and 140.1; MS, m/e 359 (M^+), 161, 132, 105, and 77 (base); HRMS calcd for $C_{19}H_{21}NO_4S$ 359.1191, found 359.1203.

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Supplementary Material Available: NMR spectra for HRMS compounds (37 pages). Ordering information is given on any current masthead page.

Rearrangement and Cleavage of the Grignard Reagent from 5-(Chloromethyl)norbornene[1]

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The Grignard reagents **1**-Mg and **2**-Mg from *endo*- and *exo*-5-(chloromethyl)norbornene rearrange with ring cleavage on heating to yield an allylcyclopentenyl organomagnesium compound (**3**-Mg). This, in turn, undergoes competitively a variety of reactions, including an alternative cyclization to a bicyclo[3.3.0]octene organomagnesium (**4**-Mg) and *formal* loss of hydrogen or propene to produce allylcyclopentadienyl- (**5**-Mg) and cyclopentadienylmagnesium compounds. Endo and exo isomers **1**-Mg and **2**-Mg rearrange at comparable rates and are partially interconverted, probably via their cleavage and recyclization. Mechanistic possibilities are discussed.

Several years ago, Freeman and co-workers[3] published a study of the reactions of *endo*- and *exo*-5-(chloromethyl)norbornene with sodium. The monomeric hydrocarbon products isolated were explained by a series of ring-cleavage and cyclization rearrangements of organosodium intermediates and their subsequent protonation.

We were interested in seeing how the organomagnesium compounds might compare with their sodium analogues in these rearrangements. Several questions, raised by features of the earlier work, were of particular relevance in this respect. First, cleavage of the five-membered ring in cyclopentylmethyl organometallic compounds is thermodynamically unfavorable,[4] and norbornylmethyl chlorides fail to cleave under similar conditions.[3] Is the double bond's effect sufficient to allow the ring cleavage of the *organomagnesium* compound to occur? The conversion of *exo*- to *endo*-5-(chloromethyl)norbornene was observed under the reaction conditions, presumably via reversal of the cleavage reaction. Would the Grignard reagents undergo the same exo-endo isomerization? Finally, the subsequent cyclization of the initial ring-opened organometallic product is of interest, since it occurs opposite to the customary orientation in organometallic cylization rearrangements.[2,4,5] Is the observed behavior unique to the highly ionic character of the organosodium derivative, or does it result from structural features independent of the metal, such as ring strain or allylic structure?

We report in this paper that norbornenylmethyl Grignard reagents do undergo analogous rearrangements when heated and that an additional reaction path, which does not appear to occur for the sodium derivatives, is important for the organomagnesium.

Results

Grignard reagents were prepared in tetrahydrofuran (THF) from a mixture of endo and exo isomers containing about 87% of *endo*-5-(chloromethyl)norbornene (**1**-Cl) and from a pure sample of the exo isomer **2**-Cl and heated to temperatures of 80–120 °C in sealed tubes. The progress of the reaction was followed by observation of the ^{13}C NMR spectrum of the Grignard solutions, and samples were also hydrolyzed after partial reaction to allow isolation and characterization of the hydrocarbon products. Less extensive studies were done in ethyl ether solution. Scheme I summarizes the observed transformations, and Table I lists ^{13}C NMR data for the Grignard reagents and related structures.

The ^{13}C NMR spectra of Grignard solutions before heating indicated nearly quantitative formation of the unrearranged organomagnesium compounds. After heating for several hours at 115 °C, both norbornenylmethyl Grignard reagent isomers had partially rearranged with ring cleavage to the allylcyclopentenyl organomagnesium compound **3**-Mg. This should exist as a mixture of rapidly equilibrating allylic isomers. Averaged ^{13}C NMR signals were readily recognized for all carbons except for the two that are rapidly interconverted between allylic and olefinic environments by the exchange. This signal may have been obscured by solvent or may have been broadened by the exchange to the point where it could not be detected. No significant change in the spectrum was observed over the temperature range 12–80 °C, except for a sharpening of several of the Grignard reagent resonances at higher temperature. Hydrolysis produced a nearly equal mixture of 3- and 4-allylcyclopentenes **3a**-H and **3b**-H, in addition to

(1) A summary of some of this material in preliminary form has been included in reviews[2] and in the M.S. thesis of K.H., University of Wisconsin—Milwaukee, 1968.

(2) (a) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123. (b) Hill, E. A. *Adv. Organomet. Chem.* **1977**, *16*, 131.

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Scheme I

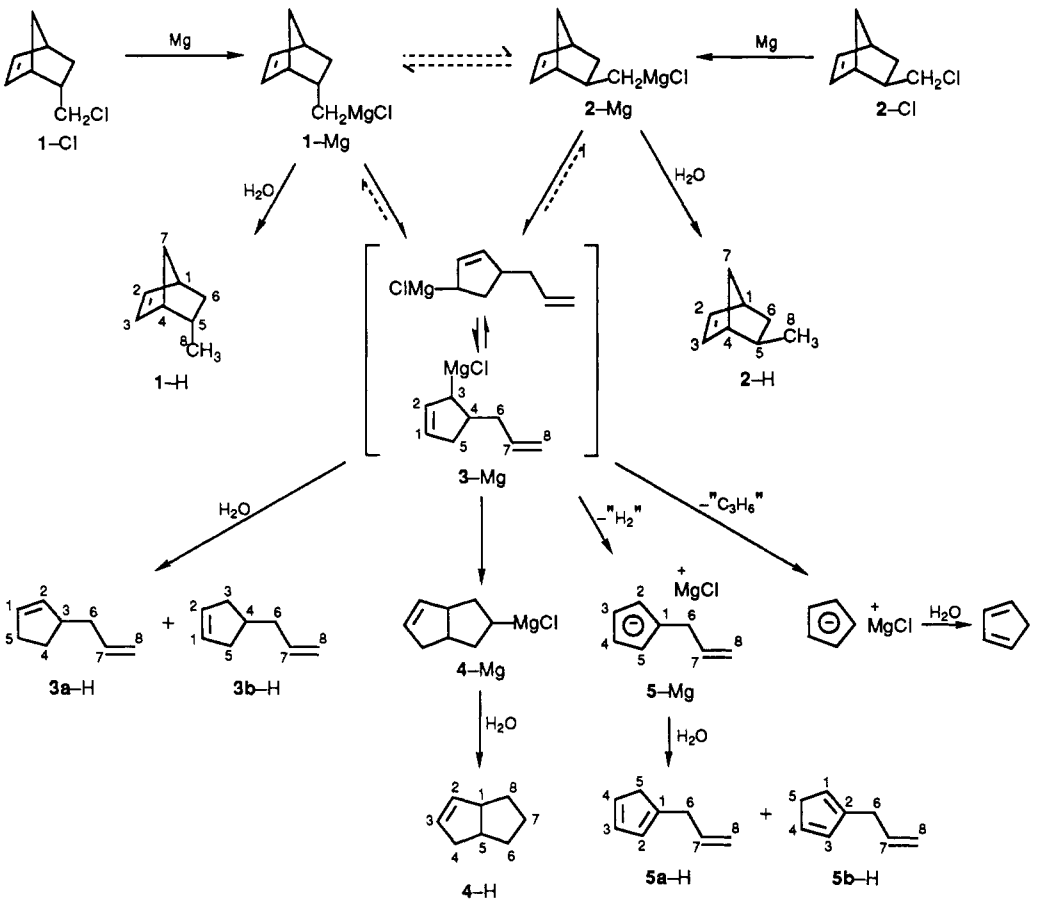


Table I. Carbon-13 NMR Spectra of Grignard Reagents and Related Structures[a]

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1-H[b]	43.62 d	137.13 d	132.45 d	47.77 d	32.94 d	34.16 t	50.45 t	19.25 q
1-Cl[c]	[42.00 d]	138.09 d	131.79 d	44.60 d	[42.75 d]	31.32 t	[49.50 t]	[48.81 t]
1-OH[c,d]	42.20	137.33	132.21	43.58	41.58	28.83	49.50	66.24
1-Mg[e]	44.23 d	135.45 d	134.08 d	51.66 d	39.72 d	39.60 t	50.62 t	14.36 t
2-H[f]	42.68 d	136.14 d	137.23 d	48.75 d	32.94 d	34.88 t	44.96 t	21.44 t
2-Cl[c]	[42.30 d]	[137.08 d]	[136.38 d]	44.77 d	[41.96 d]	32.04 t	45.01 t	49.86 t
2-OH[c,g]	[41.76]	[136.74]	[136.50]	43.28	[41.52]	29.55	44.92	67.23
2-Mg[h]	42.59 d	134.60 d	138.49 d	54.47 d	39.69 d	39.69 t	45.06 t	17.02 t
3a-H[i]	130.60 d	134.84 d	45.67 d	[29.57 t]	[32.18 t]	(40.58 t)	(138.10 d)	(115.16 t)
3b-H[i]	129.82 d	129.82 d	38.61 t	37.05 d	38.61 t	(41.00 t)	(137.75 d)	(115.06 t)
3-Mg		145.10 d		45.6 d, b	42.83 t	39.05 x	140.53 d	113.13 t
4-H[j]	51.15	134.63	129.46	41.26	40.66	35.97		32.61
5a-H[k]	147.43 s	127.50 d	[131.02 d]	[132.57 d]	43.30 t	35.49 t	137.42 d	115.00 t
5b-H[l]	126.85 d	145.24 s	[133.71 d]	[134.77 d]	41.37 t	34.63 t	136.77 d	115.25 t
5-Mg[m]	119.89 s	104.81 d	102.40 d	102.40 d	104.81 d	35.24 t	140.86 d	112.59 t

[a] Spectra reported as δ (ppm) in THF with C_6D_6 lock and reference at 128.00 ppm, unless otherwise indicated as in ethyl ether (vs C_6D_6) or $CDCl_3$ (vs TMS). Structures numbered as in Scheme I. Appearance in off-resonance decoupled spectra is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; b, broad; x, multiplicity obscured by other components. Assignment of shifts in square brackets are uncertain and may be reversed. [b] In ethyl ether: 43.59, 137.14, 132.45, 47.75, 32.96, 34.14, 50.47. In $CDCl_3$: 43.21, 136.97, 132.40, 47.34, 32.53, 33.85, 50.18, 19.36. Lit.:[29a] 43.1, 136.7, 132.1, 47.2, 32.5, 33.7, 50.1, 19.3. Lit.:[29b] 43.5, 137.0, 132.5, 48.7, 32.9, 35.0, 50.6, 19.6. [c] In $CDCl_3$. [d] *Lit.*:[29c] 42.2, 137.2, 132.2, 43.6, 41.7, 28.9, 49.5, 66.3. Lit.:[29b] 42.3, 137.1, 132.9, 44.3, 43.1, 29.8, 50.2, 66.1. [e] In ethyl ether: 44.24, 135.76, 133.85, 51.50, 39.50, 39.27, 50.68, 14.62. [f] In ethyl ether: 42.64, 136.16, 137.2, 48.72, 32.9, 34.89, 44.95, 21.45. In $CDCl_3$: 42.29, 136.01, 137.06, 48.29, 32.5, 34.56, 44.79, 21.56. Lit.:[29a] 42.3, 135.9, 137.0, 48.3, 32.5, 34.6, 44.8, 21.6. Lit.:[29b] 42.6, 136.1, 137.0, 47.7, 32.9, 34.2, 45.1, 21.8. [g] Lit.:[29c] [41.8], [136.5], [136.7], 42.3, [41.6], 29.6, 45.0, 67.3. Lit.:[29b] 41.9, 136.7, 136.7, 43.9, 41.9, 30.0, 45.4, --. [h] In ethyl ether: 42.65, 134.83, 138.37, 54.25, [39.21], [39.65], 45.05, 17.06. [i] Mixture of isomers; assignment of peaks enclosed in parentheses to isomers is uncertain. In $CDCl_3$: 130.60, 134.65, 45.14, [29.23], [31.99], (40.20), (137.94), (115.26) and 129.77, 129.77, 38.52, 36.64, 38.52, (40.64), (137.59), (115.15). [j] In $CDCl_3$: 50.61d, 134.52d, 129.42d, 41.04t, 40.09d, 35.69t, 25.22t, 32.33t. Lit.[7d] 50.8, 134.7, 129.5, 41.2, 40.4, 35.9, 25.4, 32.5. Lit.:[7e] 51.4, 134.9, 129.7, 41.6, 40.9, 36.3, 25.7, 32.9. Lit.:[7g] 51.28, 134.76, 129.65, 41.57, 40.81, 36.25, 25.77, 32.87. [k] In ethyl ether: 147.23, ca 127.5, 130.93, 132.59, 43.26, 35.61, 137.51, 115.06. In $CDCl_3$: 147.43, 127.29, 131.08, 132.48, 43.29, 35.31, 137.10, 115.32. Lit.:[8b] 147.32, 127.26, 131.08, *134.56*, 43.26, 35.35, 137.05, 115.34. [l] In ethyl ether: 126.79, 145.2, 133.61, 134.81, 41.31, ca. 34.7, 136.86, 115.30. In $CDCl_3$: 126.82, 144.98, 133.83, 134.60, 41.37, 34.43, 136.50, 115.57. Lit.[8b] 126.78, 144.92, *132.46*, 133.80, 41.35, 34.46, 136.42, 115.34. The assignments from ref 8b that are italicized are reversed from those listed above from the present study; the latter are believed to be correct, based on observation of the conversion of **5a**-H to **5b**-H. [m] At 80 °C: 120.20, 104.91, 102.61, 35.21, 140.84, 112.58. In ethyl ether: ca. 121, 105.08, 104.46, 35.18, 140.2, 113.33. From cpMgBr and allyl bromide in THF: 120.41, 105.06, 103.02, 35.30, 140.61, 112.80.

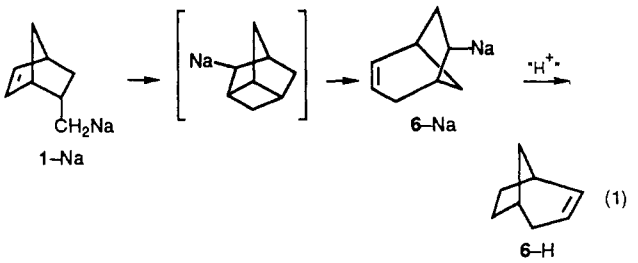
the isomeric 5-methylnorbornenes 1-H and 2-H. These were characterized by their NMR and mass spectra.[6]

On further heating, a number of additional signals in the ^{13}C NMR spectrum of the Grignard reagent increased, and additional hydrolysis products were produced. The new products were identified by partial GC separation and NMR, IR, and mass spectra as 2-bicyclo[3.3.0]octene 4-H[7] and a mixture of 1- and 2-allyl-1,3-cyclopentadienes **5a**-H and **5b**-H.[8] A similar mixture of the latter was produced by reaction of cyclopentadienylmagnesium bromide with allyl bromide.[9] The most prominent new ^{13}C NMR peaks in the spectrum of the heated Grignard reagent were assigned to (allylcyclopentadienyl)magnesium chloride (**5**-Mg); these were very similar to those in a sample prepared by reaction of the allylcyclopentadiene mixture with ethylmagnesium bromide. Unfortunately, it was not possible to convincingly assign NMR signals to the carbons of the bicyclo[3.3.0]octenyl Grignard compound (**4**-Mg) because of a profusion of minor peaks that appeared at the longer heating times. These included signals from the monomeric hydrocarbon products (probably produced at least in part by attack on solvent) and polymeric side products. Although nearly every signal in the *volatile* hydrolysis fraction could be assigned to the aforementioned components, a complex nonvolatile residue remained. It was also observed semiquantitatively that the summed intensities of the identified organomagnesium signals in the ^{13}C NMR spectrum of the Grignard reagent fell with longer heating times.

A minor ^{13}C NMR peak with the same chemical shift as cyclopentadienylmagnesium bromide was present in the spectrum of the Grignard solution, and the ^{13}C and ^{1}H NMR spectra of the crude hydrolysis mixture also had minor resonances in positions appropriate for 1,3-cyclopentadiene. In addition, a minor, rapidly eluted GC peak had the same retention time as authentic cyclopentadiene and was larger in samples that had been heated longer. The mass spectrum of this peak was consistent with literature data for cyclopentadiene.[10]

Approximate analyses of the heated Grignard reagent solutions could be derived from signal intensities in the ^{13}C NMR spectra of the Grignard reagents and hydrolysis mixtures and from gas chromatograms of the latter. Although the results were only semiquantitative, the different analyses were reasonably consistent, and certain trends were quite clear. First, the fraction of **3**-Mg grew rapidly at first and then leveled off and decreased at longer times, as expected for an intermediate component that disappears in a subsequent reaction. Second, the **4**-Mg and **5**-Mg are not formed initially but appear slowly as the concentration of **3**-Mg builds up. The major competing pathway for reaction of **3**-Mg is *formal* loss of H_2 to give **5**-Mg. Relative extents of this path, of cyclization to **4**-Mg, and of cleavage to cyclopentadienyl anion are *roughly* in the ratio of 0.75:0.20:0.05. (The formation of nonvolatile or polymeric byproducts contributes quantitative uncertainty to this analysis.) The subsequent reactions of **3**-Mg apparently are of higher activation energy than its formation; in a reaction at about 85 °C, formation of **5**-Mg was considerably less evident at similar extents of conversion to **3**-Mg.

2-Bicyclo[3.2.1]octene **6**-H was reported[3] as a minor (1–3%) product in the reaction of the chlorides with sodium (eq 1). In the present Grignard reagent study, it was not detected spectroscopically[3,11] and could have comprised no more than 2% of the total rearrangement product.



(1)

Finally, there was clearly an interconversion between endo and exo isomers of the Grignard reagent. Starting with a mostly endo reagent, the exo remained at about 10–14% of the total mixture while the endo dropped to a similar value; both fell with further heating (6.5% endo and 8.5% exo at 62 h). In the exo Grignard reagent, the endo isomer was not initially detectable (<1%), but at the time that half to two-thirds of the Grignard reagent was rearranged (19 h), exo and endo Grignard reagents were present in a ratio of about 5:1. Thus, both samples isomerized toward a predominantly exo mixture. The two rearranged at similar rates; the exo may have been slightly faster, but no more than 1.5 times as fast.

Qualitatively similar behavior was noted in ethyl ether. In this solvent, the reaction was not as clean, with more protolysis of Grignard reagent and polymer formation. Because of this, it is difficult to compare rates in the two solvents, but it is unlikely that they differed by more than a factor of 2. The initial ring-cleavage product **3**-Mg remained lower in concentration, apparently being more efficiently converted to the subsequent products than in THF. The partitioning between **4**-Mg, **5**-Mg, and cyclopentadienyl anion was similar. Another variable that appeared to have a minimal effect was the grade of magnesium used. Similar results were obtained with "Grignard reagent" grade magnesium, a 99.98% grade magnesium, and sublimed magnesium.

The formal dehydrogenation to **5**-Mg was a feature not reported in the study of the reaction of the chlorides with sodium metal.[3] In that work, the monomeric hydrocarbon product was isolated by reduced pressure distillation from the residual reaction mixture. However, any cyclopentadienyl compound would have been expected to remain behind as the sodium salt and so should have avoided detection. For this reason, we repeated the reaction of the 5-(chloromethyl)norbornene mixture with sodium metal. The volatiles distilled from the reaction consisted of **3a**-H

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(9) It has been known[8] that the presumably first-formed 5-allylcyclopentadiene rearranges with hydrogen migration to the 1-allyl isomer and more slowly to a 1:1 equilibrium mixture of 1- and 2-allyl isomers (see also the Experimental Section).

(10) *Atlas of Mass Spectral Data*; Sternhagen, E., Abrahamson, S., McLafferty, F. W., Eds.; Wiley: New York, 1969; p 49.

(11) (a) Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1977**, *55*, 841. (b) Freeman, P. K.; Ziebarth, T. D.; Rao, V. N. M. *J. Org. Chem.* **1973**, *38*, 3823. (c) By comparison of ^{1}H NMR spectrum and GC retention time with authentic material from another study.

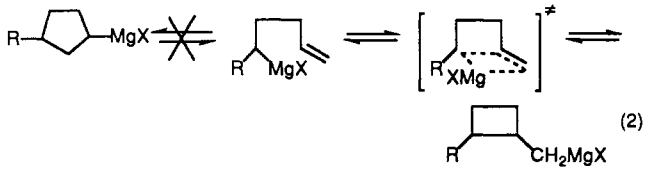
and **3b**-H (50%), 4-H (41%), 1-H and 2-H (5.5%), and 6-H (3.5%). These results are similar to those reported previously,[3] except that no 2-methylnorbornenes were found earlier and no unreacted chloride remained in the present work. No more than 0.2% of the product could have consisted of either 5-H isomer, and hydrolysis of the residue also gave no evidence for their presence.

Discussion

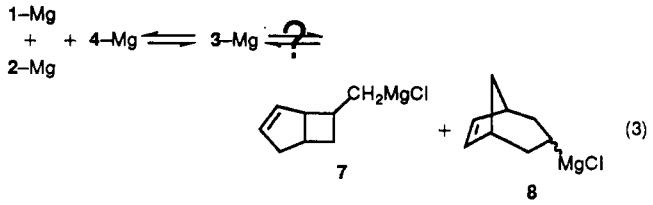
Several features of the results above might be noted. First, the observation of rearrangement with 1- and 2-Mg means that the double bond *does* provide sufficient additional driving force for ring cleavage to occur. The ring cleavage of cyclopentylmethyl derivatives is thermodynamically unfavorable,[2,4] and the added ring strain of the norbornyl skeleton is apparently insufficient to favor cleavage of either (2-norbornylmethyl)sodium[3] or 2-norbornyl organometallics.[4a] However, the cleavage product 3-Mg has an allylic organomagnesium function. This should be stabilized by resonance (σ–π conjugation[12]), though presumably to a smaller extent than the more ionic organosodium function of 3-Na. Another feature favoring cleavage is that a double bond in a norbornane skeleton is less stable than in a simple five-membered ring by about 7–8 kcal/mol,[13] leading to additional relief of strain on cleavage.

A second question concerned the possible interconversion of the exo and endo Grignard isomers. In this respect also, they resemble the corresponding organosodium reagents.[3] The simplest reasonable mechanism for this process is reversal of the ring cleavage. The relatively small extent of exo–endo isomerization observed indicates that 3-Mg partitions to products 4-Mg and 5-Mg somewhat more rapidly than it reverts to 1-Mg or 2-Mg.

The cyclization of organomagnesium compounds,[2a,4,5] as well as the corresponding free radicals,[14] generally proceeds in such a fashion as to produce the smaller of two possible rings. For example, 4-penten-1-yl Grignard compounds are interconverted with cyclobutylmethyl rather than cyclopentyl structures[2a,15] (eq 2). The most likely explanation for this orientation is that it helps to maintain maximum π-overlap as the new C–C σ-bond is forming. In the present instance (eq 3), the "smaller-ring" cyclization



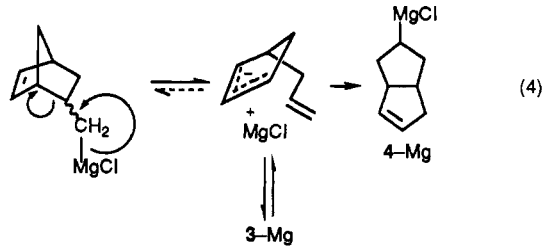
(2)



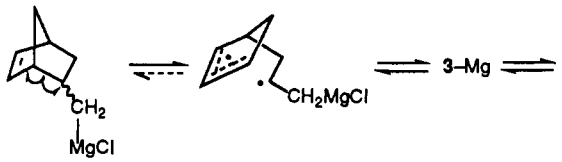
(3)

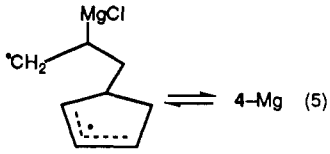
of 3-Mg would form 1- or 2-Mg and the cyclobutylmethyl organometallic 7. The latter would be less stable and so should not lead to observable products. The "abnormal" cyclization to 4-Mg, which *is* observed, might simply be an inherently slower process, seen by default because of the unfavorable equilibrium of the faster "normal" cyclization to 7. On the other hand, the formation of 4-Mg at a competitive rate may be related to the allylic nature of 3-Mg (see below). The other "larger-ring" cyclization to 8 was not detected.

The most probable mechanism for cyclization/ring cleavage rearrangements of organomagnesium compounds appears in most cases to be a concerted four-center process[2] (illustrated in eq 2). However, when the cleaving or adding group is allylic or benzylic, its enhanced stability as an anion or radical might favor an alternative mechanism. Two such possibilities, applied to the present example, are illustrated in eq 4 and 5. The first is cleavage to an allylic



(4)





(5)

carbanion/magnesium ion pair, which then collapses to 3-Mg. The second involves a homolytic bond cleavage in its first step. This is analogous to cleavages of metal alkoxides observed by Cram and co-workers[16] or to the cleavage step in the Wittig rearrangement as proposed by Lansbury and co-workers,[17] and the overall process is equivalent to the reverse of the single-electron-transfer mechanism favored by Ashby[18] for the addition of Grignard reagents to carbon–oxygen double bonds. Both of these mechanisms have been largely ruled out for the cyclization/cleavage rearrangements of simple cycloalkylmethyl Grignard reagents;[2a] groups that might be expected to stabilize carbanionic or radical intermediates generally fail to accelerate the rearrangement, and the reactions are usually somewhat faster in ethyl ether than in the more polar THF. However, it is suggested[19] that ring cleavage of the (2-phenylcyclobutyl)methyl Grignard reagent may follow a mechanism similar to eq 4, since that rearrangement appears to be substantially faster in THF than in ethyl ether.

An additional mechanistic possibility for allylic groups is a symmetry-allowed six-center process. A number of cyclizations involving intramolecular addition of an allylic

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(15) Hill, E. A.; Ni, H.-R. *J. Org. Chem.* **1971**, *36*, 4133.
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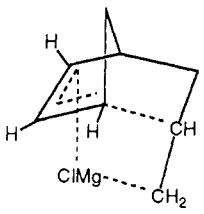
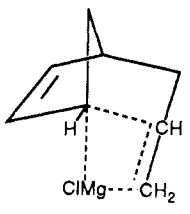
organomagnesium function to an olefinic double bond are known,[20] and recently Oppolzer has developed this into a useful synthetic sequence he refers to as the "magnesium–ene" reaction.[21] The preferred stereochemistry and regiochemistry that are reported appear to be in accord with the six-center mechanism.

Is there any indication that mechanisms other than the four-center process might be implicated in the rearrangements reported here? The lack of a significant solvent effect between ethyl ether and THF offers no support for the more polar mechanism of eq 4. A six-center transition state, illustrated in **9**, is specific to the endo



9



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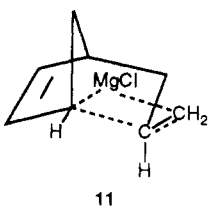

11

isomer. Therefore, the similarity in rates of the endo and exo isomers may rule out this mechanism for the interconversion of **1**- and **2**-Mg with **3**-Mg. However, the isomeric four-center transition states **10** and **11** might also be expected to differ significantly in energy, since the magnesium is differently located relative to C_1 and to the double bond of the norbornene ring. This difference in energy between the two transition states might be minimized if the reaction coordinate consists largely of bond cleavage (as in eq 4 or 5), with migration of the magnesium less important.

The "wrong" regiochemistry in the cyclization of **3**-Mg to **4**-Mg might also be consistent with alternative mechanisms. The geometric constraints that favor formation of the "smaller" ring by the four-center mechanism might be relaxed in an ion-pair or homolytic/electron-transfer mechanism (if one of these were preferred by an *allylic* organomagnesium), allowing easier formation of the larger, less-strained ring. A six-center mechanism might also be drawn.

Although we see that there is some reason to consider other mechanisms, there is no compelleing argument that the present reactions differ fundamentally in mechanism from that of simple cycloalkylmethyl Grignard reagent ring-cleavage/cyclization rearrangements. The exo–endo rate similarity may simply imply a relatively early transition state with little magnesium transfer and not a different mechanism. And as suggested above, the cyclization of **3**-Mg to **4**-Mg could be observed simply because the faster kinetically favored pathway leads to an unobserved, unstable product. In other reported examples in which allylic organomagnesium compounds cyclize by addition to an alkene function, the preference for formation of the "smaller" ring appears to have been maintained.[20,21] However, appropriate cases in which the "larger" ring is favored by other factors might, in fact, lead to a different result, and at least one example has been reported[20c] in which a benzylic Grignard function cyclize to form the "larger" cyclopentane ring (eq 2, R = C_6H_5).

The formation of **5**-Mg is formally equivalent to the loss of H_2 from **3**-Mg. This most likely occurs via elimination of "HMgCl", which then reacts as a "hydride" base with the acidic hydrogen of the resulting allylcyclopentadiene. Other Grignard reagent species present could also react as bases in the same way, leading to part of the monomeric hydrocarbons **1**-H, **2**-H, and **3**-H, which were observed before hydrolysis in the ^{13}C NMR spectra. It is curious that the analogous elimination of NaH does not occur in the sodium reaction.

There was also evidence for the alternative minor elimination from **3**-Mg that produces cyclopentadienyl anion. This reaction could be formulated similarly as elimination of allylmagnesium chloride (possibly by a symmetry-allowed six-center process) followed by deprotonation of the cyclopentadiene. Neither propene nor allylmagnesium chloride was clearly identified, but neither could small amounts be excluded with certainty. A formally similar fragmentation has been observed[22] on heating *endo*-5-norbornen-2-ol with a Grignard reagent. Cyclopentadiene (or cyclopentadienide) and acetaldehyde (or its enolate) were formed in that instance. Interestingly, the exo isomer was inert to the cleavage, and the reaction also occurred for the sodium alkoxide or for the alcohol with magnesium bromide catalysis.

Experimental Section

Boiling points are uncorrected. Gas chromatographic analyses and preparative separations utilized Varian (Aerograph) A90-P chromatographs with the following columns: A, $^1/_4$ in. × 10 ft, 25% tricresyl phosphate on firebrick; B, $^1/_4$ in. and $^1/_2$ in. × 10 ft Ucon polar on firebrick. NMR spectra were run on Varian Associates HA-100, EM-360L, and CFT-20 and Bruker WM-250 spectrometers. ^{13}C NMR assignments were assisted by single-frequency off-resonance decoupling (SFORD) spectra and by comparison with chemical shifts estimated by using additive parameters.[23] About 15% of C_6D_6 was added to Grignard solutions for a lock signal and used as reference (128.0 ppm). ^{13}C chemical shifts for organomagnesium and related organic compounds are collected for comparison in Table I. Mass spectra were obtained on a Hewlett-Packard 5985 gas chromatograph–mass spectrometer with electron impact ionization (15 eV), using a capillary column, 0.25-mm i.d. × 30 m, 0.25-μm coating of 5% diphenyl/95% dimethylpolysiloxane. Results are reported as *m/e* (abundance). THF and ethyl ether were purified by reflux and distillation under nitrogen from benzophenone ketyl or from lithium aluminum hydride. Magnesium of various grades was used: "Grignard reagent" grade, RMC-40P (99.98%) from Reade Manufacturing Co., and sublimed magnesium. Grignard reactions were run under a nitrogen atmosphere, using glassware and transfer syringes that had been oven-dried. Tubes for heating or storing Grignard solutions were dried, connected with a short length of Tygon tubing to a manifold, evacuated, refilled with nitrogen, loaded by syringe in a counterflow of nitrogen through an opening on the top of the manifold, and sealed after partial evacuation. In some cases, screw-capped, septum-sealed NMR tubes were used.

5-(Chloromethyl)norbornene. Samples consisting mostly of the endo isomer were prepared from a commercial mixture of the isomers of 5-(hydroxymethyl)norbornene by the procedure of Sauers et al.[24] GC analyses of various preparations (column A) showed two peaks in a ratio of 1:5 to 1:10, in order of retention time, corresponding to the exo and endo isomers. A similar ratio

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was deduced from ^{13}C NMR peak intensities. NMR analyses of small samples separated by preparative GC were consistent with the assigned structures. The ^1H NMR spectrum of the endo isomer agreed with published data.[25] No data for the exo isomer were located, but the observed spectrum had features in common with those of related endo isomers;[26] ^1H NMR (CCl_4) δ 6.05 (br s, 2, olefinic), 3.44 (AB part of ABX system, A 3.50_5, B 3.40, J_{AB} = 10.7, J_{AX} = 8.90, J_{BX} = 6.66 Hz), 2.80 (br s, 2, bridgeheads), 1.9–1.6 (m, 1, H_{5N}), 1.5–1.0 (m, 4). In some preparations, an additional component identified as 4-oxatricyclo[4.2.1.$0^{3,7}$]nonane was isolated; mp 91 °C [lit.[27] mp 105, 117–119 °C]; IR and ^1H NMR spectra consistent with literature data;[27] ^{13}C NMR ($CDCl_3$) δ 79.56 (d), 74.03 (t), 46.52 (d), 40.75 (t), 38.52 (d), 38.30 (t), 38.17 (t), 34.17 (d) ppm; MS, M^+ 124 (71), with major fragments at 109 (12), 106 (5), 95 (15), 93 (14), 91 (14), 82 (66), 81 (56), 80 (100), 69 (40). The pure exo isomer was prepared by a route starting with base-catalyzed equilibration of the isomers of methyl 5-norbornene-2-carboxylate, hydrolysis, and removal of remaining endo isomer as the iodolactone.[28] Lithium aluminum hydride reduction and conversion to the chloride produced the exo chloride without detectable contamination (<1%) by the endo.

Grignard Reagent Preparation and Rearrangement. Magnesium turnings (0.65 g, 27 mmol) were activated by addition of bromoethane (0.15 mL, 2 mmol) in 2 mL of THF. After completion of reaction, the supernatant liquid was withdrawn by syringe, and the turnings were washed once with a small portion of solvent. A sample of the chloride (2.84 g, 20 mmol), shown by NMR and GC to have a ratio of endo:exo = 87:13, was added with 15 mL of THF, and the solution was heated to gentle reflux until Grignard reagent formation occurred. Portions of the solution were transferred to NMR tubes and to a larger storage tube. These were heated at 115 °C for periods of time up to 62 h with periodic observation of the ^{13}C NMR spectrum. Samples were opened and hydrolyzed after 0, 1200, 2540, and 3725 min. The volatile solvent and monomeric hydrolysis products were transferred by vacuum to a trap and then examined by NMR, GC, and GC-MS. A number of additional runs on similar scale were performed that used different chloride samples, solvent (ethyl ether), or grade and activation of the magnesium and in some cases by following changes in the ^1H NMR. The following description of experimental results incorporates data from other runs where relevant and notes any details that are dependent on these variations.

The ^{13}C NMR spectrum of the original Grignard reagent had signals assigned to 1- and 2-Mg (see Table I); two signals of 2-Mg were nearly coincident and were obscured in mixtures by one from 1-Mg. Resonances from hydrocarbons 1- and 2-H amounted to less than 2% of the Grignard reagent, and yields from coupling or other side reactions were comparably small. The ^1H NMR spectrum had high-field doublets (CH_2Mg) at –0.70 and –0.44 ppm for the endo and exo isomers, J = 7.7 Hz (–0.52 and –0.25 ppm in ethyl ether). Olefinic protons of the principal (endo) isomer were seen as a triplet at 5.96 ppm (6.04 in ethyl ether), with an *apparent* J = 1.8 Hz. Another multiplet (assigned as H_{6N}) was clearly seen at 0.25 ppm (0.34 in ethyl ether), with coupling constants of 2.5, 4.9, and 10.9 Hz. In THF, additional multiplets were at 2.56 and 2.42 (probable bridgeheads), 2.2, and 1.22 ppm (AB pattern of H_{8a},H_{8s}) (2.65, 2.55, 2.31, and 1.96 ppm in ethyl ether). On heating, the ^{13}C signals of 1-Mg and 2-Mg decreased in intensity, and new resonances assigned to 3-Mg and 5-Mg grew in (see Table I). On long heating, numerous minor peaks appeared. In the ^1H NMR, reactant signals also decreased and were replaced by relatively broad new resonances at 6.00 and 5.83 (singlets over indistinct absorption from 6.2 to 5.5), 5.05–4.75 (m), and –0.3 to –0.6 ppm [6.15–5.4 (m), 5.15–4.75 (m), 2.0 (br), and –0.35 ppm (br) in ethyl ether].

The ^{13}C NMR spectrum of the volatile product of hydrolysis at times from 0 to 62 h could be almost completely assigned to components 1-H–5-H (see Table I and below), although at the longest periods of heating and especially in ethyl ether, there were increasing numbers of quite minor unidentified resonances. Spectra of the crude hydrolysis product and the residue from vacuum transfer indicated the presence of additional less volatile material.

Preparative gas chromatography (column B) led to the isolation of three cleanly separable peaks, each of which was in turn seen by GC (at lower temperature on column B or on column A) and by ^{13}C NMR to be a mixture. In other earlier runs, small-scale preparative separation was done on column A. The first to be eluted were the *endo*- and *exo*-5-methylnorbornenes 1- and 2-H. These were the only products from the unheated Grignard reagent and were further identified by comparison with literature ^1H and ^{13}C NMR data;[26a,29] MS, M^+ 108 (12), with major fragments at 93 (3), 79 (5), 66 (100).

The second peak to be eluted contained nearly equal amounts of 3- and 4-allylcyclopentenes. The ^1H NMR and IR spectra were consistent with published data,[6] and the GC retention time and ^{13}C NMR spectra were identical with those from a sample isolated from a repetition of the reaction of 1-Cl and 2-Cl with sodium (vide infra): GC-MS (partial resolution), 3a-H: M^+ at 108 (2), with fragments at 67 (100), 66 (24), and 41 (3); 3b-H: M^+ at 108 (1) with fragments at 93 (3), 79 (17), 67 (60), 66 (100), 54 (8), 41 (3).

The third peak to be eluted was further partially resolved into two components by chromatography at a lower temperature. The first of these was identified as 2-bicyclo[3.3.0]octene (4-H) by comparison of ^1H and ^{13}C NMR spectra with published data.[7] Its GC retention time and ^{13}C NMR spectrum were also the same as those of a sample from the reaction of 1-Cl and 2-Cl with sodium; MS, M^+ at 108 (50), with major fragments at 93 (26), 80 (86), 79 (100), 67 (24), 66 (20). The second component had GC retention time and ^{13}C NMR spectrum identical with those of a mixture produced by the reaction of cyclopentadienylmagnesium bromide with allyl bromide (vide infra), and ^1H and ^{13}C NMR and IR spectra were in agreement with literature data[8] for a mixture of 1- and 2-allyl-1,3-cyclopentadienes, 5a-H and 5b-H; MS, M^+ at 106 (80), with major fragments at 105 (25), 91 (100), 79 (28), 78 (71). In addition to the C-8 components isolated by preparative GC, a small, rapidly eluted peak coincided in retention time with 1,3-cyclopentadiene; too little was present for successful isolation and spectra. However, both ^1H and ^{13}C NMR spectra of the total volatile product had peaks at appropriate chemical shifts for 1,3-cyclopentadiene, the mass spectrum (by GC-MS) was consistent with the published spectrum,[10] and the ^{13}C NMR spectrum of the Grignard reagent had a resonance at about the same shift as observed for cyclopentadienylmagnesium bromide (see below).

Alkylation of Cyclopentadienylmagnesium Bromide with Allyl Bromide. An ethylmagnesium bromide solution in THF was prepared, about 1.5 M in the organometallic. A portion of this solution (70 mL, about 0.1 mol) was added to 0.1 mol of 1,3-cyclopentadiene. Disappearance of the ethylmagnesium

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bromide (13.75 and −2.0 ppm) and the cyclopentadiene (133.04, 132.55, and 41.63 ppm) and appearance of the cyclopentadienide (104.9 ppm) and ethane (6.56 ppm) were monitored in ^{13}C NMR spectra of the solution. After 20 h of heating at about 45 °C, the reaction was nearly complete. Allyl bromide (12.1 g, 0.1 mol) was added; the solution warmed slightly, and precipitate gradually formed. After about 1 h, the ^{13}C NMR spectrum of the supernatant solution showed the disappearance of the cyclopentadienylmagnesium bromide and the residual ethylmagnesium bromide, the presence of the resonances of 1-pentene, and the appearance of a new set of resonances (see Table I) assigned to 1-allyl-1,3-cyclopentadiene. After 2 days at room temperature, an additional set of peaks attributed to 2-allyl-1,3-cyclopentadiene had grown to comparable size. A portion of the solution was worked up by addition of water and extraction with pentane. The pentane extract was washed with water and saturated salt solution, dried (Na_2SO_4), and distilled under vacuum (about 10 mmHg). The material distilling below 30 °C, collected on an ice bath, had a ^{13}C NMR spectrum identical with the mixture of allylcyclopentadiene isomers.[8] The remainder of the solution was treated with excess ethylmagnesium bromide. After about 2 days of gentle heating (35–40 °C), about half of the allylcyclopentadiene had reacted, and a new set of resonances assigned to allylcyclopentadienylmagnesium bromide was present (see Table I). A similar spectrum was obtained by treatment of the distilled allylcyclopentadiene mixture with ethylmagnesium bromide.

Reaction of 5-(Chloromethyl)norbornene with Sodium. In a reaction vessel with a glass stirring paddle, sodium metal (0.97 g, 42 mmol) and 4 mL of *n*-hexadecane were heated to 110 °C. Over a period of 20 min, 5-(chloromethyl)norbornene (3 mL, 20 mmol) was added dropwise. After an additional hour, the temperature was dropped to 80–90 °C, and volatile material was distilled to a cold trap under vacuum (10 mmHg). Most of the residual liquid was removed and added to water for hydrolysis. *tert*-Butyl alcohol was added to the remaining sodium, and the solvent and suspended material were again removed and hydrolyzed. The volatile products were examined by GC and ^{13}C NMR, as described above for reaction products from the Grignard reagent. Compounds **1**-H, **2**-H, **3a**-H, **3b**-H, **4**-H, and **6**-H were identified, but there was no indication of the presence of **5a**-H or **5b**-H in any of the product fractions.

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Ruthenium(II)-Catalyzed Reactions of 1,4-Epiperoxides

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The behavior of 1,4-epiperoxides in the presence of transition-metal complexes is highly dependent on the structures of the substrates and the nature of the metal catalysts. Reaction of saturated epiperoxides such as 1,3-epiperoxycyclopentane, 1,4-epiperoxycyclohexane, or dihydroascaridole catalyzed by $RuCl_2(PPh_3)_3$ in dichloromethane gives a mixture of products arising from fragmentation, rearrangement, reduction, disproportionation, etc. Prostaglandin H_2 methyl ester undergoes clean and stereospecific fragmentation to afford methyl (5*Z*,8*E*,10*E*,12*S*)-12-hydroxy-5,8,10-heptadecatrienoate and malonaldehyde. Bicyclic 2,3-didehydro 1,4-epiperoxides give the *syn*-1,2:3,4-diepoxides by the same catalyst. The monocyclic analogues are transformed to a mixture of diepoxides and furan products. The stereochemical outcome of the epoxide formation reflects unique differences in the ground-state geometry of the starting epiperoxide substrates. $FeCl_2(PPh_3)_2$ serves as a useful catalyst for the skeletal change of sterically hindered bicyclic 2,3-didehydro 1,4-epiperoxides to the *syn*-diepoxides. In addition, the Fe complex best effects the conversion of 1,4-unsubstituted 2,3-didehydro epiperoxides to furans. The Ru-catalyzed reactions are interpreted in terms of the intermediacy of inner-sphere radicals formed by atom transfer of the Ru(II) species to peroxy substrates, in contrast to the Fe-catalyzed reactions proceeding via free, outer-sphere radicals generated by an electron-transfer mechanism.

1,4-Epiperoxides (endoperoxides) have become increasingly significant as synthetic[1] and biosynthetic[2] intermediates. The diverse chemical behavior induced by the O–O bond cleavage is bewitching.[1] Mild and selective decomposition of the epiperoxides provides a synthetically useful tool for the site-specific 1,4-dioxygenation of 1,3-diene carbon frameworks.[1,3] Also, an opportunity for the interpretation of biosynthetic mechanisms may be given by chemical simulation, particularly with well-defined metallic reagents.[1g] In light of this, detailed studies have been done on the behavior of 1,4-epiperoxides in the presence of various kinds of transition-metal salts or complexes[4,5] as well as under thermal and photochemical

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