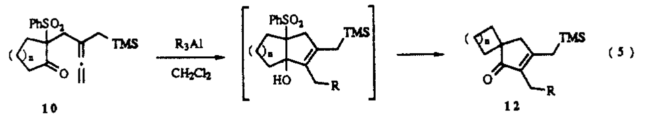
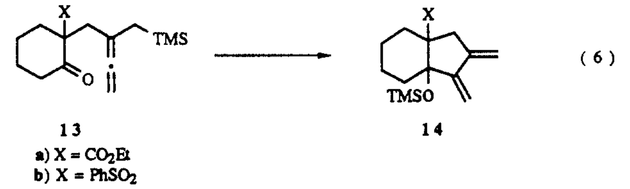
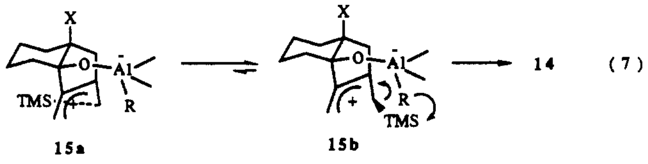
kylative cyclorearrangement of eq 5. Thus, using the eight-membered (**10**, $n = 4$) or twelve-membered (**10**, $n = 8$) substrates directly produces the spiro cyclopentenones **12** under the above conditions [R = CH_3, $n = 4$ (71%), $n = 8$ (67%); R = C_2H_5, $n = 8$ (71%)].[2]



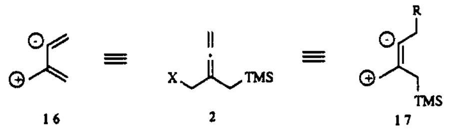
The behavior of the cyclohexyl substrates **13a** and **13b** contrasts with the behavior observed for all of the other ring sizes (eq 6).

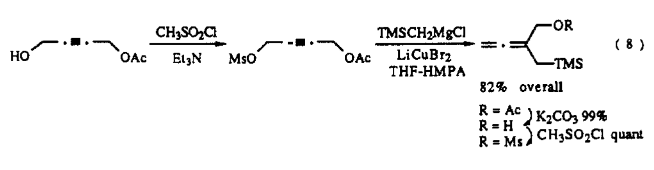


Only the products of desilylative cyclization **14a** (77%) and **14b** (82%) were observed with trimethylaluminum under conditions that produce only alkylative cyclization in the five-, seven-, eight-, and 12-membered rings. The conformational rigidity imposed by the cyclohexyl systems may account for this effect. In contrast to the other ring sizes, steric factors strongly destabilize conformer **15a**. The poising of the trimethylsilyl group for desilylation in **15b** allows the normal kinetic advantage of silyl transfer versus group transfer from aluminum to carbon to dominate, and only the diene **14** is obtained (eq 7).



The bifunctional conjunctive reagent **2**, which is readily available from butyne-1,4-diol (eq 8), thus becomes a versatile synthon for cyclopentane annulation as summarized in structures **16** and **17**. Further, the results clearly indicate that, in such Lewis acid promoted additions of (allenylmethyl)silanes to carbonyl partners, the desilylation does not accompany carbon–carbon bond formation. The enhanced stability of the silyl-stabilized allyl cation allows its interception to provide an alkylative cyclization or desilylation simply by choice of Lewis acid. This is the first report of such a successful competition. This approach should allow creation of other alkylative cyclizations, as well as new bifunctional conjunctive reagents, to create different ring sizes and substitution patterns.





Acknowledgment. We thank the National Science Foundation for its generous support of our programs.

Supplementary Material Available: Summary of spectral data including ^1H and ^{13}C NMR and IR data for compounds **2–7** and **11–14** (8 pages). Ordering information is given on any current masthead page.

Structures of Organomagnesiate Ions Formed from Dialkylmagnesium Compounds and Alkali-Metal Alkoxides

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This study[1] was stimulated by observations that cryptands and crown ethers alter the reactivity of diorganomagnesium compounds. These additives are now known to cause disproportionation of R_2Mg to magnesiate ions such as R_3Mg^-, the reactive species, and coordinated RMg^+ cations, such as $RMg(cryptand)^+$.[2] We thought that appropriate salts could alter diorganomagnesium compounds in a similar fashion by forming magnesiate anions in which the anion of the salt is bonded to Mg, for example, $R_2Mg + KOMe \rightleftarrows$ "R_2MgOMe^-,K^+".

By dissolving organosodium or potassium compounds in solutions of $Mg(OR)_2$ (OR = OCH_2CH_2OEt), Screttas and Screttas have prepared solutions of composition $Na_2MgPh_2(OR)_2$,[3] $KMgPh(OR)_2$,[3] $Na_2MgBu_2(OR)_2$,[4] and $NaMgBu(OR)_2$.[4] In principle these might be the same as solutions prepared from Ph_2Mg or Bu_2Mg and NaOR or KOR, and in the case of $Na_2MgPh_2(OR)_2$, they concluded that both modes of preparation led to identical solutions.[5] They observed only single sets of ^1H and ^{13}C NMR absorptions for the solutions they studied and reached no structural conclusions. In earlier work, Ashby, Arnott, and Srivastava concluded that the major species in solutions formed from equimolar amounts of KH and R_2Mg had the molecular formula $K_2Mg_2R_4H_2$.[6]

We find that additions of alkali-metal alkoxides or some other salts to R_2Mg lead to behavior in some reactions resembling that of R_2Mg–cryptand preparations. This includes relatively ready addition to pyridine leading to 4-R-substituted as well as 2-R-substituted pyridines,[1,7] additions to ketones in which the accompanying reduction of the ketone is lessened or even eliminated,[8] and halogen–metal exchange with aryl bromides and iodides.[1,9]

Low solubility of many R_2Mg–salt combinations and chemical instability of some (RH is formed) limits systems suitable for structural studies. Systems having sufficient solubility (most studies have been in benzene), however, generally provide evidence for a species containing the elements of R_2Mg and the salt in equal amounts. When a salt itself is insoluble, solutions with a 1:1 composition commonly are attained, even when an excess of salt is used. At salt:R_2Mg ratios above about 0.5, a specific set of NMR absorptions often is seen that can be attributed to a 1:1 species; at a ratio of 1, only this set of absorptions remains. The ^1H NMR absorption of α-H's of R of a 1:1 species is at higher field than the equivalent absorption of R_2Mg.[10] At salt:R_2Mg ratios below 1, additional sets of NMR absorptions often are seen that are due to species having lower salt:R_2Mg ratios.

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[1] Farkas, J., Jr.; Hanawalt, E. M., The Pennsylvania State University, unpublished observations.

[2] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660. Squiller, E. P.; Kushlan, D. M.; Pajerski, A. D., The Pennsylvania State University, unpublished observations.

[3] Screttas, C. G.; Micha-Screttas, M. *Organometallics* **1984**, *3*, 904.

[4] Screttas, C. G.; Micha-Screttas, M. *J. Organomet. Chem.* **1986**, *316*, 1.

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

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

[7] For related reactions of pyridine with solutions prepared from R_2Mg and RLi, see: Richey, H. G., Jr.; Farkas, J., Jr. *Organometallics*, in press.

[8] Richey, H. G., Jr.; DeStephano, J. P. *J. Org. Chem.*, in press.

[9] Stoudt, S. J., The Pennsylvania State University, unpublished results.

[10] For example, (CH_2Mg): (benzene-d_6) Hex_2Mg, δ 0.18; 1:1 Hex_2Mg–KOMe, δ −0.76.

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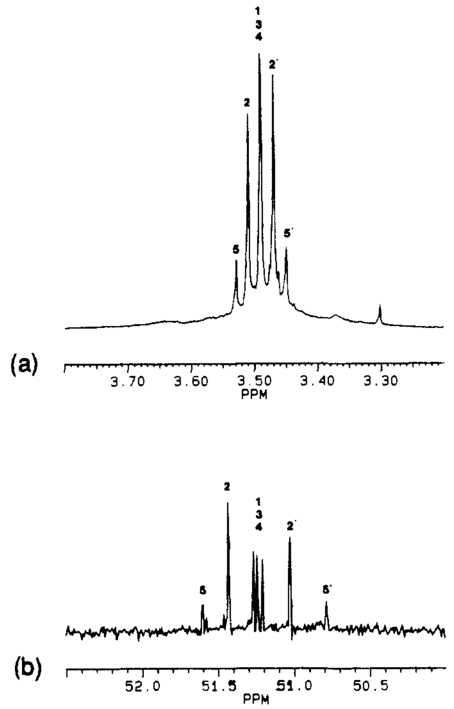


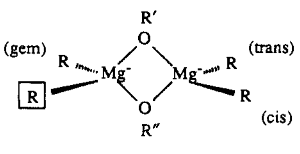
Figure 1. NMR absorptions of OMe in solutions of (*sec*-Bu)$_2$Mg–KOMe in benzene-d_6. (a) ^{1}H NMR spectrum of a 0.4 M solution (500 MHz). Chemical shifts are relative to benzene-d_5 (δ 7.15). (b) ^{13}C NMR spectrum of a 0.3 M solution (125 MHz). Chemical shifts are relative to benzene-d_6 (δ 128.0). The numbers over the peaks are the assignments of each to a particular isomer that is listed in Table I.

Table I. Properties of Isomers Having Structure **1**

configns of *sec*-Bu groups	statistical wt	NMR wt	OMe's	isomer designatn (Fig. 1)
R_4	1	2	identical	1
S_4	1			
R_3S	4	8	diastereotopic	2
RS_3	4			
R_2S_2 gem	2	2	identical	3
R_2S_2 cis	2	2	identical	4
R_2S_2 trans	2	2	diastereotopic	5

NMR absorptions of most R$_2$Mg–salt species provide only limited information useful for defining structure. This communication presents some results of applying to R$_2$Mg–MOR′ (M = K or Na) systems the idea that reducing symmetry can furnish much more information. One approach is to use chiral R or R′ groups. When R is *sec*-butyl rather than an achiral group (e.g., hexyl), all absorptions are more complicated. The OMe absorption (Figure 1a) in the ^{1}H NMR spectrum of a solution prepared from (*sec*-Bu)$_2$Mg and KOMe has the appearance of a quintet,[11] but is indicated by spectra obtained at different field strengths to consist of independent absorptions. In fact, the central absorption appears as two absorptions of unequal size if the solvent is Et$_2$O-d_{10} and also is partially resolved if the salt is NaOMe and tetramethylethylenediamine (TMEDA) is added. The broad band decoupled ^{13}C NMR spectrum of OMe (Figure 1b) is similar, except that the central region has three closely spaced absorptions.

If (*R*)- and (*S*)-*sec*-butyl groups are distributed in an approximately statistical manner, then structure **1a** is consistent with these observations. Two pairs of enantiomers and three meso compounds, listed in Table I, have this structure,[12] and two of these possibilities have diastereotopic methoxyl groups. Assignments of absorptions to particular isomers are indicated on Figure 1. The "diastereotopic shift" is approximately twice as great in the trans R_2S_2 isomer as in the R_3S and RS_3 isomers, consistent with this shift being due in the former to the effects of all four *sec*-butyl groups, but in the latter to the net effects of only two groups.



1a R = *sec*-butyl, R′ = R″ = OMe

1b R = hexyl, R′ = OMe, R″ = ONp

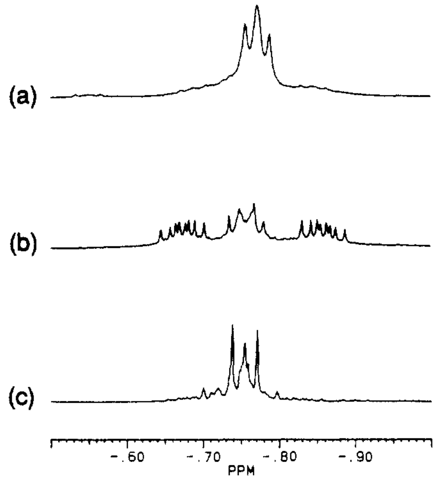


Figure 2. ^{1}H NMR absorptions of CH_2Mg in 0.3 M solutions of Hex$_2$Mg–KOR in benzene-d_6. Chemical shifts are relative to benzene-d_5 (δ 7.15). (a) OR = OMe. (b) Approximately one-half of OR is OMe, and the other one-half is Np (Np = neopentyl). (c) OR = ONp.

Structure **1a** provides eight environments for a *sec*-butyl group since the geminate, cis, and trans *sec*-butyl groups can each be *R* or *S* (**1** indicates these relationships for the boxed group). Eight ^{1}H NMR absorptions having approximately equal areas are seen for CHCH_3.[13]

Another approach is to use two different R or OR′ groups. Figure 2 shows the ^{1}H NMR absorption of CH$_2$Mg of solutions prepared from Hex$_2$Mg plus KOMe or KONp (Np = neopentyl) or a mixture of both. Decoupling shows that the two widely spaced absorptions of CH$_2$ seen when both salts are used represent spin-coupled H's (J = 12 Hz). The 1:1 R$_2$Mg–MOR′ species must have at least two alkoxide groups, and when they are different, then the two H's of each RCH$_2$Mg must also be different. In fact, the H's of each RCH$_2$Mg in **1b** are diastereotopic.

We think structure **1** to be the simplest that accords with the observations about the dominant 1:1 species. Observation of chemical shifts as small as 0.6 Hz in the spectrum of **1a**[13] indicate that any processes inverting or exchanging *sec*-butyl groups have rates less than 3 s^{-1}. Although steric factors must limit approach of the alkali-metal cations to the oxygens, the chemical shifts of **1a** differ slightly when Na$^+$ is used instead of K$^+$ and, probably because of more efficient coordination to the K$^+$ or Na$^+$, more significantly when TMEDA is added.[14]

R$_2$Mg–MOR′ preparations used for chemical reactions have been in Et$_2$O. The ^{1}H NMR spectrum of a Et$_2$O-d_{10} solution containing equal parts of the elements of (*sec*-Bu)$_2$Mg and KOMe is so similar to that of a benzene solution that **1a** must also be its dominant component.

Acknowledgment. We are indebted to the National Science Foundation for support of this work and for aiding in the purchase of the NMR spectrometers.

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(11) The relative areas are not significantly concentration dependent.

(12) The C's of the OMe groups in **1a** probably are not in the plane of the O–Mg bonds, in which case cis and trans arrangements are possible but perhaps interconvert rapidly.

(13) Seven doublets (J's = 7.7–7.9 Hz) are resolved (300 MHz): (benzene-d_6) δ 1.560, 1.569, 1.573, 1.582 (approximately twice the size of the others and somewhat broader), 1.593, 1.595, 1.604.

(14) For example: ^{1}H NMR (benzene-d_6, 300 MHz, the OMe chemical shifts are for the central OMe absorption) (*sec*-Bu)$_2$Mg–KOMe (1:1), δ −0.99 (CHMg), 3.49 (OMe); (*sec*-Bu)$_2$Mg–NaOMe (1:1), δ −1.02 (CHMg), 3.39 (OMe); (*sec*-Bu)$_2$Mg–KOMe–TMEDA (1:1:2.5), δ −0.47 (CHMg), 3.83 (OMe); (*sec*-Bu)$_2$Mg–NaOMe–TMEDA (1:1:2.5), δ −0.63 (CHMg), 3.80 (OMe).