Concerning the Structure of Allylic Grignard Reagents

D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received May 23, 1973*

Abstract: A series of γ-substituted allylic Grignard reagents (Me, Et, *i*-Pr, *t*-Bu) and α,γ-dimethylallylmagnesium chloride were studied by proton nmr spectroscopy. These Grignards exist as a rapidly equilibrating mixture of *Z* and *E* primary stereoisomers (structure **1**). Temperatures as low as $-80°$ were not sufficient to stop this rapid interconversion. Protonation and coupling constant studies show that the percentage of *Z* isomer decreases as the size of the alkyl substituent increases: methyl, 57%; ethyl, 42%; isopropyl, 27%; *tert*-butyl, ~1%. At low temperatures, the Schlenk equilibrium was detected. The stereochemical behavior of the diallylmagnesium compound was found to be similar to the corresponding allylmagnesium chloride.

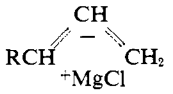
The chemistry and structure of allylic Grignard reagents have intrigued chemists for many years.[1-3] In the last decade, nmr techniques have been utilized to expand our knowledge of the structure of these compounds in solution.[4] There are at least three fundamental problems associated with these reagents.

(A) Their chemical composition. *I.e.*, what is the state of aggregation of the reagent and where is the position of the Schlenk equilibrium (eq 1) in solution?

$$R_2Mg + MgCl_2 \rightleftharpoons 2\,RMgCl \qquad (1)$$

(B) The position at which the magnesium atom is bonded. Does the Grignard reagent exist with a terminally bonded magnesium (**1**), an internally bonded magnesium (**2**), an intermediate bridged carbanion-type structure (**3**), or an equilibrium mixture of all of these types?

$RCH{=}CHCH_2MgCl$ **1** $\quad RCH(MgCl)CH{=}CH_2$ **2**



3

(C) The stereochemistry around the partial double bonds in the molecule. In structures **1** and **3** geometric isomerism is possible. If these isomers do exist, what is their preferred stereochemistry?

In their pioneering work on the crotyl Grignard reagent, Roberts and coworkers[5] contributed considerably to our knowledge of the bonding position of the magnesium atom. They conclude that, within the limits of their detection, the reagent existed as structure **1** (R = Me). In later work with 3-methyl-2-butenylmagnesium bromide (V)[6] they concluded that the internal isomer [$Me_2C(MgCl)CH{=}CH_2$] must be energetically accessible to account for the interchange of the methyl groups at room temperature on the nmr time scale. The internal isomer responsible for this interchange escaped detection because of its low concentration. In both the crotyl and the 3-methyl-2-butenyl reagents, structure **3** was ruled out because of their distinctly different chemical shifts and coupling patterns.[5,6] The results obtained in our laboratory are in agreement with, but elaborate on, these conclusions.

As part of a continuing study of the chemistry of allylic Grignard reagents,[7] the nmr spectra of a series of such reagents were examined. Systematic variation of the γ-alkyl substituent ($R^{\gamma}CH{=}^{\beta}CH^{\alpha}CH_2MgX$) on the Grignard reagent and of the temperature at which the spectra were obtained has provided a detailed picture of the nature of these reagents in solution. These data also provided answers to most of the structural problems outlined with the exception of the state of aggregation of the reagent.

The alkyl substituent on the γ carbon of the Grignard was varied in the series methyl (I), ethyl (II), isopropyl (III), and *tert*-butyl (IV).[3] α,γ-Dimethylallylmagnesium chloride (VI) was also examined under the same conditions. Table I summarizes the chemical shifts obtained for these reagents together with the previous data of Roberts. In each case, the individual resonances are readily assigned from their relative intensities and coupling patterns (see Figures 1 and 2).

$CH_3CH{=}CHCH_2MgCl$ I

$(CH_3)_3CCH{=}CHCH_2MgCl$ IV

$CH_3CH_2CH{=}CHCH_2MgCl$ II

$(CH_3)_2C{=}CHCH_2MgCl$ V

$(CH_3)_2CHCH{=}CHCH_2MgCl$ III

$CH_3CH{=}CHCHCH_3MgCl$ VI

$CH_2{=}CHCH_2MgCl$ VII

The chemical shifts in Table I clearly show the distinction between unsymmetrically substituted reagents (I–V) and the symmetrically substituted ones (VI and VII). For the unsymmetrical cases, the chemical shifts are characteristic of structure **1**. If there is any of structure **2** present in the solution, it must be in rapid equilibrium with structure **1** because no separate resonances attributable to such species were detected under any conditions (2% limit of detectability). The observed chemical shifts place an upper limit of 5% on the amount of **2** which can be in rapid equilibrium with **1**. The invariance of these shifts over a 100° tempera-

---

[1] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, New York, N. Y., 1954, Chapter XVII.

[2] R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

[3] R. A. Benkeser, *Synthesis*, **3**, 347 (1971).

[4] G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discuss. Faraday Soc.*, **No. 34**, 185 (1962).

[5] J. E. Nordlander, W. G. Young, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 494 (1961).

[6] G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 2010 (1962).

[7] The term allylic Grignard will be used as a generic name in this paper and it does not imply any preferred chemical form either with respect to the Schlenk equilibrium or to the nature of the allyl anion. It should also be noted that commercial Grignard-grade magnesium was employed in the preparations. All statements with regard to rate processes should be interpreted in this light.

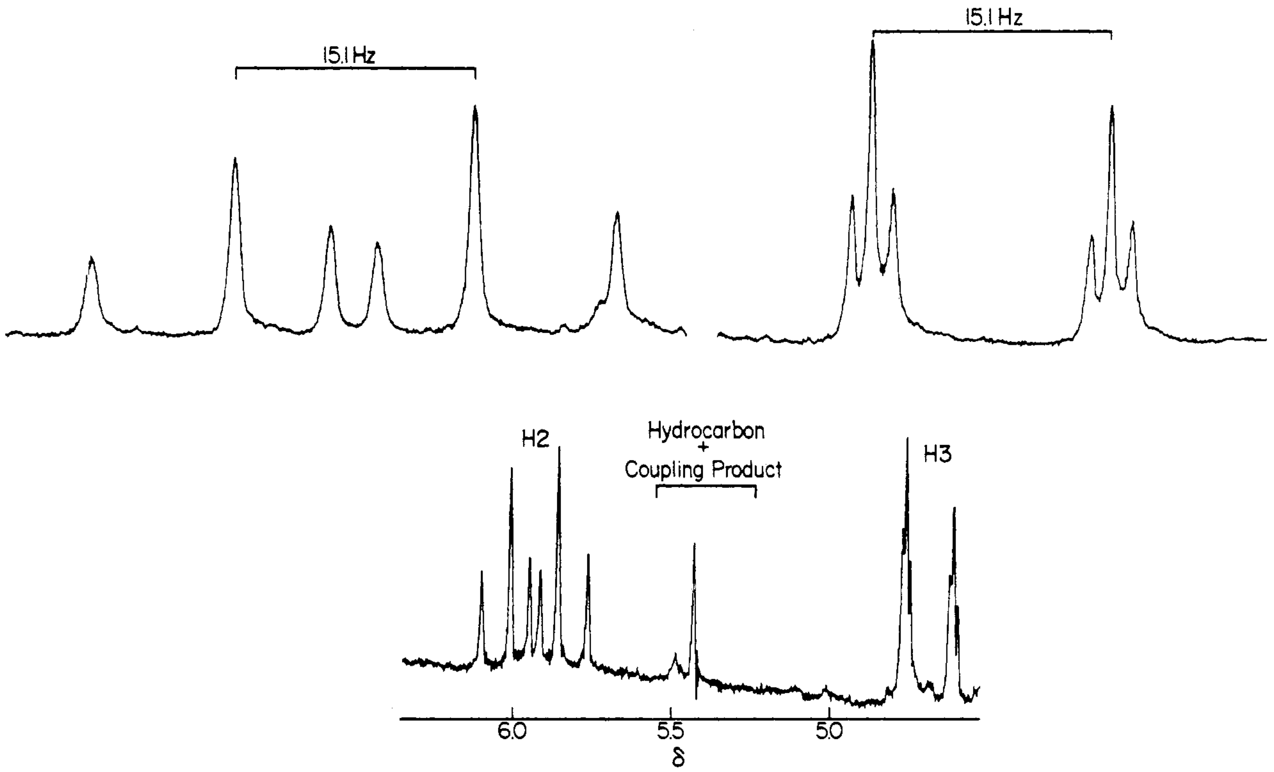
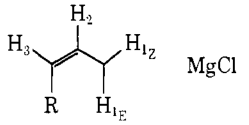


Figure 1. The proton nmr spectrum of (0.5 *M*) γ-*tert*-butylallylmagnesium chloride (IV) in Et_2O at probe temperature (32°). The upper spectra show each multiplet on an expanded scale. Signals due to the small amount of hydrocarbon impurities are indicated.

Table I. Chemical Shifts of Allylic Grignards[a]



Substituent, R	H_{1Z}, H_{1E}	H_2	H_3	R	Ref
H	2.50	6.38	2.50		4
Me	0.81	5.98	4.53	1.58	
	0.72	5.88	4.48	1.53	4, 5
Et	0.79	5.94	4.56	2.09 CH_2 0.97 CH_3	
i-Pr	0.78	5.91	4.57	2.26 CH 0.96 CH_3	
t-Bu	0.71	5.95	4.73	0.98 CH_3	
3,3-Me_2	0.57	5.58		1.55 CH_3	4, 6
1,3-Me_2	2.82	6.20	2.82	1.76 CH_3	

[a] In δ units using the diethyl ether solvent peaks as secondary reference at probe temperature (32°).

ture range provides a further check that the amount of **2** must be small (see also ref 5).

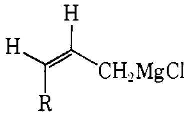
From the chemical shift data alone, no decision can be made as to the structure of the symmetrically substituted reagents. The data are equally consistent with a bridged structure **3** or a rapid equilibrium between two equivalent structures related to **1**. An attempt was made to freeze out this potential equilibrium by observing the α,γ-dimethylallyl Grignard (VI) spectrum at −100°. At this temperature viscosity broadening became significant, but no evidence for exchange line broadening was detected. It is possible to calculate an upper limit to the activation energy for the equilibration from these data. Experience with these and other Grignards suggests that rate data derived from such calculations are not reliable since the coalescence temperatures of different samples varied (see below).

Table II lists the coupling constants for compounds I–IV and VI. The striking feature of these data is the steady increase in J_{23} as the size of the alkyl substituent increases, while the other coupling constants remain virtually constant. Based on the magnitude of J_{23}, the similarity of the other spectral parameters across the series and the fact that all Grignard species in solution are equilibrating rapidly to give a single averaged spectrum, it is reasonable to conclude that J_{23} is reflecting a change in equilibrium population with substituent. This average coupling constant reveals a rapid equilibrium between *Z* (cis) (VIII) and *E* (trans) (IX) stereoisomers about the double bond of structure **1**. The magnitude of the coupling constant provides a measure of the equilibrium population of isomers. Values of

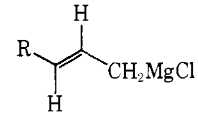
Table II. Coupling Constants of Allylic Grignards[a]

Substituent	J_{12}	J_{13}	J_{23}	J_{2R}	J_{3R}
Me	9.6	1.2	11.7	1.5	6.4
Et	9.45	1.5	12.4	1.25	6.5
i-Pr	9.4	1.3	13.55	1.1	7.25
t-Bu	9.1	1.3	15.1		
1,3-Me_2	11.0		11.0	~0.8	7.0

[a] See Table I for conditions.



VIII
Z (cis)



IX
E (trans)

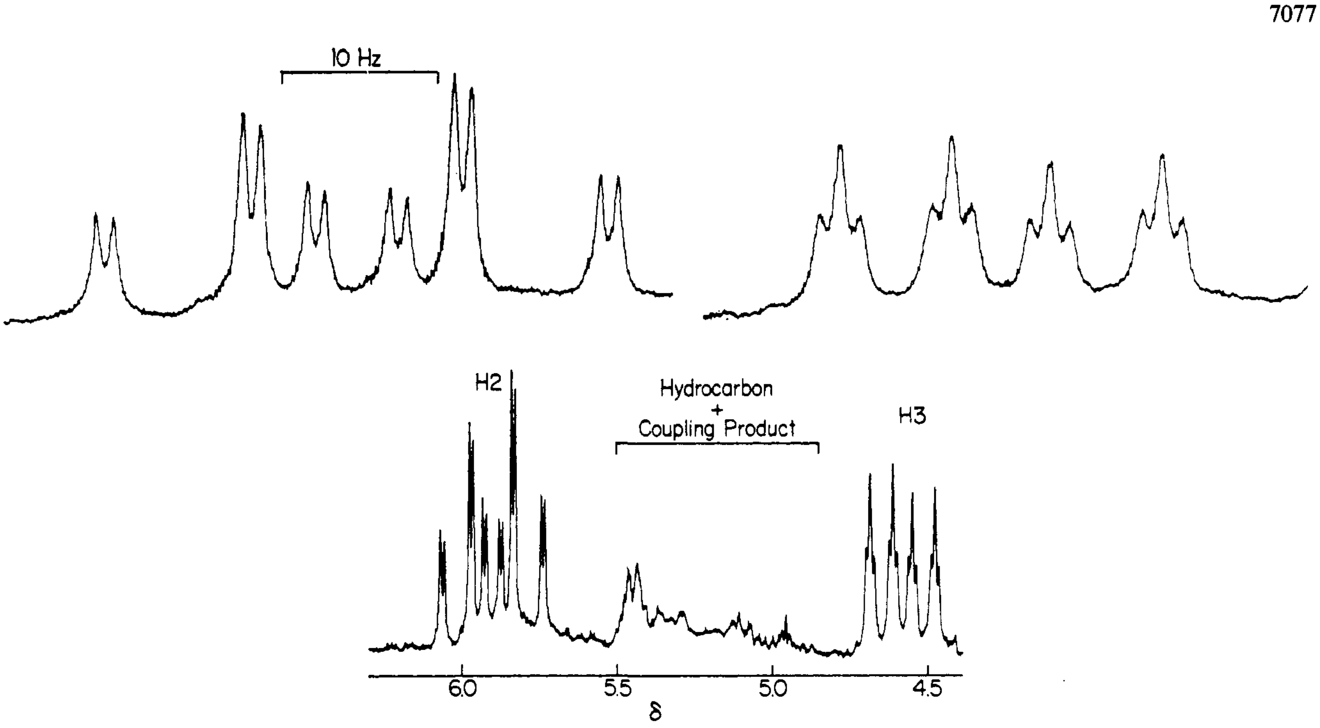


Figure 2. The proton nmr spectrum of (0.5 *M*) γ-isopropylallylmagnesium chloride (III) in Et_2O at probe temperature (32°). The upper spectra show each multiplet on an expanded sacle. Signals due to the small amount of hydrocarbon impurity are indicated.

J_{23} for allylic anions where equilibration has been unequivocally slowed or stopped have been reported by several workers.[8-13] The cis coupling constants range from 8.6 to 9.6 Hz and the trans coupling constants from 15.1 to 15.4 Hz. We have used these allylic anions as models for allylic Grignards. Support for this physical behavior comes from both nmr data and chemical quenching studies. The amounts of (*Z*)- and (*E*)-2-butenes formed after reaction of the allylic Grignards with excess numerous strong and weak acids indicate that the *Z*:*E* ratios tend to vary little with protonation conditions from an average value. If one accepts that the protonation reaction to form the 2-butenes is rapid compared to the stereochemical equilibrium rate, then one has an independent check on the validity of the ratios derived from coupling constants. Assuming average values within the aforementioned ranges for J_{23}(cis and trans), one can calculate equilibrium ratios of *Z* and *E* isomers. Those compare well with those average 2-butene values found from the protonation reactions and hence support our assumptions. Table III shows such a comparison.

Alternatively if one takes those amounts of *Z* and *E* isomers from the protonation experiments, a system of simultaneous linear equations can be solved for J_{23}(cis) and J_{23}(trans). In this way, a J_{23}(cis) value of 8.6 Hz (range 8.0–9.5 Hz) and a J_{23}(trans) value of 15.1 Hz (range 14.8–15.3 Hz) can be calculated. These values fall precisely within the lower end of the model allylic anion systems studied previously.[8-13] From Table III, one can see the empirical "cis rule" in this system as it has been shown in other allylic systems. In the absence of steric hindrance, the allylic Grignard prefers the *Z* configuration: (I) *Z*:*E* = 60:40 and (II) *Z*:*E* = 45:55. When steric hindrance becomes significant, the *Z* preference gives way to *E* preference. In contrast to I and II, *tert*-butylallyl Grignard (IV) exists predominately, if not exclusively, in the *E* configuration.

Table III. Stereochemical Equilibria of Allylic Grignards

Substituent	*Z*:*E* from J_{23}[a]	*Z*:*E* from quenching reaction
Me (I)	60:40	54:46
Et (II)	45:55	39:61
i-Pr (III)	30:70	23:77
t-Bu (IV)	3:97	0.2:99.8

[a] Assuming $J_{23}(cis)$ = 9.2 Hz and $J_{23}(trans)$ = 15.25 Hz.

A consideration of the H_1–H_2 coupling constant also leads to some interesting conclusions about the geometry of the allylic Grignard system. H_2 is coupled equally to both of the protons of C_1, and it was impossible to differentiate or freeze out these inherently nonequivalent hydrogens under any of the experimental conditions used. Thus there must be rapid rotation about the C_1–C_2 bond on the nmr time scale. However, the magnitude of J_{12} clearly shows that this rotation is *not* just an equilibrium between *Z* and *E* hydrogens on C_1 in the planar allylic system **3**. An equilibrating system of this type should have an average coupling constant of about 12 Hz, as found in model allylic carbanion systems (averaging J_{12}(cis) = 8.6–9.6 Hz and J_{12}(trans) = 13.8–15.1 Hz.[7-13]). The apparent low value cannot be attributed to unequal isomer populations favoring the form with a cis coupling because any

---

(8) (a) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968); (b) P. West, J. I. Purmort, and S. V. McKinley, *ibid.*, **90**, 797 (1968).

(9) G. J. Heiszwolf, J. A. A. Van Drunen, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **88**, 1377 (1969).

(10) (a) H. Kloosterziel and J. A. A. Van Drunen, *Recl. Trav. Chim. Pays-Bas*, **89**, 270 (1970); (b) *ibid.*, **89**, 37 (1970); (c) *ibid.*, **89**, 32 (1970).

(11) (a) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **86**, 1345 (1967); (b) *ibid.*, **86**, 807 (1967).

(12) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

(13) W. H. Glaze, J. E. Hanicak, M. L. Moore, and J. Chaudhuri, *J. Organometal. Chem.*, **44**, 39 (1972).

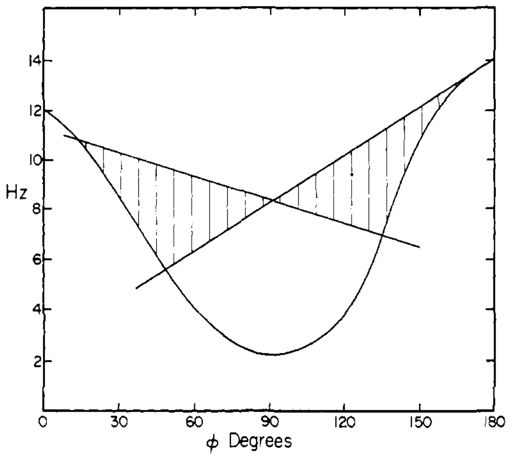
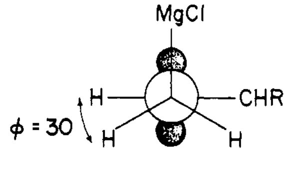


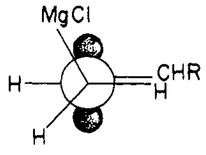
Figure 3. The Karplus curve constructed for determination of the conformation of allyl Grignards. The angle ϕ is defined in structure X. The shaded areas represent the conformations where the theoretical averaged coupling constant (J_{12}) matches the observed value.

planar structure must have equal numbers of hydrogens with cis and trans couplings. Even with rapid rotation about the C_1–C_2 bond, an average of one cis and one trans coupling will be observed. Thus, the compounds cannot have *exclusively* a rigid planar allylic carbanion system of type **3** between C_1 and C_2 unless our choice of reference coupling constants is substantially in error, which seems unlikely.

The question arises whether the observed coupling constants are consistent with a single bond between C_1 and C_2. To answer this, we have assumed that vicinal coupling constants in alkyl systems should provide a suitable model for the C_1–C_2 coupling constants in the corresponding allylic systems. The coupling constants for alkyl Grignards have been reported by Roberts[14,15] and Fraenkel.[16] An anti coupling constant (dihedral angle H–C–C–H of 180°) of 14.2 Hz and a gauche coupling constant (dihedral angle of 60°) of 4.0 Hz were reported. Previous workers have shown that the replacement of one sp^3-hybridized carbon by an sp^2-hybridized center has only a very small effect on the vicinal coupling constants[17a] and this was taken into account in the treatment of the data. Assuming a Karplus relationship is valid,[17] namely that the J_{12} is a function of the dihedral angle between H_1 and H_2, then the two alkyl Grignard coupling constants define a working Karplus curve (see Figure 3).[17] The conformational preference can now be deduced within the following constraints. The observed coupling constant of about 9 Hz must represent the average of the couplings of both hydrogens at C_1 with H_2 since individual splitting patterns were not observed. The average is taken over all preferred conformations weighted according to their populations. Also, it is assumed that the H–C–H angle does not differ appreciably from 120°. These limitations require that the major conformer be close to structure X because at least one of the dihedral angles must be close to 0 or 180°. Distortion toward structure XI would also be compatible with the data. However, conformations close to XII cannot contribute significantly because the average coupling constant would be about 6 Hz. It should be noted that rotation by 180° around the C_1–C_2 bond in X leads to an energetically equivalent conformer in which the C_1 hydrogens have been interchanged. Interconversion between the two equivalent X conformers can account for the observed spectrum. If steric interaction between the γ-alkyl group and the magnesium distorts the molecule toward structure XI, the observed coupling constant should decrease. In this context, it is interesting to note the small but real decrease in J_{12} from 9.6 to 9.1 Hz, as R increases in size from methyl to *tert*-butyl. Further qualitative support for the conformational preference comes from the long-range allylic coupling J_{13}. Although no good quantitative models exist for our systems, data for other allylic compounds[18] suggest that conformations related to XII should have J_{13} ~2.5 Hz. Conformations related to X and XI should have J_{13} ~1–1.5 Hz in accord with the observed values.

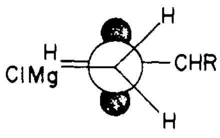


X



XI

An alternative model which cannot be rigorously excluded is that the Grignard exists as a rapidly equilibrating mixture (*ca.* 50:50) of the planar structure **3** and structure **1** in conformation XII. For reasons of simplicity and the data for the Schlenk equilibrium (see below), this latter possibility seems remote. The



XII

data presented are therefore consistent with the structure having substantial single bond character in the C_1–C_2 bond and C_1 having substantial sp^3 character. There can be little doubt that the magnesium is localized at C_1 and that its presence controls the geometry at C_1.

While no single definitive structure can be delineated for the symmetrical systems allylmagnesium chloride (VII) and 1,3-dimethylallylmagnesium chloride (VI), any proposed structure must meet several spectral criteria. The structure must account for the symmetry of the spectrum, the equivalence of the terminal hydrogens in the allyl system and of the methyl groups in the 1,3-dimethylallyl system, as well as the magnitude of the coupling constants. All of these requirements demand that there be rapid rotation around both the C_1–C_2 and the C_2–C_3 bonds. Assuming a delocalized planar allylic structure (**3**), the 1,3-dimethylallyl compound must exist predominantly as rapidly interconverting

---

[14] G. M. Whitesides, M. Witanowski, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 2854 (1965).

[15] M. Witanowski and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 737 (1966).

[16] G. Fraenkel and D. T. Dix, *J. Amer. Chem. Soc.*, **88**, 979 (1966).

[17] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969: (a) p 284; (b) p 282; (c) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 104.

[18] (a) M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971); (b) G. P. Newsoroff and S. Sternhell, *Aust. J. Chem.*, **25**, 1669 (1972).

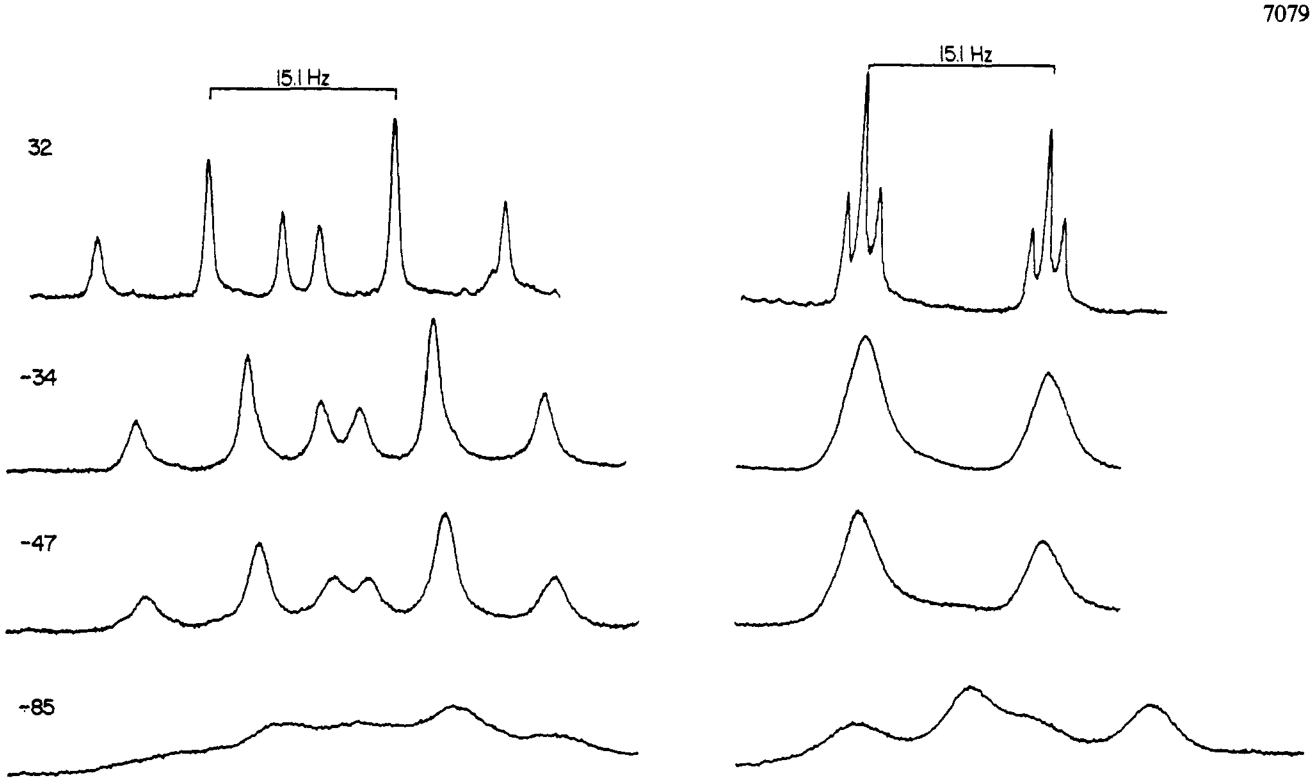
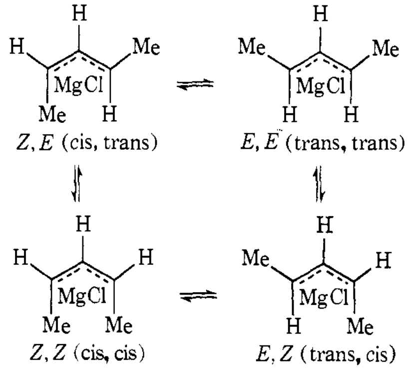
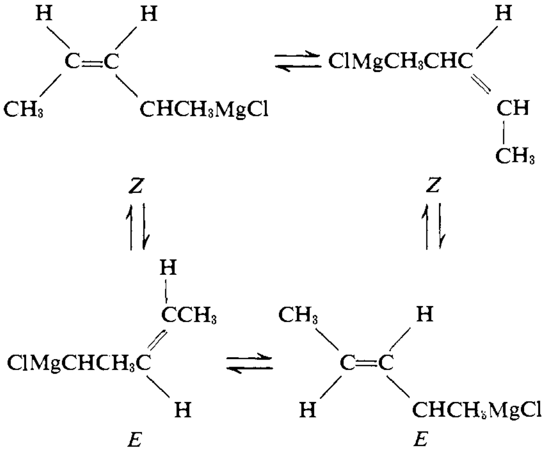


Figure 4. The spectra of H_2 (left) and H_3 (right) of (0.13 *M*) γ-*tert*-butylallylmagnesium chloride (IV) in Et_2O as a function of temperature. Note particularly the −85° spectrum for H_3 which shows the pair of doublets attributed to the R_2Mg species (major) and the RMgX species (minor).

Scheme I



Scheme II



isomers (Scheme I). From the magnitude of the coupling constant it would appear that there is about a 70% *Z* and 30% *E* isomer ratio present. The exact ratios of the *Z–Z*, *Z–E*, and *E–E* forms cannot be found from the coupling constant without some idea as to the relative stabilities of the individual isomers. An alternative explanation of this behavior is that there is present a series of degenerate positional isomers related to structure **1**, as was discussed for the monosubstituted compounds, with about 70% *Z* and 30% *E* isomers present (Scheme II). This latter interpretation involving a localized magnesium atom seems preferable on the basis of the Schlenk equilibrium data (see below).

Variable-temperature studies were done in order to try to freeze out individual stereoisomers of the Grignards and to obtain their relative energies (see, for example, Figure 4). Surprisingly, there was no variation of the coupling constants over a temperature range of 100°. Each Grignard was cooled to at least −70° and some to −100°, and the low-temperature coupling constants were within ±0.2 Hz of the room-temperature ones. The uncertainty in the coupling constants was due to considerable line broadening and signal overlap which occurred at low temperatures. The line broadening was due to viscosity effects because the signals arising from hydrocarbon side products showed similar broadening. Although the coupling constants remained nearly constant, marked changes did take place in the spectrum as the temperature was lowered. Upon cooling the sample, the signals due to H_2 and H_3 broadened and then separated into two sets of signals for each proton. Because of solvent interference and peak overlap, the high-field region of the spectrum (containing H_1 and the alkyl group signals) was not examined in detail. This discussion will focus on the changes in the H_2 and H_3 region where spectral changes were clearly monitored. Line broadening was significant at low temperatures, and peaks were often too broad to resolve long-range couplings. However, careful comparison of spectra for a number of temperatures combined with computer simulation of the broadening (chemical shifts and coupling constants constant) allowed straightforward analysis of the three bond couplings. At low temperature, each multiplet showed two components, slightly different in chemical shift but with the same coupling pattern as the room-temperature spectrum. The relative intensities of the two components varied significantly with temperature. This behavior can be interpreted as a slowing of the Schlenk equilibrium so that the individual resonances of R_2Mg and RMgCl can be observed. This interpretation was confirmed by showing that the component assigned to R_2Mg had the same chemical shift and coupling constants as an authentic sample of R_2Mg and that the equilibrium could be shifted in favor of the R_2Mg component by the addition of dioxane. It was also shown that these spectral changes were probably not due to the presence of an adventitious alkoxide equilibrium. The addition of 10 mol % of isopropyl alcohol simply increased the intensity of the hydrocarbon signals without changing the position or coupling pattern of the signals associated with the Grignard. The coupling constants observed in the R_2Mg component were the same within ±0.3 Hz as those for the Grignard itself. Thus, any conclusions drawn about the stereochemistry of the Grignard RMgCl *apply as well* to the R_2Mg.

A quantitative determination of the position of the Schlenk equilibrium was made on the *tert*-butylallyl Grignard (IV) and on the α,γ-dimethylallyl Grignard (VI). The results are shown in Table IV and representative spectra are given in Figure 4. The other Grignards (I–III) could not be precisely quantitated due to extensive signal overlap, but the spectral changes agreed qualitatively with those for compounds IV and VI. The magnitude of the equilibrium constant provided additional support for the suggestion that the allyl Grignards exist predominantly as localized structures (**1** or **2**). By combination of the published data for localized and delocalized Grignards and extrapolation of these data to a common temperature in diethyl ether solvent, the following Schlenk equilibrium constants (eq 1) were obtained. In comparison with the experimental equilibrium constant of about 50 for the allylic systems investigated here, completely localized *tert*-butylmagnesium chloride[19] has an equilibrium constant of 16 and extremely delocalized cyclopentadienylmagnesium chloride[20] has an equilibrium constant of 200,000. These results would indicate that the allylic systems in this study largely favor the vinyl carbinyl structure **1** and not the delocalized structure **3**.

Table IV. Equilibrium Constants[a] in Et_2O for $R_2Mg + MgCl_2 \rightleftharpoons 2RMgCl$

Temp, °C	$\mathrm{R = (CH_3)_3CCH{=}CHCH_2{-}}$	$\mathrm{R = CH_3CH{=}CH\underset{\vert}{C}HCH_3}$
−47	14	
−56		9
−65	2.3	6.8
−75	1	3.4
−86	0.44	2.5

[a] Note that because of signal overlap and the formation of a precipitate at low temperature, these constants may be in error by as much as a factor of 2.

No attempt was made to obtain rate data for the exchange processes because apparently equivalent samples prepared at different times showed coalescence temperatures which differed by as much as 40°. All Grignard samples did show line-broadening effects due to slowing of the Schlenk equilibrium in the region 0 to −80°, and in each case H_1 broadened at a higher temperature than H_2. This behavior is expected because the chemical shift difference between R_2Mg and RMgCl is greater for H_1 than for H_2. Probably the most important feature of the rate data is that the *Z–E* interconversion is rapid on the nmr time scale at temperatures as low as −80°. This rapid interconversion must be taken into account when interpreting the stereochemistry of any reaction products derived from these Grignards.

Discussion

Many of our conclusions about the structure of allylic Grignards in ether solution are based on interpreting the H_2–H_3 coupling constant in terms of a rapid *Z–E* interconversion. The premise for this conclusion is that the cis and trans ethylenic coupling constants are essentially invariant with different alkyl substituents in molecules of fixed geometry. Suitable model systems exist in the literature in support of this premise.[21] Ideally, 1,2-disubstituted ethylenes should have been chosen as models for the coupling constant analysis. However, the dependence of ethylenic coupling constants on substituent electronegativity is well known[22] and the question of the electronegativity of the CH_2MgCl group presents an unanswered problem. Within the general range of expected electronegativities of this group, the cis and trans coupling constants differ by 4–7 Hz. At worst, the analysis given in Table III may be in error by underestimating the amount of *Z* isomer present if the spread of *J* values was 4 Hz or if the assumed trans coupling constant was low. However, such numerical errors do not alter the general trends. The use of protonation results may be regarded as purely circumstantial in such rapidly equilibrating systems, but the close match between protonation results (obtained with a wide range of protonating agents[23]) and coupling constant analysis provides some support for our conclusions. Unfortunately there are no definitive nmr studies of model Grignard systems published which would provide suitable reference data to allow a check on our assumptions.

A number of allylic anion examples are available to provide models for cis and trans allylic coupling. A survey of the published data is shown in Table V. The data of Dolinskaya, *et al.*,[24] for crotyllithium have not been included in this survey because of their inconsistent allylic coupling constants, splitting patterns, and variable-temperature data. It is clear from Table V that where bond rotation has been unequivocally

---

(19) G. E. Parris and E. C. Ashby, *J. Amer. Chem. Soc.*, **93**, 1206 (1971).

(20) W. T. Ford and J. B. Grutzner, *J. Org. Chem.*, 37, 2561 (1972).

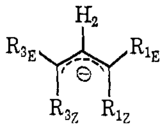
(21) A. A. Bothner-By, *Advan. Magn. Resonance*, 1, 195 (1965).

(22) Reference 17, p 302.

(23) D. A. Hutchinson and R. A. Benkeser, unpublished observations.

(24) E. R. Dolinskaya, I. Y. Poddufnyi, and I. U. Tsereteli, *Dokl. Akad. Nauk SSSR*, **191**, 862 (1970).

Table V. Coupling Constants in Allyl Anions



Counter-ion	Solvent	R_{1E}	R_{1Z}	R_{3E}	R_{3Z}	J_{1E2} (cis)	J_{1Z2} (trans)	J_{23E} (cis)	J_{23Z} (trans)	Ref
Li^+	THF	H	H	H	H	8.6	15.2	8.6	15.2	8b
Li^+	THF	H	H	Ph	H	9.4	15.4		12.2	8a
K^+	NH_3	H	H	Ph	H	9.3	15.4		12.2	11a
K^+	NH_3	CH_3	H	Ph	H		13.8		11.4	9
K^+	NH_3	H	CH_3	Ph	H	9.8			12.5	9
K^+	NH_3	H	H	Ph	CH_3	9.4	15.2			10b
K^+	NH_3	H	H	Vinyl	H	9.0	15.1		11.5	11b
Li^+	THF	H	H	Vinyl	H	9	16		11	12
K^+	NH_3	H	CH_3	Vinyl	H	8.7			11.5	9
K^+	NH_3	CH_3	H	Vinyl	H		13.7		11.2	10a
K^+	NH_3	H	H	C_3H_5	H	8.8	15.1		11.5	9
K^+	NH_3	H	H	C_3H_5	H	9.0	15.2		11.2	10a
K^+	NH_3	H	H	Ph	Ph	10.4	16.4			11a
K^+	NH_3	H	OCH_3	Ph	H	5.5			12.1	10c
K^+	NH_3	OCH_3	H	Ph	H		11.2		11.6	10c
Li^+	Toluene	H	C_5H_{11}	H	H	10.0			10.0	13
Li^+	Toluene	C_5H_{11}	H	H	H		14.5		9.4	13

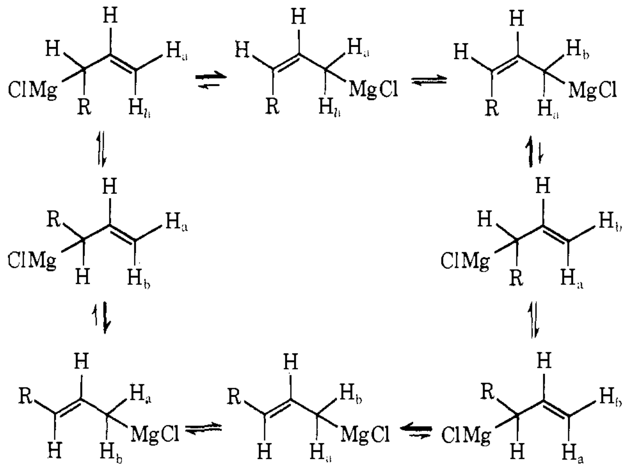
slowed, the cis and trans coupling constants are about 9 and 14 Hz, respectively.

In the literature examples, the proof that bond rotation had been stopped on the nmr time scale was the observation of discrete cis and trans coupling constants of a terminal vinyl group. In the more heavily substituted systems, proof that bond rotation has been slowed relied on the differentiation and detection of the signals due to the individual stereoisomers. The data in Table V show that, where separate isomers had apparently been detected, the trans coupling constant had a somewhat lower value than those found here and those reported for terminal vinyl groups. Furthermore, for internal double bonds where the substituents are presumably in the *E* orientation, markedly lower trans coupling constants (11–12 Hz) have been found. There are two possible explanations for these observations. First, increased delocalization leads to lower bond orders in internal bonds and hence to smaller coupling constants.[12,25] Substituents could also act to lower the bond orders of some substituted allylic systems. Second, the observed couplings may represent the average of a rapidly equilibrating *Z* and *E* isomeric mixture. Whatever the explanation, the literature examples of internal coupling constants do not provide a definitive model, and so the values for the terminal vinyl group have been taken as a reference point. Therefore, there can be little doubt in the conclusion that a rapid *Z*–*E* interconversion is taking place in our reported alkyl-substituted allylic Grignards. The preference of these systems for a *Z* geometry at equilibrium was discussed previously. The propensity of anionic species for *Z* stereochemistry even in the presence of bulky groups has been noted and discussed by many authors, but no generally accepted rationale has been developed.[26,27]

Another major conclusion drawn from the coupling constants is that the Grignards exist as a vinyl carbinyl group (structure **1**) rather than a completely delocalized carbanionic group (structure **3**). Schlenk equilibria data support this conclusion for both the symmetrically and the unsymmetrically substituted compounds. The equilibrium constant of 50 for the allylic Grignards is similar to that of 2,2-dimethylpropylmagnesium chloride, 16, and not of cyclopentadienylmagnesium chloride, 200,000. There is no completely satisfying rationale for this dependence of the Schlenk equilibrium on the nature of R.

Accounting for all of these observations, the mechanistic pathway of Scheme III is suggested. At least one and probably all of these species must be in equilibrium with the corresponding diallylmagnesium, which itself is undergoing rapid 1,3 shifts and bond rotation. No conclusions can be drawn about the state of aggregation of the Grignards studied. This proposed reaction scheme should be regarded as the simplest representation of a process which may be occurring in higher aggregates. The internal rearrangements are faster than the Schlenk equilibrium rate for both the allylmagnesium chloride compounds and the diallylmagnesium compounds. Accordingly, the bond rotations must occur independently in each type of com-

Scheme III



---

(25) H. Kloosterzeil, *Recl. Trav. Chim. Pays-Bas*, **89**, 300 (1970).
(26) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).
(27) S. Bank, *J. Amer. Chem. Soc.*, **87**, 3245 (1965).

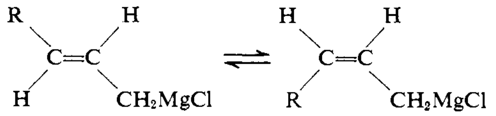
pound. The data presented are consistent with a polar, localized magnesium atom bonded to the carbon atom either with a very polar σ bond or, as discussed previously, as a tight ion pair. The latter interpretation is also consistent with the upfield shift of H_3, the steric effects due to the magnesium atom at C_1, the somewhat larger Schlenk equilibrium constant, and the facile configurational equilibria. The inclusion of secondary Grignards as intermediates is reasonable because of the indirect evidence for tertiary intermediates.[4] Our inability to freeze out this equilibrium is understandable because a 1–2° interconversion should have a lower activation barrier than a 1–3° interconversion. Further support for these conclusions comes from Kwart's study[28] of allyltrimethylsilanes, where 5% of the secondary isomer was isolated after thermal equilibration.

No attempt was made to quantify these various kinetic processes because of considerable variation in the line-broadening characteristics of apparently identical samples prepared on different days. This was not a concentration effect because a threefold change in concentration had no effect on the spectra of samples prepared from the same batch. Similar observations have been made by other workers.[19,20] Catalytic amounts of transition metal alkyls may catalyze these interconversions and their presence may explain this anomalous behavior. Unlike kinetic data, thermodynamic data are independent of these influences. The invariance of the ratio of *Z* to *E* stereoisomers over the 100° temperature range studied requires that the enthalpic and entropic contributions to the stereoisomers' free energy difference be equal and opposite or zero.

Although the rate data are lacking, the inability to freeze out the *Z*–*E* interconversions at temperatures as low as −80° is important to the chemistry of these species. Based on line-shape arguments, the lifetime of each discrete species must be less than 10^{-3} sec at −80°. Any products from a reaction involving the allylic Grignards that takes longer than 10^{-3} sec to occur will not reflect the composition of the reagent. The product composition will reflect not only the equilibrium populations but also the relative kinetics for reaction of each component.

Conclusion

From these data it can be concluded that alkyl-substituted allylic Grignard reagents in diethyl ether solution exist as a rapidly equilibrating mixture of *Z* and *E* primary isomers to the limits of the detectability of proton nmr. The work reported here shows that the allylic Grignards are better represented as localized vinyl carbinyl systems (structure **1**) rather than delocalized allylic anions (structure **3**). There is rapid rotation around the C_1–C_2 bond at temperatures down to −100°. These vinyl carbinyl reagents show rapid isomerization on the nmr time scale about the formal double bond and exist as a mixture of *Z* and *E* primary isomers. This "bond rotation" is suggested to occur *via* the intermediacy of an undetectably low concentration of the secondary vinyl carbinyl system (Scheme III) by analogy with previous work. Thus the dominant species in these reagents are best formally represented by the equilibrium shown below. When the substituent R is small, such as methyl, the *Z* form is favored. As R increases in bulk, the proportion of *E* isomer increases until, when R is *tert*-butyl, there is almost exclusively *E* isomer present. Indirect measurement has estimated a cis vinyl coupling constant of about 8.6 Hz and a trans coupling of 15.1 Hz. With decreasing temperature the Schlenk equilibrium has been found to shift, increasing the amount of the diallylmagnesium compound. The stereochemistry of the diallylmagnesium compound is identical with that of the Grignard reagent in all cases observed. The magnitude of the Schlenk equilibrium constant suggests that the 1,3-dimethylallyl Grignard reagent also exists in the vinyl carbinyl form.[29]



Experimental Section

All spectra were recorded on a Varian XL-100 spectrometer with 12-mm samples. Sweep widths of 250 Hz or less were used to obtain spectral parameters with sweep rates of 0.5 Hz/sec or less. The diethyl ether solvent peaks were used for the lock signal and as a secondary reference for chemical shift measurements. Temperatures were measured with a Wilmad long-stem thermometer accurate to ±3°. No stem corrections were made. In many cases, lowering the temperature resulted in precipitation of a solid. This behavior is exactly analogous to the behavior of simple alkyl Grignards discussed in detail by Ashby.[19] The nmr studies were performed on samples of 0.1–0.5 *M* formal Grignard concentration. Samples were prepared by distilling from $LiAlH_4$, under a nitrogen atmosphere, diethyl ether (A. R. Mallinckrodt anhydrous) into a tenfold molar excess of magnesium turnings (Dow 99.8% minimum). The chloride was added over a 3-hr period. Each chloride was prepared and characterized as the *trans*-3-alkyl-1-chloro-2-butene with less than 3% of the 3-alkyl-3-chloro-1-butene isomer. The chlorides were distilled prior to use and stored over anhydrous $MgSO_4$. The samples were originally 0.13 *M* as prepared and concentrated by removal of solvent at reduced pressure. The solutions were centrifuged and only the clear supernatant was used. All solution handling was done by syringe under nitrogen and the nmr tubes were sealed. Complete details of the quenching reactions will be published at a later date. In all cases, small amounts (<10%) of hydrocarbon side products (butenes and coupling products) were present in solution. These impurities had no observable effect on the spectral parameters discussed. In a few cases the Grignards were also prepared in THF and the spectra were essentially equivalent to those obtained in ether.

Acknowledgment. The authors are grateful to the National Science Foundation and Eli Lilly & Co. (J. B. G.), whose financial assistance made this work possible.

---

[28] H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.*, **94**, 2515 (1972).

[29] NOTE ADDED IN PROOF. Since this paper was submitted the work of Glaze and coworkers[30] became available to us. Their results and conclusions are in close agreement with those reported here. The neopentyl group appears to have about the same effective size as the isopropyl group in our studies. The correlation between coupling constant and protonation has been verified by these workers by freezing out the individual stereoisomers. While the rate difference of isomer interchange varies considerably between the work of Glaze and our own, this probably is due to differences in sample preparation methods. It is worth noting that Zeiger and Roberts[31] were unable to stop rotation in diallylmagnesium at temperatures as low as −120°. It is tempting to ascribe the chemical shift and coupling constant variation of the neopentylallyllithium to an increasing amount of the delocalized anion compared with the vinyl carbinyl form as solvent polarity increases.

[30] (a) W. H. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, *J. Organometal. Chem.*, **51**, 13 (1973); (b) W. H. Glaze and C. R. McDaniel, *ibid.*, **51**, 23 (1973).

[31] H. E. Zieger and J. D. Roberts, *J. Org. Chem.*, **34**, 1975 (1969).