of workers (5, 6) have now found that mixtures of labelled magnesium bromide with either diethylmagnesium or ethylmagnesium bromide both result in statistical exchange among the various forms of magnesium present. However, the stereochemistry of the Schlenk equilibrium is still unknown.

It is proposed that an exchange experiment be carried out using the optically active Grignard reagent and magnesium-25 bromide. This experiment should allow a conclusion to be drawn concerning the stereochemistry of the Schlenk equilibrium.

The experiment can be carried out in the simplest manner by forming the optically active Grignard reagent from (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane. Unfortunately the Grignard reagent prepared in this manner is only 12% optically pure, but it is known (3) that the racemization occurs during the formation of the Grignard reagent and once formed the Grignard reagent is optically stable.

The Grignard reagent can be prepared with complete optical purity from the lithium compound, but this introduces the problem of having unlabelled magnesium bromide in the solution. This

problem can be effectively overcome by adding an excess of magnesium-25 bromide after the Grignard reagent has been formed.

After a period of time the magnesium bromide present can be precipitated from the solution with dioxane. Mass spectrometry can be used as the means of determining the composition of the precipitated magnesium bromide. If a Schlenk equilibrium has been proceeding, we will find that statistical equilibrium has been achieved among the various forms of magnesium present. If this result is obtained, then it can be firmly stated that, at least in this system, the Schlenk equilibrium must be proceeding with retention. If statistical equilibrium among the different isomers of magnesium is not obtained, then the Schlenk equilibrium does not proceed in this system, and presumably proceeds with inversion in other systems.

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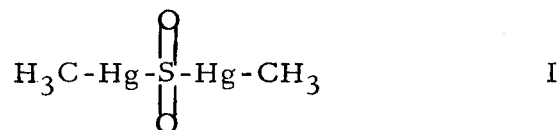
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Proposition IV

The use of ^{17}O nmr spectroscopy is proposed to ascertain the structure of one of the products formed in the reaction between dimethylmercury and sulfur dioxide.

Carbon-metal bonds can in some cases be cleaved by sulfur dioxide. Hartman and Wojcicki (1) observed that $\text{CH}_3\text{Mn}(\text{CO})_5$ reacts with SO_2 to give the sulfone, $\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{Mn}(\text{CO})_5$. However, it is conceivable that in some cases the ester might form; the reaction of sulfur dioxide with triethylaluminum is thought to yield the ester-type product tris-(ethylsulfinato-)aluminum $(\text{C}_2\text{H}_5-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O})_3\text{Al}$ (2).

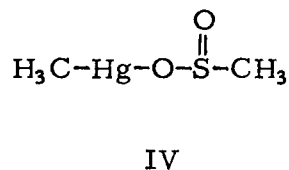
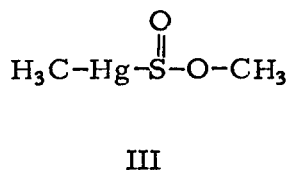
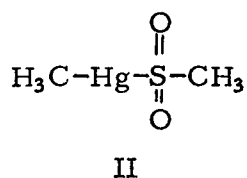
Dimethylmercury reacts with sulfur dioxide to form two compounds in a ratio of 3:1 (3). The compound formed in the predominant amount was identified as I. The structure of I was based on infrared and nmr evidence and an analysis. The proton nmr spectrum showed



a single peak at $\delta = 0.8$ ppm. The infrared showed strong bands at 1245 and 1085 cm^{-1} which can be assigned to the $\text{S}=\text{O}$ stretching vibrations. Structure I was not soluble in common solvents,

indicating that perhaps association was occurring through S-Hg coordination or through $\text{S}=\text{O} \rightarrow \text{Hg}$ coordination. The band present at the 940 cm^{-1} in the infrared spectrum is consistent with the latter type of association.

The compound formed in smaller amount analyzed for $\text{C}_2\text{H}_6\text{O}_2\text{SHg}$. This compound was soluble in organic solvents and gave a sharp melting point indicating that it was not polymeric. A molecular weight determination should be carried out, prior to the experiments outlined below, to verify that the compound is a monomer. Three possible structures for this compound are (II), (III), and (IV).



The infrared spectrum of this compound showed strong bands at 980 and 950 cm^{-1} which can be assigned to either $\text{>S}=\text{O} \rightarrow$ or $\text{S}-\text{O}$. Strong bands were also found at 1230 and 1115 cm^{-1} suggesting $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$ or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$. The proton nmr spectrum showed two peaks at $\delta = 1.32$ and $\delta = 2.99$ ppm, indicating that there are two nonequivalent methyl groups. However, neither the infrared nor the proton nmr spectrum can be used to decide between structures (II), (III), and (IV).

It is proposed that the ^{17}O nmr spectrum (4) of $\text{C}_2\text{H}_6^{17}\text{O SHg}$ be examined to determine whether the structure of this compound is (II), (III), or (IV). Structure (II) can be distinguished from (III) and (IV) by observing the number of chemically shifted lines in the ^{17}O spectrum.

If (II) is the correct structure, then only one line (assuming decoupling of the protons present) will be found in the ^{17}O spectrum. However, if either (III) or (IV) is the proper choice, two lines (again assuming decoupling of the protons) will be observable in the ^{17}O spectrum. There should be no problem in observing shift differences between the non-equivalent oxygens in (III) and (IV) because the two oxygens in a typical ester show a shift difference of 200 ppm (5).

In order to distinguish between (III) and (IV) it is proposed to examine the proton nmr spectrum of $\text{H}_3\text{C}-^{17}\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{CH}_3$ (V). The two important points to be made concerning this compound are the position of the non-equivalent methyl protons and their respective splitting with the ^{17}O nucleus. Although ^{17}O has a nuclear quadrupole moment, spin-spin splitting of this nucleus with other nuclei not having a quadrupole moment such as ^1H have been observed (4, 5).

An estimate of the magnitude of the $^{17}\text{O}-^1\text{H}$ coupling constants in (V) can be obtained from the $^{31}\text{P}-\text{H}$ coupling constants in triethylphosphine. The phosphorous coupling constants in triethylphosphine are $J_{\text{P}-\text{CH}_2} = 0.5 \text{ Hz}$ and $J_{\text{P}-\text{CH}_3} = 13.7 \text{ Hz}$. The magnetic moment μ of ^{17}O is 1.89 (in units of nuclear magnetons) and for ^{31}P $\mu = 1.13$. This leads to an estimate of $J_{^{17}\text{O}-\text{C}-\text{H}} = 0.9$ and $J_{^{17}\text{O}-\text{S}-\text{C}-\text{H}} = 26$. If the $^{17}\text{O} - ^1\text{H}$ coupling constants prove too small to measure, the experiment described below utilizing the proton chemical shift of the methyl groups should still allow a distinction to be made between (III) and (IV).

The methyl groups in (V) correspond to the methyl groups

bonded to the oxygen in (III) and to the sulfur in (IV). Hence, a comparison of the proton shifts observed from (V) with the shift observed for the downfield methyl group in $C_2H_6O_2 SHg$ should allow a distinction to be made between (III) and (IV).

A comparison of the magnitude of the $^1H-^{17}O$ spin-spin splittings in (V) with the $^1H-^{17}O$ splitting of the downfield methyl group in $C_2H_6O_2SHg$ should also allow a distinction to be made between (III) and (IV). In (III) the $^1H-^{17}O$ splitting with the downfield methyl is over two bonds and if the same pattern is followed here as in triethylphosphine this splitting should be smaller than the splitting in (IV) which is over three bonds. The above argument assumes that the $^1H-^{17}O$ coupling is influenced more by the separation between the oxygen and the proton than by the interchange of a H_3C-Hg- group by a H_3C- group. This assumption is supported by the fact that the $^{13}C-C-H$ coupling in diethylmercury is similar in magnitude to the $^{13}C-C-H$ coupling in propane (6), whereas, the $^{13}C-C-H$ coupling in propane is quite different from the $^{13}C-C-C-H$ coupling.

$C_2H_6^{17}O_2SHg$ could be formed in the reaction between $(CH_3)_2Hg$ and $S^{17}O_2$ can be prepared from sulfur and oxygen-17 which is commercially available.

$H_3C^{17}O-S-CH_3$ can be prepared by reacting $H_3CMg-Cl$ with $S^{17}O_2$ to yield $H_3C-\overset{\overset{O}{\parallel}}{S}-OMgCl$ which upon reaction with H_3CCl should yield the desired product.

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Proposition V

A spectroscopic study is proposed to determine the extent of π bonding in the C-M bond of vinyl lithium, divinylmagnesium, and divinylcadmium.

Bonding of the p_{π} - p_{π} type can exist between a vinyl group and a metal atom having a vacant p-orbital. Indeed, experimental evidence for this type of bonding has been found for some of the Group III vinylmetallics (1).

Stone and co-workers (1) have presented evidence for the existence of π -bonding in vinylboron derivatives. Chemical and spectroscopic evidence was offered in support of the idea of carbon-boron π -bonding. For example, the C=C stretching band in the infrared spectrum of various vinylboron compounds occurs at a lower wave number than a typical unconjugated double bond. This shift, considered together with the greater intensity of the band in the boron compounds relative to unconjugated systems, provides strong evidence that these double bonds are conjugated with a group which removes electrons by π -delocalization. The ultraviolet spectral properties of unsaturated organoboron compounds have also suggested resonance interaction between π -electrons of the carbon-carbon double bond and the p_{π} -orbital of an adjacent boron atom. The

observation by Letsinger and Skoog (2) of an absorption maximum at 223 m μ ($\epsilon = 1000$) in the spectrum of 2-methylprop-1-enylboronic acid is an example. Neither alkenes nor alkylboronic acids absorb in this region. Trivinylboron shows an eight line multiplet centered at $\delta = 6.55$ in the nmr spectrum. The nmr absorption of ethylene occurs at $\delta = 5.3$. The downfield shift of the absorptions in trivinylboron relative to ethylene presumably indicates a transfer of electrons from the C-C bond into the C-B bond.

The metal atoms of vinyl lithium, divinylmagnesium, and divinylcadmium all have vacant p-orbitals. There appears to be no reason why a p_{π} - p_{π} interaction similar to that in the vinylboron derivatives could not also occur in these compounds. In this connection it is significant that the nmr spectra of the vinylmetallics indicated immediately above show that the protons in these compounds are shifted downfield with respect to the protons in ethylene. Taking into account only the inductive effect of the above metals (Li, Mg, and Cd) one would expect an opposite shift, i. e., that the protons in the vinylmetallics would be shifted upfield of ethylene.

Vinyl lithium reagents are less reactive than their saturated counterparts; delocalization of the vinyl group's electrons into the lithium p_{π} -orbital could account for the diminished reactivity of this compound.

A lithium π -electron interaction has been proposed to account for the stereospecificity in the polymerizations of butadienes initiated by alkyllithium compounds (3). Oliver, et al. (4) have presented evidence for an interaction between the vacant orbitals on the hexameric lithium framework in but-3-enyllithium and the π -orbitals on the butene moiety in this compound.

A spectroscopic study of the above vinylmetallics is proposed in order to measure the extent of p_{π} - p_{π} bonding in these compounds.

The extended conjugation in vinylolithium can be measured by observing the position and intensity of the $C=C$ stretching band in the infrared spectrum. A shift to lower wave numbers from the normal position of the band at 1650 cm^{-1} indicates that the double bond is conjugated (5) with a group which removes electrons by π -delocalization. A greater intensity of the band is also observed when the double bond is conjugated. Hence, if p_{π} - p_{π} bonding is present in a hydrocarbon solution of vinylolithium, the $C=C$ stretching band will occur at a wave number less than 1650 cm^{-1} .

The addition of a coupling agent such as N,N,N',N' -tetramethylethylenediamine to a hydrocarbon solution of vinylolithium should decrease the p_{π} - p_{π} interaction because the diamine will presumably interact with the vacant p -orbital of the metal. This phenomenon then provides an additional tool for the observation of the p_{π} - p_{π} interaction

because the addition of diamine should shift the C=C band to higher wave numbers relative to a solution of vinyl lithium without diamine.

The ultraviolet spectrum can also be used as an indication of conjugation between the vinyl electrons and the lithium atom. A shift to higher wavelength indicates increasing conjugation. A comparison of the absorptions obtained from a hydrocarbon solution of vinyl lithium with and without diamine should indicate whether conjugation is present.

Finally the ^7Li nmr spectrum of vinyl lithium can also serve as a measure of the p_{π} - p_{π} overlap. The ^7Li shift should be related, at least in part, to the degree to which the p-orbital on the lithium is occupied. Based solely on an inductive argument, one would expect the ^7Li resonance in vinyl lithium to fall downfield of that in ethyl lithium since the vinyl group is more electron-withdrawing than an ethyl group. However, if the p_{π} - p_{π} interaction occurs to an appreciable extent, then the ^7Li resonance in vinyl lithium should fall upfield of the ^7Li resonance in ethyl lithium. Here again the observation of the ^7Li spectra of vinyl lithium both in the presence and absence of N,N,N',N'-tetramethylethylenediamine should prove interesting.

The experiments outlined above should be conclusive in deciding whether C-Li π -bonding does occur in vinyl lithium.

Similar experiments could be carried out with the vinyl compounds of magnesium and cadmium, thus giving information about the extent of carbon-metal π -bonding in these compounds.

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