Organomagnesates from Reactions of Dialkylmagnesium Compounds with Alkali-Metal Alkoxides, Potassium Hydride, and Other Salts

Erin M. Hanawalt, Julius Farkas, Jr., and Herman G. Richey, Jr.*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received July 21, 2003

Reactions of R_2Mg and KOR′ in benzene form solutions containing organomagnesates that incorporate equal amounts of the reactants. NMR spectra of preparations in which the choice of R and R′ leads to stereoisomers are consistent with a dimeric organomagnesate structure in which the magnesium atoms of two R_2Mg units are bridged by the oxygen atoms of two OR′ groups. Similar species result when NaOR′ is the salt or diethyl ether is the solvent. When less than 1 equiv of KOR′ is used, other species also are present. Reactions in benzene of R_2Mg with some other salts, including tetrabutylammonium halides and $LiNR'_2$ compounds, also furnish 1:1 organomagnesates, but reactions with KH can lead to solutions of R_3MgK.

Organomagnesate ions such as R_3Mg^- are known in crystalline solids and in solutions.[1] Solutions containing such organomagnesates exhibit reactivities different from those of RMgX (Grignard reagents) or R_2Mg.[1] With ketones, for example, such solutions furnish addition products but very much less of the reduction products that often are significant or even major products when the organic group of RMgX or R_2Mg has a β-hydrogen.[2] Reaction of R_2Mg with a salt having an anion (A^-) that might bind to the magnesium (eq 1) is a possible way

$$R_2Mg + M^+A^- \rightarrow R_2MgA^- + M^+ \qquad (1)$$

of generating an organomagnesate ion and the associated reactivities. Indeed, addition to R_2Mg of an alkali-metal alkoxide[2,3] or a tetraalkylammonium halide[2,4] increases the addition/reduction ratio in R_2Mg−ketone reactions. This paper describes efforts to determine compositions and structures of species in solutions formed by combining R_2Mg and salts.

Results and Discussion

R_2Mg + KOR′ (1:1).[5] Much of the work concerned solutions containing the elements of equimolar amounts of R_2Mg and an alkali-metal alkoxide (or aryloxide). The cation usually was potassium, the temperature was ca. 23 °C, and, except where specifically noted, the solvent was benzene (benzene-d_6).

Table 1. R_2Mg−MOR′ Preparations[a]

R	M	OR′	^1H NMR, δ(α- or *o*-H)
Hex	K	OMe	−0.76
Hex	K	OEt	−0.79
Hex	K	O-*t*-Bu	−0.82
Hex	K	OPh	−0.74
Hex	K	OCHMePr	−0.80[c]
Hex	K	OCH_2CMe_3	−0.75
Hex	K	$OC(Me_2)Et$	−0.80
Np	K	OMe	−0.59
Np	K	O-*t*-Bu	−0.49
Np	Na	OMe	−0.28
2-EtBu	K	OMe	−0.93
2-EtBu	K	OPh	−0.78
3,3-Me_2Bu	K	OEt	−0.99
3,3-Me_2Bu	K	OPh	−0.90
s-Bu	K	OMe	−0.99[c]
s-Bu[b]	K	OMe	−0.92[c]
s-Bu	Na	OMe	−1.02[c]
p-*t*-BuPh	K	OMe	8.12

[a] Except where noted, the solvent is benzene-d_6. NMR absorption areas of all preparations are consistent with an R:OR′ ratio of 2. [b] The solvent is Et_2O-d_{10}. [c] Average position of a cluster of absorptions (see text).

When a benzene solution of an R_2Mg compound was stirred with ≥1 equiv of a KOR′ compound that is relatively insoluble in benzene (e.g., KOMe, KOEt, KONp (Np = neopentyl = $(CH_3)_3CCH_2$), KOPh), R:OR′ ratios of 2 found from relative areas of ^1H NMR absorptions indicate that 1 equiv *but never more* of KOR′ dissolved. Significant amounts of some R_2Mg compounds relatively insoluble in benzene (e.g., Et_2Mg, $(2\text{-EtBu})_2Mg$ (2-EtBu = 2-ethylbutyl), $(3,3\text{-}Me_2Bu)_2Mg$ (3,3-Me_2Bu = 3,3-dimethylbutyl)) dissolved in the presence of some KOR′ compounds.[6] Table 1 lists solutions that were prepared. Aliquots of some solutions were hydrolyzed and then analyzed for base, K, and Mg. For a solution

---

* To whom correspondence should be addressed. E-mail: hgr@chem.psu.edu.

(1) Richey, H. G., Jr. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, U.K., 1996; Vol. 1 (Gokel, G. W., Vol. Ed.), Chapter 21.

(2) Richey, H. G., Jr.; DeStephano, J. P. *J. Org. Chem.* **1990**, *55*, 3281.

(3) Georgoulis, C.; Gross. B.; Ziegler, J.-C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1971**, *273*, 378. Ziegler, J.-C. Doctoral Dissertation, L'Université de Nancy I (undated).

(4) Chastrette, M.; Amouroux, R. *Bull. Soc. Chim. Fr.* **1970**, 4348.

(5) Some preliminary work with alkoxides: Hanawalt, E. M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4983.

(6) Ph_2Mg, itself insoluble in benzene, was reported to dissolve in the presence of some alkali-metal alkoxide salts.[7]

10.1021/om030544k CCC: $27.50

prepared from Np_2Mg and excess KOMe in benzene, total base:Mg:K was 3:1:1. Since the base determination includes RMg and OR′ groups, these results combined with the R:OR′ ratio of 2 indicate the solution to have a 1:1 R_2Mg:KOR′ composition. The rate of dissolution depended on the alkoxide. With Hex_2Mg (Hex = hexyl), for example, dissolution took as long as 24 h with KOMe and 5 h with KOEt but 30 min with KOPh and only a few minutes with KONp, KOCHMePr, or $KOCMe_2Et$; even with KOMe, which is particularly insoluble, concentrations of at least 0.4 M were ultimately obtained. The rate of dissolution also depended on R_2Mg; dissolution of KOMe took as long as 24 h with Hex_2Mg but only 30 min with Np_2Mg and 5 min with *s*-Bu_2Mg.

One entry in Table 1 is for *s*-Bu_2Mg and KOMe in diethyl ether-d_{10}; although excess KOMe (a compound not significantly soluble in diethyl ether) was used, the solution's composition is 1:1. Analysis of solutions prepared in diethyl ether from Np_2Mg and excess KOMe and from Et_2Mg and excess KOMe or KOPh found total base:Mg:K to be 3:1:1.[8]

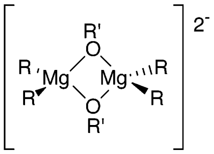
A ^1H NMR absorption of each 1:1 solution is listed in Table 1. Except for solutions (prepared with *s*-Bu_2Mg or KOCHMePr as one component) in which a reactant has a chiral group, only a single ^1H NMR absorption is found for each structural type of H. Concentrations were mainly in the range 0.1−0.8 M, and the spectra vary little with concentration. Absorptions generally are as sharp as expected for routine small molecules;[9] this contrasts to broader absorptions of some of the R_2Mg compounds (especially Hex_2Mg) in the absence of alkoxides, probably due to the presence of associated species, between which exchange of R groups is not very rapid relative to the NMR time scale. ^{13}C NMR spectra of Hex_2Mg−KOR′ solutions also show only a single sharp absorption for each structural type of C. The ^1H NMR absorptions of CH_2CH_2Mg in the solutions with Hex_2Mg and $(3,3\text{-}Me_2Bu)_2Mg$ generally are of the type AA′XX′ rather than A_2X_2, indicating that inversion of the hexyl groups is slow relative to the NMR time scale.[10]

Monitoring ^1H NMR absorptions indicated that many solutions underwent little decomposition over a period of several days. Some solutions prepared with *s*-Bu_2Mg and with Np_2Mg, however, decomposed slowly. Mes_2Mg (Mes = 2,4,6-trimethylphenyl) preparations were unstable; the principal NMR absorptions were of mesitylene. Preparations of Np_2Mg with $KOCH(CH_2NMe_2)_2$, an alkoxide with N atoms that might coordinate to K, also led to decomposition (even when excess Np_2Mg was used).

The solubility of KO-*t*-Bu in benzene permits the preparation of solutions containing more KO-*t*-Bu than R_2Mg. While 1:1 KO-*t*-Bu−Np_2Mg solutions underwent significant decomposition within 1 h, preparations with excess KO-*t*-Bu decomposed much more rapidly: within 15 min the CH_2Mg absorption had disappeared and a large neopentane absorption had appeared.

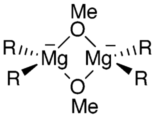
The NMR and analytical results indicate that a species having a 1:1 MOR′/R_2Mg composition is the only significant component in many solutions. The positions of the CHMg absorptions in ^1H NMR spectra are consistent with such species being organomagnesates. These absorptions are significantly upfield from the corresponding absorptions[11] of R_2Mg (for example, the CH_2Mg absorption of Hex_2Mg is at δ 0.19 but those of 1:1 KOR′−Hex_2Mg preparations are between δ −0.7 and −0.8) just as CHZn absorptions of 1:1 KO-*t*-Bu−R_2Zn organozincates are significantly upfield from those of R_2Zn.[12] Reports by Screttas and Micha-Screttas are relevant.[13] They found, for example, that PhK and PhNa, themselves insoluble in benzene, dissolve in benzene solutions of $Mg(OCH_2CH_2OEt)_2$ to form solutions with K:Mg and Na:Mg ratios of 1 and 2, respectively.[14] For the sodium case, an identical solution was prepared from Ph_2Mg and $NaOCH_2CH_2OEt$ (1:2).[15] ^1H and ^{13}C NMR spectra of the solutions they studied had only single sets of absorptions, however, and hence provided no structural information.[16]

As described below, NMR spectra of solutions in which the choice of R and R′ leads to stereoisomeric 1:1 R_2Mg−KOR′ species are consistent with structure **1** for the organomagnesates.

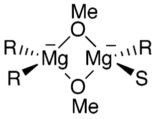


1

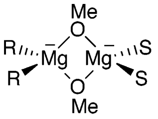
R_2Mg (R Chiral) and KOR′. When R is chiral (e.g., *sec*-butyl), seven stereoisomers have structure **1**: two pairs of enantiomers (**2** and its *S*,*S*,*S*,*S* enantiomer; **3** and its *R*,*S*,*S*,*S* enantiomer) and three other stereoisomers (**4**−**6**). Table 2 lists the relative amounts of these stereoisomers that are expected if *R* and *S* groups are distributed randomly (i.e., if isomers have equal stabilities). As indicated in the table, alkoxyl and R groups of some stereoisomers are diastereotopic; con-



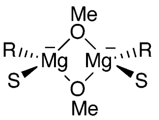
2



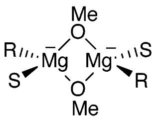
3



4



5



6

R = (*R*)-*s*-butyl

S = (*S*)-*s*-butyl

---

[7] Screttas, C. G.; Micha-Screttas, M. *J. Organomet. Chem.* **1985**, *290*, 1.

[8] Reactions of Np_2Mg and KOPh in benzene or diethyl ether resulted in large amounts of precipitate; the remaining solutions had virtually no solute (analysis after hydrolysis found the solutions to contain no base, Mg, or K).

[9] (*p*-tolyl)$_2$Mg (itself not very soluble in benzene) dissolved in the presence of some KOR′ compounds, but ^1H NMR absorptions of the resulting solutions were broad. Absorptions of solutions prepared with (*p*-*tert*-butylphenyl)$_2$Mg also were broad.

[10] The AA′XX′ pattern is particularly striking for the 3,3-Me_2Bu systems; because there is no additional coupling to their H's, the two CH_2 groups exhibit identical patterns. Some observations of AA′XX′ spectra for RCH_2CH_2Mg compounds: Whitesides, G. M.; Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 2854. Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878. Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 737.

Table 2. Properties of Stereosomers Having Structure 1 and a Chiral R Group

composition of R	statistical wt	NMR wt	OR′ groups	R groups
R,*R*,*R*,*R* (**2**)	1	2	identical	identical
S,*S*,*S*,*S*	1			
R,*R*,*R*,*S* (**3**)	4	8	diastereotopic	diastereotopic (4)
R,*S*,*S*,*S*	4			
R,*R*,*S*,*S* (**4**)	2	2	identical	identical
R,*R*,*S*,*S* (**5**)	2	2	identical	identical
R,*R*,*S*,*S* (**6**)	2	2	diastereotopic	identical

Table 3. ^{13}C NMR (125 MHz) Absorptions of Methoxide in a Benzene-d_6 Solution Formed from s-Bu$_2$Mg and KOMe

δ(CH$_3$O)	assignt	rel intens[a]
50.785	**6** and enantiomer[b]	1.81 (2)
51.601		
51.025	**3** and enantiomer[b]	7.29 (8)
51.430		
51.204	**2**, **4**, or **5**	2.17 (2)
51.241	**2**, **4**, or **5**	2.30 (2)
51.265	**2**, **4**, or **5**	2.43 (2)

[a] The total of the values is normalized to 16. The numbers in parentheses are the values expected if isomers have identical stabilities. [b] Two absorptions are observed because the methoxyl groups of this pair of enantiomers are diastereotopic.

Table 4. ^{1}H NMR Absorptions[a] of Benzene-d_6 Solutions Formed from s-Bu$_2$Mg and MOMe in the Absence or Presence of TMEDA[b]

	δ(*sec*-butyl)					δ(TMEDA)	
M	CH_3CH[c]	CH[d]	CH$_2$[d]	CH_3CH$_2$	δ(OMe)[e]	CH$_2$[e]	CH$_3$[e]
K	1.604 (1)	−0.99	1.95	1.33[d]	3.53 (1)		
	1.595 (1)				3.51 (4)		
	1.592 (1)				3.49 (6)		
	1.582 (2)				3.47 (4)		
	1.573 (1)				3.45 (1)		
	1.569 (1)						
	1.565 (1)						
Na	1.534 (1)	−1.02	1.90	1.26[f] (1)	3.43 (1)		
	1.526 (1)			1.25[f] (1)	3.41 (4)		
					3.39 (6)		
					3.36 (4)		
					3.34 (1)		
K	1.816 (1)	−0.47	2.13	1.45[d]	3.87 (1)	2.05	1.98
	1.809 (1)				3.85 (4)		
	1.809 (1)				3.83 (6)		
	1.804 (1)				3.81 (4)		
	1.791 (1)				3.79 (1)		
Na	1.813 (1)	−0.63	2.16	1.44[d]	3.86 (1)	2.11	2.04
	1.797 (1)				3.82 (4)		
					3.80 (2)		
					3.79 (4)		
					3.76 (4)		
					3.73 (1)		

[a] Spectra taken at 300 MHz. [b] s-Bu$_2$Mg (ca. 0.4 M), MOMe, and (when present) TMEDA were in the ratio 1:1:2.5. The approximate relative areas of absorptions for a particular hydrogen or group of hydrogens are given in parentheses. [c] All are doublets; $J \cong 7.7$ Hz. [d] Average position of a complex absorption. [e] All are singlets. [f] A triplet, $J \cong 7.2$ Hz.

sequently, seven NMR absorptions of alkoxyl and eight of R are potentially distinguishable.

NMR spectra of solutions prepared from s-Bu$_2$Mg and KOMe have multiple absorptions, in accord with the expectations for structure **1**. Seven methoxyl absorptions (Table 3)[17] were resolved in ^{13}C spectra (no more than five ^{13}C NMR absorptions, however, were resolved for any *sec*-butyl carbon). The absorption areas are relatively close to those expected if isomers had equal stabilities, permitting some assignments: the two largest absorptions must be due to the diastereotopic methoxyl groups of the *R*,*R*,*R*,*S* (**3**) and *R*,*S*,*S*,*S* enantiomers and the two smallest absorptions to the diastereotopic methoxyl groups of **6**. The *average* absorption position of each diastereotopic pair is close to the positions of the other three methoxyl absorptions, which must be due to the other three stereoisomers (**2**, **4**, and **5**). Except for the fact that the absorptions of **2**, **4**, and **5** coincide, the ^{1}H methoxyl absorptions mirror the ^{13}C absorptions: four noncentral absorptions due to the diastereotopic groups of **3** and **6** and the average position of each diastereotopic pair close to the common absorptions of **2**, **4**, and **5**. Both the ^{13}C and ^{1}H NMR spectra suggest that internal differences in environment of methoxyl groups are greater within the *R*,*R*,*S*,*S* isomer (**6**) and the *R*,*R*,*R*,*S*−*R*,*S*,*S*,*S* isomers (**3** and its enantiomer) than between stereoisomers. Models indicate that this is reasonable, as is the larger $\Delta\delta$ for the absorptions of the diastereotopic groups of **6** as compared to those of **3**. Surprisingly, more discrete absorptions for *sec*-butyl groups are evident in ^{1}H NMR spectra (Table 4) than in ^{13}C NMR spectra: seven sets of CH_3-CH absorptions are resolved.

Processes that could destroy the stereochemical integrity of **2**−**6** include (1) inversion of *sec*-butyl groups, (2) cleavage of the dimer structures followed by recombination, (3) exchange of *sec*-butyl groups between dimers, and (4) exchange of *sec*-butyl groups within dimers. If the first three processes were rapid relative to the NMR time scale, then the absorptions of the stereoisomers would be averaged. Since seven methoxyl absorptions (^{13}C NMR) and seven out of eight *sec*-butyl absorptions (^{1}H NMR) are resolved, none of these processes is rapid relative to the NMR time scale. The smallest $\Delta\delta$ resolved is 0.6 Hz (α-CH$_3$, ^{1}H NMR); thus, the configurations persist for at least 1 s. Even process 4, internal exchange of *sec*-butyl groups, cannot be rapid, since it would erase the diastereotopic differences in **3** and in **6** and result in identical absorptions for **4**−**6**.

Spectra also were taken in diethyl ether-d_{10}. Solubility was less than in benzene, but the absorption positions and the absorption patterns due to the presence of stereoisomers are remarkably similar to those in the spectra of benzene solutions. Six of the seven possible ^{1}H NMR methoxyl absorptions are resolved versus only five in benzene, but only four of the eight possible CH_3-CH doublets are resolved versus seven in benzene; in the ^{13}C NMR spectrum six methoxyl absorptions are resolved versus all of the possible seven in benzene.

R$_2$Mg and KOR′ (R′ Chiral). When R′ is chiral, stereoisomers **7**−**9** have structure **1**. NMR spectra potentially have one set of alkoxide absorptions for the

---

(11) This could not be verified for those R$_2$Mg compounds (Et$_2$Mg, (2-EtBu)$_2$Mg, (3,3-Me$_2$Bu)$_2$Mg) too insoluble in benzene for NMR spectra.

(12) Fabicon, R. M.; Richey, H. G., Jr. *J. Chem. Soc., Dalton Trans.* **2001**, 783.

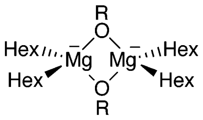
(13) A recent review, including applications in synthesis: Screttas, C. G.; Steele, B. R. *Appl. Organomet. Chem.* **2000**, *14*, 653.

(14) Screttas, C. G.; Micha-Screttas, M. *Organometallics* **1984**, *3*, 904.

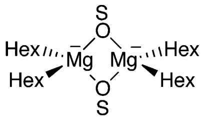
(15) Screttas, C. G.; Micha-Screttas, M. *J. Organomet. Chem.* **1985**, *290*, 1.

(16) A study of the use of R$_2$Mg−KOC(Me)$_2$Et systems in cyclohexane−hexane as polymerization catalysts concluded that R$_3$MgK or RK was formed (Patterson, D. B.; Halasa, A. F. *Macromolecules* **1991**, *24*, 1583).

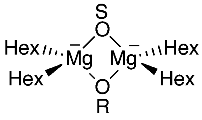
(17) The ^{1}H and ^{13}C NMR absorptions of OMe are shown in ref 5.



7

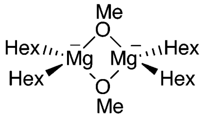


8

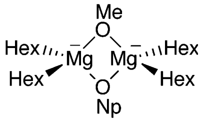


9

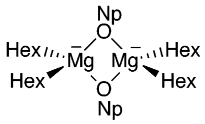
R = (*R*)-2-pentoxide S = (*S*)-2-pentoxide



10



11



12

7 and **8** pair of enantiomers and another for **9**. If *R* and *S* groups are distributed randomly, then **7**:**8**:**9** would be 1:1:2 and the two sets of absorptions would be of equal intensity. In fact, when Hex_2Mg and racemic KOCHMePr were used, the ^1H NMR spectrum (benzene-d_6) had two doublets (δ 1.14 and 1.15) of equal intensity for CH_3CH of the alkoxide. Because the geminal hexyl groups of **9** are diastereotopic, there are potentially three sets of hexyl absorptions; if the stereoisomers have equal stabilities, these sets of absorptions would have 2:1:1 intensities (2 (**7** + **8**), 1 and 1 (**9**)). A ^{13}C NMR spectrum indeed has three CMg absorptions (δ 13.92, 13.98, 14.06) with the predicted 1:2:1 intensities. Discrete absorptions due to diastereotopic hexyl groups of **9**, however, are not evident even in 500 MHz ^1H NMR spectra; ^1H NMR spectra show two overlapping triplets (δ −0.800 and −0.810, reduced to two singlets by irradiation of the CH_2CH_2Mg hydrogens) of equal intensity for CH_2Mg, corresponding to the diastereoisomeric hexyl groups of **7** and **8** and of **9**.

Processes that might exchange hexyl groups among **7**−**9** include (1) cleavage of the dimers (**7**−**9**) followed by recombination of the monomeric units and (2) direct hexyl exchange among **7**−**9**. A chemical shift difference of 1.5 Hz resolved for an absorption of diastereoisomeric hexyl groups indicates that any exchange of hexyl groups among **7**−**9** has a half-time >0.2 s. Similarly, resolution of a chemical shift difference of 1.3 Hz for an absorption of isomeric alkoxide groups indicates that any exchange of alkoxide groups also must have a half-time >0.2 s. Rapid exchange of hexyl groups *within* **7**−**9** would not interconvert these isomers but would eliminate the distinction in NMR spectra between the diastereotopic hexyl groups of **9**. Resolution of a chemical shift difference of 10.5 Hz for diastereotopic hexyl groups indicates that the lifetime of a hexyl group in a given position within **9** is >0.02 s.

R_2Mg, KOR′, and KOR″. When two alkoxides (KOMe and KONp) and Hex_2Mg are used, three constitutions (**10**−**12**) have structure **1**: assuming equal stabilities, **10**−**12** would be in 1:2:1 amounts when equimolar amounts of the alkoxides are used. Indeed, the ^{13}C NMR spectrum of such a solution shows ca. 1:2:1 absorptions for C_1, C_2, C_3, and C_4 of the hexyl group and ca. 1:1 absorptions for COMg of methoxyl and of neopentoxyl. Separations of 15−20 Hz resolved for these absorptions indicate that lifetimes of alkoxyl and hexyl groups in a given compound exceed 0.01 s, setting an upper limit to the rate to any process (e.g., cleavage of a dimer to monomeric units followed by recombination) interchanging **10**−**12.** Slow interconversion occurs, however, since equilibrium concentrations of **10**−**12** had been reached when a solution prepared by combining solutions of **10** and of **12** was first examined after 24 h.

The H's of each hexyl CH_2 of **11** are diastereotopic, and consequences of this are evident, particularly in the CH_2Mg absorption.[18] About half of the total CH_2Mg absorption corresponds to a superposition (ca. δ −0.75) of the absorptions observed for solutions prepared using only one alkoxide. This absorption of **10** and **12** is flanked, however, by two equal multiplets (δ −0.65 and −0.85) that constitute the other half of the total CH_2Mg absorption. Irradiation of the CH_2CH_2Mg H's to remove the vicinal coupling provides simpler spectra exhibiting only a single (coincident) CH_2Mg absorption for **10** and **12**, but doublets (J = 12 Hz, geminal coupling) remain for the diastereotopic CH_2Mg hydrogens of **11**.[19]

R_2Mg + NaOR′ or LiOR′ (1:1). NMR spectra (Table 4) of solutions of *s*-Bu_2Mg with NaOMe in benzene are remarkably similar to those with KOMe.[20] LiOMe did not dissolve in benzene solutions of Np_2Mg or *s*-Bu_2Mg. LiO-*t*-Bu is soluble in benzene, but NMR spectra of LiO-*t*-Bu−Np_2Mg preparations had many *t*-Bu absorptions and only feeble absorptions that might be due to CH_2Mg (or CH_2Li).

R_2Mg + MOR (1:1) + TMEDA. Solutions obtained by adding TMEDA to 1:1 Np_2Mg−KOMe solutions were stable.[21] Figure 1 shows plots of the positions of the CH_2Mg and OCH_3 ^1H NMR absorptions as a function of the TMEDA:Np_2Mg−KOMe ratio.[22] The observations are consistent with conversion of most of the K to $K(TMEDA)_2^+$ by sufficient TMEDA. Absorptions (Table 4) of 1:1 *s*-Bu_2Mg−KOMe and *s*-Bu_2Mg−NaOMe solutions to which excess TMEDA was added are very similar (as are the absorptions of the solutions without TMEDA) but not identical.

---

(18) The ^1H NMR absorptions of CH_2Mg are shown in ref 5.

(19) Resolution of a 100 Hz difference between the absorptions of the diastereotopic CH_2Mg H's indicates their stereochemistries to have a lifetime >0.002 s, setting an upper limit to the rate of any process that inverts the α-C of hexyl and hence exchanges these H's.

(20) NaOPh did not dissolve in benzene solutions of Np_2Mg.

(21) Addition of 18-crown-6, 2,2,2-cryptand, or $Me_2N(CH_2)_2N(Me)(CH_2)_2N(Me)(CH_2)_2NMe_2$ to 1:1 Np_2Mg−KOMe solutions, however, led to decomposition (^1H NMR spectra had a large neopentane absorption and no absorption attributable to CH_2Mg). Solutions of these coordinating agents with Np_2Mg alone were stable.

(22) When the TMEDA/Np_2Mg−KOMe ratio is low, the positions of the two TMEDA absorptions are reversed compared to those of free TMEDA. The absorptions approach one another as the ratio increases, coincide at a ratio of ca. 2, and approach those of free TMEDA at higher ratios.

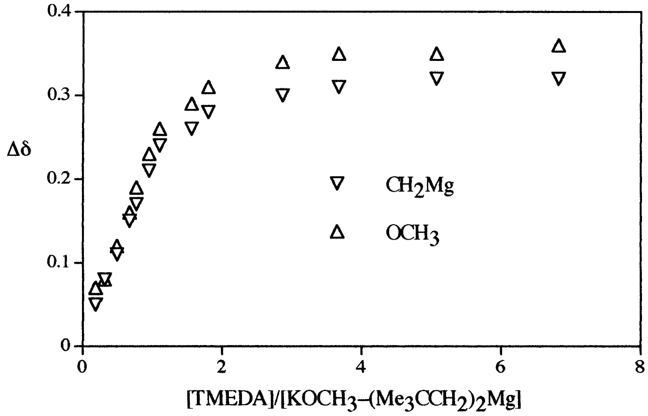


Figure 1. Plot of the downfield change in positions of the ^{1}H NMR absorptions of CH_2Mg and CH_3O as TMEDA is added to a 1:1 benzene-d_6 solution of $((CH_3)_3CCH_2)_2Mg$ and $KOCH_3$ (the TMEDA is added as a 0.09 M benzene-d_6 solution to a 0.09 M $KOCH_3-((CH_3)_3CCH_2)_2Mg$ solution).

R_2Mg + KOR′ (1:(<1)). NMR spectra of solutions having KOR′:R_2Mg ratios <1 often indicated the presence of several species. Spectra of solutions having the same ratio were identical regardless of the mode of preparation: (1) using <1 equiv of KOR′, (2) stirring for insufficient time to dissolve 1 equiv of KOR′, or (3) adding R_2Mg to a 1:1 KOR′$-R_2Mg$ solution.

The complex observations are exemplified by some results with s-Bu_2Mg−KOMe preparations. Preparations having KOMe:s-Bu_2Mg ratios <0.5 (s-Bu_2Mg initially ca. 0.2 M) had two liquid phases, the denser considerably smaller than the other.[23] In a preparation with a KOMe:s-Bu_2Mg ratio of 0.33, for example, ^{1}H and ^{13}C NMR spectra of the denser phase show only a single methoxyl absorption and a single set of *sec*-butyl absorptions; the ^{1}H NMR absorptions correspond to a OMe:s-Bu_2Mg ratio of ca. 0.3. Individual ^{1}H NMR absorptions seen for the two CH_2CHMg hydrogens (in contrast to the common absorption for these hydrogens in spectra of s-Bu_2Mg or 1:1 KOMe−s-Bu_2Mg solutions) indicate that inversion at the chiral center is slow relative to the NMR time scale.[24] The ^{1}H NMR spectrum of the less dense phase indicates a ca. 0.5 OMe:s-Bu_2Mg ratio; broad, overlapping absorptions indicate several environments for methoxyl and butyl groups.

Preparations with KOMe:s-Bu_2Mg ratios >0.5 seemed to be homogeneous. As many as four CHMg absorptions were evident in the ^{1}H NMR spectra. A solution having a ratio of 0.7, for example, exhibited four absorptions having similar intensities. One (δ −0.96) was identical with that (assigned to **2**−**6**) of 1:1 solutions; the corresponding set of OMe absorptions was present. A second (δ 0.10) and a corresponding OMe absorption (δ 4.00) were similar to those observed for the dense phase. The third CHMg absorption (δ −0.29) was sharp; the fourth (δ ca. −0.5) shifted upfield upon addition of more KOMe, suggesting it to be an exchange-averaged absorption of species containing different amounts of KOMe.[25] Since the broadness of some absorptions complicated interpretation of these spectra, TMEDA was used as an additional component in some preparations in the hope that it might slow any exchange. ^{1}H NMR spectra of preparations having various KOMe:s-Bu_2Mg ratios and excess TMEDA had only two sets of absorptions: (1) the set assigned to **2**−**6** and (2) a set identical with that obtained when TMEDA is added to s-Bu_2Mg. When TMEDA was added to a s-Bu_2Mg−KOMe solution exhibiting four CHMg absorptions, the spectrum also showed only absorptions of **2**−**6** and of s-Bu_2Mg(TMEDA). TMEDA evidently does not disrupt **2**−**6** but converts the other species to s-Bu_2Mg(TMEDA), an indication that these species are less stable than **2**−**6**.

R_2Mg + Other Salts. Exploratory reactions of R_2Mg compounds with several other salts (MA) also suggest the formation of organomagnesates having 1:1 compositions ($(R_2MgA^-)_n$). $KPPh_2$ has only limited solubility in benzene, but enough dissolved in dilute Hex_2Mg solutions to permit taking NMR spectra.[26] ^{1}H NMR absorption areas indicate a 1:1 ratio of the components of the reactants, and the CH_2Mg absorption is at δ −0.29. The absorptions are too broad to yield information about coupling to ^{31}P. KS(p-tolyl), insoluble in benzene, dissolved in a dilute s-Bu_2Mg solution.[27] ^{1}H NMR absorption areas indicate a 1:1 composition, and the CHMg absorption is at δ −0.59; the broadness of the absorptions, however, obscures all coupling to C*H*Mg. Because of its two O atoms, acetate might form magnesates with structures different from those formed with the other anions that were studied. A KOAc−Hex_2Mg (1:1) preparation exhibited an upfield ^{1}H NMR absorption (δ −0.73) of CH_2Mg, but all other absorptions are broad and overlapping in the δ 1.0−2.0 region. An $LiNR_2$ compound (R = ethyl, isopropyl, cyclohexyl), itself soluble in benzene, when combined (1:1) with Hex_2Mg gave a solution having a significantly upfield ^{1}H NMR absorption of CH_2Mg (e.g., δ −0.47 when R = ethyl).[28] Other absorptions, however, were too broad and overlapping to provide additional information.[29]

Reactions (1:1) of Bu_4NBr (which is quite soluble in benzene) and Et_2Mg, Hex_2Mg, Np_2Mg, or s-Bu_2Mg often led to two liquid phases (formation of two phases with Np_2Mg was noted over a concentration range of 0.10−1.0 M),[30] the denser containing most of the solute. ^{1}H NMR spectra of the denser phases show the components of R_2Mg and Bu_4N^+ to be in a 1:1 ratio.[31] ^{1}H NMR

---

[23] Separation into two phases was perhaps sometimes missed in experiments with other R_2Mg−KOR′ preparations. Separation was sometimes not observed until after a sample had been sealed in an NMR tube, a procedure that involved submerging in liquid nitrogen, sealing, and then warming the NMR tube to ambient temperature.

[24] This does not rule out exchange of *sec*-butyl groups, since exchange of RMg groups can be much faster than inversion. For example: House, H. O.; Latham, R. A.; Whitesides, G. M. *J. Org. Chem.* **1967**, *32*, 2481.

[25] Preparations using Hex_2Mg and <1 equiv of a KOR′ compound were homogeneous, but their ^{1}H NMR absorptions were too broad and overlapping to provide useful information. Preparations using Np_2Mg and between 0.5 and 1 equiv of KOMe generally exhibited two or three sets of ^{1}H NMR absorptions; one set corresponded to the spectrum of the 1:1 species (**1**). Preparations using Np_2Mg and 0.5 equiv of KO-t-Bu also exhibited multiple absorptions (as many as 4 for CH_2Mg) in contrast to the single set of absorptions for 1:1 preparations.

[26] Combination of $KPPh_2$ and a solution of s-Bu_2Mg led to precipitation. The only NMR absorptions were for traces of butane.

[27] KS(p-tolyl) did not dissolve significantly in a Hex_2Mg solution.

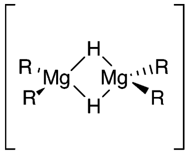
[28] A similar combination of Hex_2Mg with $KN(cyclohexyl)_2$ resulted in decomposition (large hexane absorptions and only weak absorptions attributable to CH_2Mg).

[29] KF, CsF, or KBr did not dissolve in a Hex_2Mg solution, even if 18-crown-6 or TMEDA also was present. Similar results were obtained with KF, Np_2Mg, and 18-crown-6 or TMEDA.

[30] Some Np_2Mg−Bu_4NBr preparations having much lower concentration levels exhibited more than one set of absorptions and may have been homogeneous. Such preparations may merit further investigation.

absorptions of CHMg are broad and somewhat upfield from those of R_2Mg,[11] but absorptions of Bu_4N^+ are little changed from those of Bu_4NBr. Combinations (1:1) of Bu_4NCl with *s*-Bu_2Mg or Hex_2Mg and of Bu_4NI with Np_2Mg also resulted in two phases. Decomposition of Bu_4N^+ (e.g., to form butene and trimethylamine) was never significant, even after several days.

Results with KH were very different than with the other salts. KH with Bu_2Mg or *s*-Bu_2Mg in benzene had earlier been reported to form solutions of composition Bu_2MgKH and *s*-Bu_2MgKH.[32] ^1H NMR absorptions at ca. δ 3.5 were attributed to MgH, and cryoscopic molecular weight measurements found these species to be dimeric over a wide concentration range. Presumably they have structure **13**.[33] In our work, stirring benzene solutions of R_2Mg with excess KH (itself insoluble in benzene) led eventually to solutions containing principally R_3MgK (eq 2). After an Np_2Mg solution was stirred with KH, for example, the ^1H NMR spectrum showed a single set of neopentyl absorptions (δ −0.82 for CH_2Mg and δ 1.29 for $(CH_3)_3C$)) *but no new absorption in the δ 3−4 region*.[34] Analysis (titration and AAS) of a solution (after filtration and hydrolysis) showed total base:Mg:K to be 3:1:1. If hydride is absent, then this analysis suggests the composition Np_3MgK. Solutions of composition R_3MgK had been prepared previously from reactions of R_2Mg and K in hydrocarbon solvents.[35] Indeed, we found a reaction of Np_2Mg and K in benzene[36] to produce a solution (K:Mg = 1:1 by analysis) whose major NMR absorptions were similar to those of the solution prepared from Np_2Mg and KH.[37] Similar reactions of Hex_2Mg or *s*-Bu_2Mg with KH also led to solutions also exhibiting (1) single sets of ^1H NMR absorptions[38] for the organic groups, (2) α-H absorptions markedly upfield from those of the R_2Mg reactants (δ −0.35 for CH_2Mg of hexyl, δ −1.00 for CHMg of *sec*-butyl), and (3) no absorptions attributable to hydride. As another test for the presence of hydride, a Hex_2Mg−KH preparation thought to be Hex_3MgK was transferred to a vacuum line and degassed by a series of freeze−pump−thaw cycles. The pressure did not increase upon addition of ethanol, which should have converted any magnesium hydrides to H_2; more than 0.05 H per magnesium would have been detected. That the elements of MgH_2 precipitated from our preparations but not those in the earlier work may be related to the KH source; we used commercial KH (as did the earlier work), although we obtained similar results with “active”[39] KH.[40]



13

$$3R_2Mg + 2KH \rightarrow 2R_3MGK + MgH_2\downarrow \qquad (2)$$

Some reactions of R_2Mg with less than 1 equiv of KH or with stirring with KH for periods of time short enough that much less than 1 equiv of KH dissolved did exhibit weak ^1H NMR absorptions that probably are due to hydride-containing species. When a Hex_2Mg solution was stirred with excess KH, for example, some spectra recorded at intermediate times showed a weak absorption (H:Hex <0.05) at δ 3.5; the CH_2Mg absorption was broad and with increasing stirring times shifted progressively upfield from its initial position of δ 0.18. Addition of TMEDA to such solutions converted species other than Hex_3MgK to $Hex_2Mg(TMEDA)$: ^1H NMR spectra recorded after adding TMEDA to Hex_2Mg−KH preparations (1) with short stirring times show principally absorptions identical with those of $Hex_2Mg(TMEDA)$, (2) with stirring times sufficiently long that no further change was occurring show only a single but different set of absorptions (CH_2Mg at δ −0.46), and (3) with intermediate stirring times show both sets of absorptions. When an *s*-Bu_2Mg solution was stirred with 0.5 equiv of KH, ^1H NMR spectra showed only a single set of *s*-Bu absorptions, intermediate in position between those of *s*-Bu_2Mg and of *s*-Bu_3MgK, and also a sharp but weak (H:*s*-Bu ca. 0.1) absorption at δ 3.98. Spectra of preparations in which somewhat more KH had reacted (evidenced by absorptions nearer to those of *s*-Bu_3MgK) had weak, very broad absorptions in the δ 3.5−4.2 region.

Reaction rates depended on the R_2Mg compound and KH source. With the same KH source, reactions with *s*-Bu_2Mg were much faster than with Hex_2Mg or Np_2Mg. With Hex_2Mg, 9 days were required with one commercial KH sample to achieve the composition achieved in 1 day with another commercial sample. Preparations using freshly prepared, “active”[39] KH were much more rapid—the maximum spectral changes were achieved in 10 min. Solutions prepared with the active KH did not show greater absorptions at δ 3−4 (that might indicate formation of a R_2MgHK species) than did solutions with other KH samples.

The stability of R_3MgK solutions depended on R. Hex_3MgK solutions showed little decomposition after several days, but Np_3MgK solutions decomposed completely (large neopentane ^1H NMR absorption) within 2 days. *s*-Bu_2Mg preparations with 1 equiv of KH decomposed significantly (*sec*-butylbenzene and butane were major

---

[31] Solids (1:1) have been obtained from reactions of tetramethylammonium salts and Me_2Mg: Klopsch, A.; Dehnicke, K. *Chem. Ber.* **1975**, *108*, 420. Müller, J.; Schmock, F.; Klopsch, A.; Dehnicke, K. *Chem. Ber.* **1975**, *108*, 664.

[32] Ashby, E. C.; Arnott, R.; Srivastava, S. *Inorg. Chem.* **1975**, *14*, 2422.

[33] Ashby, E. C.; Goel, A. B. *Inorg. Chem.* **1978**, *17*, 322.

[34] Traces of the dioxane used to precipitate MgX_2 from RMgX in the preparation of R_2Mg sometimes remained in the R_2Mg reactants and exhibited a sharp absorption at ca. δ 3.4 (absorption position somewhat dependent on the particular R) which could obscure a small peak due to hydride; the dioxane absorption, however, never had more than 5−10% of the intensity expected for one H per R_2Mg.

[35] Malpass, D. B.; Eastham, J. F. *J. Org. Chem.* **1973**, *38*, 3718.

[36] Analysis of a hydrolyzed portion of a similar reaction in diethyl ether also found total base:Mg:K to be ca. 3:1:1.

[37] In solution, R_3MgK compounds might have structure **13** (with R in place of H). The ^1H NMR spectrum (toluene-d_8) of a Np_3MgK preparation, however, was unchanged, as the temperature was lowered until broadening of *all* absorptions became significant at −80 °C. ^{13}C NMR spectra of Hex_3MgK solutions to which TMEDA was added had only single sets of hexyl absorptions.

[38] ^{13}C NMR spectra of *s*-Bu_2Mg reactions also show only a single set of absorptions.

[39] Klusener, P. A. A.; Brandsma, L.; Verkruijsse, H. D.; Schleyer, P. v. R.; Friedl, T.; Pi, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 465.

[40] The differences between our results and those reported previously are not due to the concentration level. The R_2Mg concentration in our experiments did not exceed that in previous work (0.20 M) and generally was lower.

products) in 1 day, but preparations with <1 equiv of KH were stable for days.

Conclusions

Exploratory studies of reactions of R_2Mg compounds with $KPPh_2$, KSTol, KOAc, $LiNR'_2$ compounds, and R'_4NX compounds suggest that 1:1 organomagnesates form. Reactions with KH instead form principally R_3MgK. The most comprehensive results were obtained with alkali-metal alkoxides. R_2Mg and KOR′ compounds in benzene form well-defined 1:1 species. Some observations indicate that the same species form with NaOR′ (though not with LiOR′) and when the solvent is diethyl ether. NMR spectra of preparations that result in stereoisomers are consistent with structure **1**.[41,42] Magnesium in **1** is four-coordinate; although higher coordination numbers are well-known, 4 is the most common for organomagnesium compounds (at least in solids), particularly when bulky groups are involved.[43] The somewhat different absorption positions in NMR spectra of solutions of equivalent potassium and sodium species indicate some influence of the cations on dianion **1**. The differences may result from interactions other than specific bonding; absorption positions remain different in the presence of TMEDA, which is indicated by an NMR study (Figure 1) of a potassium system to coordinate with the potassium.

Studies of solutions with KOR′:R_2Mg ratios less than 1 detected several species that do not equilibrate rapidly relative to the NMR time scale. We had hoped that effects of long-range coupling in NMR spectra of MA−R_2Mg solutions in which the coordinating atom of A^- was NMR active (e.g. ^{19}F, ^{31}P, etc.) might provide additional structural information. Such efforts were unsuccessful, however, as were efforts to obtain crystals suitable for X-ray diffraction studies.

Reactions of RLi and KOR′ can synthesize RK (eq 3).[44]

$$RLi + KOR' \rightarrow RK + LiOR' \qquad (3)$$

$$R_2Mg + KOR' \rightarrow RK + RMgOR' \qquad (4)$$

This work indicates that similar reactions of R_2Mg (e.g., eq 4) are not generally significant. The instability of some R_2Mg−KOR′ preparations, however, may be due to formation of some RK (RK is known[45] to metalate benzene). Bulky R and R′ groups seem to decrease the stability of the R_2Mg−KOR′ preparations. Bulky groups may make structure **1** less stable, permitting formation of other species to become significant. The instability of solutions having more than one KOR′ per R_2Mg also was noted. Excess KOR′ perhaps leads to replacement of an R of **1** by an OR′ group, releasing RK.

Experimental Section

Procedures involving organometallic compounds were performed under an atmosphere of purified nitrogen using Schlenk techniques, a glovebox, and a vacuum line. NMR spectra were recorded at ca. 23 °C; the solvent was benzene-d_6, except where otherwise noted. ^1H NMR absorption positions for benzene-d_6 solutions are relative to internal C_6D_5H (δ 7.15) and for diethyl ether-d_{10} solutions to internal $CD_3CDHOCD_2CD_3$ (δ 3.34); ^{13}C NMR absorption positions for benzene-d_6 solutions are relative to internal C_6D_6 (δ 128.0). Solutions for NMR analysis were prepared in a glovebox and transferred into NMR tubes to which an extension of routine glass tubing had been added to facilitate sealing with a flame. An NMR tube was capped temporarily with a septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension. Dialkylmagnesium compounds were prepared from Grignard reagents using the dioxane precipitation method.[46]

Preparation of NMR Solutions. The general procedure is as follows. In a glovebox, the salt and dialkylmagnesium compound were weighed into a vial equipped with a magnetic stirring bar. The solvent (typically 0.5 mL) was added, and the mixture was stirred. If a homogeneous solution was present after the preparation had been stirred for a few minutes, it was transferred into an NMR tube. A preparation which remained heterogeneous was sometimes stirred for a longer time (2−24 h) before transfer. When solid was evident, the suspension was filtered into the NMR tube through a Kimwipe plug in a pipet. Preparations resulting in two liquid phases were done on a larger scale (e.g., 1−2 mL of solvent) so that enough of the lower phase would be present to permit taking routine NMR spectra. Preparations with KH often were done on a larger scale (1−5 mL) and with a considerable excess of KH (up to 10 equiv).

To prepare the solutions used to provide the data shown in Figure 1, a benzene-d_6 solution of Np_2Mg (2.5 mL, 0.45 mmol, 0.18 M) was added dropwise to a stirred mixture of KOMe (124 mg, 1.77 mmol) and benzene-d_6 (2.5 mL). Stirring was continued for 5 h, and then the preparation was filtered through a fritted funnel. Appropriate volumes (syringe) of the resulting solution and of a benzene-d_6 solution of TMEDA (0.090 M) were combined. The solutions containing Hex_2Mg, KOMe, and KONp were prepared by combining equal volumes of benzene-d_6 solutions (each 0.27 M) of Hex_2Mg−KOMe (1:1) and of Hex_2Mg−KONp (1:1). The solutions of *s*-Bu_2Mg, KOMe, or NaOMe and TMEDA were prepared by adding TMEDA to already prepared *s*-Bu_2Mg−MOMe solutions. Solutions containing less than 1 equiv of the components of KOMe/equiv of R_2Mg compound were prepared by (1) lengthy stirring of <1 equiv of KOMe with a solution of R_2Mg, (2) briefer stirring of 1 equiv of KOMe with a solution of R_2Mg, or (3) adding R_2Mg (either neat or a solution) to a 1:1 R_2Mg−KOR′ solution.

Acknowledgment. We thank the National Science Foundation for supporting this work, John Chubb for critical control experiments, and anonymous reviewers for helpful suggestions.

Supporting Information Available: Text giving experimental information, including preparations and NMR spectra of the R_2Mg compounds and of some of the salts, NMR spectra of many R_2Mg−salt solutions, and analyses of R_2Mg−alkoxide and R_3MgK solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030544K

---

[41] Neither ^1H nor ^{13}C NMR spectra of MOR′−R_2Mg species provide any indication of permanent cis/trans relationships of R′ groups. (Inversion at tricoordinate oxygen generally is rapid, although the barrier to inversion is higher in strained cyclic systems. Lambert, J. B. *Top. Stereochem.* **1971**, *6*, 19. Schlosser, M. In *Organometallics in Synthesis, A Manual*; Schlosser, M., Ed.; Wiley: Chichester, U.K., 2002; Chapter 1, Section 2.3.3.)

[42] A relevant crystal structure is of a species formed from Et_2Zn and KO-*t*-Bu that has structure **1** (Zn instead of Mg); one K−O distance (2.626(5) Å) is quite short, but of course this relationship is not likely to persist in solution. Fabicon, R. M.; Parvez, M.; Richey, Jr., H. G. *J. Am. Chem. Soc.* **1991**, *113*, 1412.

[43] Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *32*, 147. Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1994**, *465*, 1. Bicklelhaupt, F. In *Grignard Reagents: New Developments*; Richey, H. G., Jr., Ed.; Wiley: Chichester, U.K., 2000; Chapter 9.

[44] Lochmann, L. *Eur. J. Inorg. Chem.* **2000**, 1115.

[45] Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 362.

[46] Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic: London, 1995; Section 3.4.1.