ratio of **25/24** was 17/83 after 15 min; the ratio did not change after an additional 40 min at −100 °C. An additional 1.1 equiv of *n*-butyllithium was added. After 15 min the above ratio was 75/16; compound **26** was also detected. The mixture was continually stirred at −100 °C; examination of aliquots showed that the amount of **24** decreased while the amount of butylated products (**26** and **27**) increased. The mixture was quenched with water after a total of 4 h after the second addition of n-C_4H_9Li. The mixture of products obtained contained phenylpropionitrile (**25**, 62%), α-butyl-β-phenylpropionitrile (**26**, 19%), α-butyl-β-(*p*-butylphenyl)propionitrile (**27**, 13%), and an unidentified product. Products were collected by preparative GLC.

α-Butyl-β-phenylpropionitrile (26): NMR ($CDCl_3$) δ 0.9 (t, 3, aliphatic H), 1.55 (m, 6, aliphatic H), 2.9 (m, 3, aliphatic H), 7.3 (m, 5, aromatic H).

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37, H, 9.15; N, 7.48. Found: C, 83.55; H, 9.05; N, 7.55.

α-Butyl-β-(*p*-butylphenyl)propionitrile (27): NMR ($CDCl_3$) δ 0.70–1.9 (m, 16, aliphatic H), 2.2 (m, 2, CH_2), 2.85 (m, 3, aliphatic H), 7.2 (m, 4, aromatic H).

Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35. Found: C, 83.79; H, 10.60.

***p*-Iodobenzylnitrile (28).** Examination[4b] of an aliquot, quenched with water taken after 15 min from reaction of **28**[27] with 1 equiv of n-C_4H_9Li at −100 °C, showed the ratio of benzylnitrile to starting material (**28**) to be 80/20; starting material immediately disappeared upon addition of an additional 0.5 equiv of n-C_4H_9Li. Attempts to trap the anionic products from the reaction mixture with cyclohexanone gave a multicomponent mixture (GLC) which was not resolved.

Registry No.—**1**, 6952-59-6; **2**, 100-47-0; **3**, 57775-02-7; **4**, 6136-62-5; **5**, 623-00-7; **6**, 57808-43-2; **7**, 1503-49-7; **8**, 2042-37-7; **9**, 57775-03-8; **10**, 28873-85-0; **11**, 57775-04-9; **12**, 34446-14-5; **15**, 1009-14-9; **16**, 57775-05-0; **17a**, 19472-74-3; **17b**, 31938-07,5; **17c**, 16532-79-9; **20**, 57775-06-1; **23**, 57775-07-2; **24**, 57775-08-3; **26**, 54321-42-5; **27**, 57775-09-4; **28**, 51628-12-7; *n*-butyllithium, 109-72-8; benzophenone, 119-61-9; methyl benzoate, 93-58-3; cyclohexanone, 108-94-1; methyl acrylate, 96-33-3; phenyl isocyanate, 103-71-9; phenylacetonitrile, 140-29-4; *n*-butyl bromide, 109-65-9; α-butylphenylacetonitrile, 3508-98-3; α,α-dibutylphenylacetonitrile, 3508-99-4; 2-(*o*-bromophenyl)propionitrile, 57775-10-7; β-(*p*-bromophenyl)propionamide, 57775-11-8; β-(*p*-bromophenyl)propionic acid, 1643-30-7.

References and Notes

(1) Supported by U.S. Army Research Office, Grant DAHCO4 74 GD128.
(2) H. Gilman and G. Melstrom, *J. Am. Chem. Soc.*, **70**, 4177 (1948).
(3) (a) W. E. Parham and Y. A. Sayed, *J. Org. Chem.*, **39**, 2051 (1974); (b) *ibid.*, **39**, 2053 (1974).
(4) The degree of metalation was determined by treating aliquots with water and analyzing the dried organic products by (a) GLC [20% SE-30 on Chromosorb W (60/80 mesh), 6 ft × 0.25 in., or 5% SE-30 on Chromosorb W (60/80 mesh), 3 ft × 0.25 in., including injection of authentic starting halides and reduced products], (b) NMR, the benzylic protons of *p*-iodobenzyl nitrile and benzyl nitrile appear as sharp singlets at δ 3.75 and 3.65, respectively.
(5) Dr. Robert Piccirilli, Duke University, private communication.
(6) Thin layer chromatography showed it to be multicomponent.
(7) Imino anthraquinones (or *N*-butyl derivatives) were anticipated as possible products of self-condensation of **13** by analogy to products of self-condensation of lithium *o*-lithiobenzoates (cf. ref 3b).
(8) Reaction of **18a**, formed from **17a** and 1 equiv of *n*-butyllithium, with methyl iodide, gave a 79% yield of nearly pure 2-(*o*-bromophenyl)propionitrile (see Experimental Section).
(9) Analysis of the organic products obtained by decomposition of aliquots with water showed 17% halogen–metal exchange after 0.5 h with 1 equiv of *n*-butyllithium.
(10) Butylation is assumed to occur by reaction of *n*-butyl bromide, formed by exchange, with the dilithio derivative formed from **24**.
(11) Studies of aliquots showed that 80% iodine–lithium exchange occurs when **28** is treated with 1 equiv of *n*-butyllithium.
(12) *o*-, *m*-, and *p*-bromobenzonitrile are commercially available.
(13) Practical grade stored over molecular sieves.
(14) G. W. A. Kahlbaum and G. von Wirkner, *Ber.*, **27**, 1894 (1894).
(15) (a) bp 90–110 °C; (b) bp 60–90 °C; (c) bp 30–60 °C.
(16) L. Novak and M. Protiva, *Collect. Czech. Chem. Commun.*, **24**, 3966 (1959).
(17) F. Ahrens, *Ber.*, **20**, 2957 (1887).
(18) W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **29**, 853 (1964).
(19) Freshly distilled from hydroquinone.
(20) M. P. H. van der Meulen, *Recl. Trav. Chim. Pays-Bas*, **15**, 282 (1896).
(21) (a) C. L. Jackson and J. F. White, *Am. Chem. J.*, **2**, 315 (1880); (b) N. Campbell and J. E. McKail, *J. Chem. Soc.*, 1251 (1948).
(22) R. C. Fuson et al., *J. Org. Chem.*, **23**, 1161 (1958).
(23) (a) W. E. Parham and D. C. Egberg, *J. Org. Chem.*, **37**, 1545 (1972); (b) L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 450.
(24) Shown by coinjection of an authentic sample prepared from benzyl nitrile (1 equiv), sodium hydride (2 equiv), and methyl iodide (2 equiv) in dimethylformamide; bp 226 °C (754 mm); $n^{25}D$ 1.5016 (lit.[25] bp 232 °C; n_D 1.50665).
(25) O. Wallach, *Chem. Zentralbl.*, 1047 (1899).
(26) (a) S. Gabriel and Z. Zimmerman, *Ber.*, **13**, 1683 (1880); (b) J. V. Braun and J. Nelles, *Chem Ber.*, **66**, 1464 (1933).
(27) (a) C. F. Maybery and C. L. Jackson, *Am. Chem. J.*, **2**, 253 (1880); (b) C. L. Jackson, *ibid.*, **1**, 100 (1879).

Ring Cleavage Rearrangements of 2-Bicyclo[3.2.0]heptyl and Related Grignard Reagents

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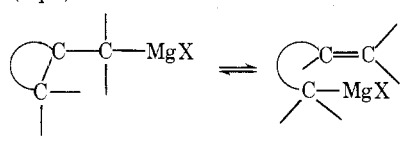
The Grignard reagent (**12**) from 2-bromobicyclo[3.2.0]heptane undergoes a ring cleavage rearrangement to cyclopentenylethyl (**13**) and cycloheptenyl (**14**) Grignard reagents. Grignard **14** is slowly converted to **13**. The rate of rearrangement of **12** is thought to be somewhat retarded by geometric restrictions introduced by the bicyclic skeleton. The facility of the rearrangement of **12** → **14** may indicate that the preferred transition state for rearrangement is nonplanar. Rearrangement of the Grignard reagent **25** from 3-chlorotricyclo[5.3.0.$0^{2,6}$]decane occurs in analogous fashion. Grignard reagents **31** from 2-bromo-6-alkoxybicyclo[3.2.0]heptanes decompose with elimination of the alkoxy group and ring cleavage to 3-vinylcyclopentene and 1,4-cycloheptadiene.

The rearrangement of appropriate organomagnesium compounds, either by cleavage of a strained ring or its reverse (intramolecular addition to a multiple bond), is well established (eq 1):[2]

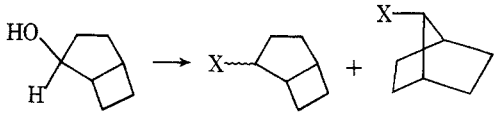


(1)

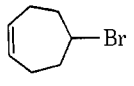
Experimental results have been interpreted as being most consistent with a synchronous four-center process for this rearrangement.[2-4] In the present paper, we report Grignard cleavage studies in the bicyclo[3.2.0]heptyl and tricyclo[5.3.0.$0^{2,6}$]decyl systems. These studies were undertaken to probe the effects of geometric constraints imposed on the transition state by the bicyclic system, and to assess the influence of a polar substituent, an alkoxy group.

Preparation of Halides. Bicyclo[3.2.0]heptan-2-ol (**1**)

was synthesized as reported by Winstein and Stafford.[5] Reaction of the alcohol with thionyl chloride in pyridine yielded a mixture containing *exo*-2-chlorobicyclo-[3.2.0]heptane and 7-chloronorbornane in a ratio of about 1:2. Bromide formation with bromine and triphenylphosphine was more successful in producing product without rearrangement. *endo*-2-Bromobicyclo[3.2.0]heptane, *exo*-2-bromobicyclo[3.2.0]heptane, and 7-bromonorbornane were formed in a ratio of 5:2:1, respectively. The mixture could be resolved by gas chromatography, but was used without separation for the Grignard studies.



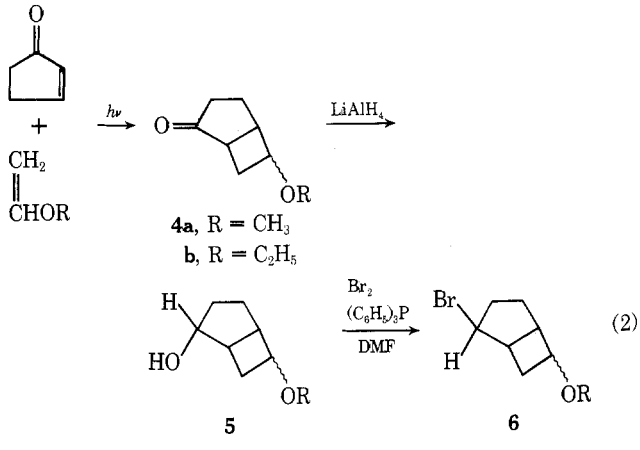
1 **2a**, X = Br; **b**, X = Cl



3

5-Bromocycloheptene (**3**) was synthesized from the corresponding alcohol.[6] It also contained a small amount (~10%) of 7-bromonorbornane, undoubtedly produced via carbonium ion rearrangement in the reaction of the alcohol with phosphorus tribromide.

The photochemical cycloaddition of cyclopentenone to methyl or ethyl vinyl ether produced the corresponding 6-alkoxybicyclo[3.2.0]heptan-2-ones **4**, which were converted to the respective bromides **6** (eq 2). Each of the compounds

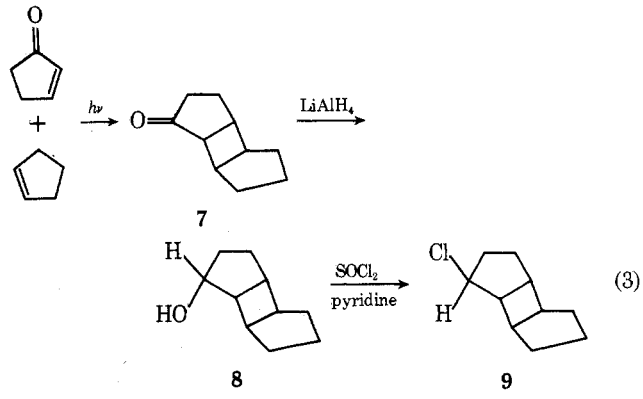


4a, R = CH_3; **b**, R = C_2H_5

5 **6** (2)

4–**6** was obtained as a mixture of two isomers present in nearly equal amounts. These are epimers differing in configuration at the alkoxy group, rather than a mixture of 6- and 7-alkoxy derivatives, since either Wolff–Kishner reduction of ketones **4a** or **4b** or tri-*n*-butyltin hydride reduction of **6a** led to a mixture of saturated bicyclic ethers, rather than a single ether product. Hydrolysis of the Grignard reagent from **6a** or **6b**, or reduction of **6a** with sodium in alcohol, led to a mixture which contained unsaturated components also, as a result of disproportionation and/or elimination. The epimers of **4**–**6** were separated on a small scale for spectroscopic characterization, but most of the work was done with the mixture. Attempted preparation of the chloride corresponding to **6b** (thionyl chloride–pyridine) led to a mixture of products, including one lacking the ethoxy group, and was not pursued further.

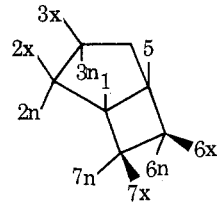
Tricyclo[5.3.0.$0^{2,6}$]decan-3-one (**7**), prepared by photocycloaddition of cyclopentenone to cyclopentene,[7] was reduced and converted to the chloride **9** (eq 3).



7 **8** **9** (3)

Stereochemical Considerations. From the results of x-ray crystallographic[8] and electron diffraction[9] studies, it appears that there is a pronounced tendency toward twisting or folding of the five-membered ring of the bicycloheptyl and tricyclodecyl systems. Folding of the four-membered ring is also likely. The precise manner of distortion from planarity may depend upon substitution and unsaturation present, as well as crystal forces in the x-ray studies.

NMR spectra provide further evidence for nonplanar geometry, and also for the configuration of substituents. In the 2-substituted bicyclo[3.2.0]heptanes, H-2n generally appears as a doublet,[10] with J_{2n-3n} as the only coupling of significant magnitude (see **10**). In the present work, dou-



10

blet absorption was noted for alcohol **1** and halides *exo*-**2a**, **6**, and **9** ($J \sim 3$–4 Hz). Small values for J_{2n-1} and J_{2n-3x} are found also in unsaturated analogues.[11] These require a conformation in which carbon 2 is rotated in the exo direction and carbon 3 endo, in order to obtain the implied dihedral angles of about 90°. With an endo 2 substituent, coupling of H-2x is more extensive. In the present work, spectra of alcohols **5** and **8** showed absorption resembling a broadened first order (1–3–3–1) quartet, suggesting coupling to three hydrogens (1, 3x, 3n) with similar coupling constants of 7–8 Hz. Similar results have been reported for some more heavily substituted or unsaturated analogues,[10b,11,12] though a different interpretation has also been given.[10a]

The configurations of compounds in this study are consistent with chemical expectations, as well as with the NMR spectra. Thus, reaction of **1** with thionyl chloride gives largely carbonium ion rearrangement to 7-chloronorbornane; most of the product of unrearranged structure appears to be exo isomer, formed with retention of configuration. Reaction with triphenylphosphine dibromide gives much less rearrangement, and most of the unrearranged product is now formed with inversion (endo), as expected from the greater tendency of this reagent to react by direct displacement. Reaction of **1** with triphenylphosphine–carbon tetrachloride also gives unrearranged endo isomer, but much more rearrangement.[10a] In the preparative sequence of eq 2 and 3, hydride reduction of ketones occurs as expected from the exo direction to yield endo alcohol. Conversion to halides without rearrangement was much more successful, since displacement by halide ion can occur from the less hindered exo side of the ring, and the C–C bond

Table I. Rearrangement Rates of Bicyclo[3.2.0]heptyl and Related Grignard Reagents in Ether

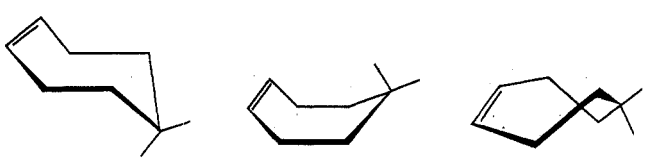
Grignard rearrangement	Concn, M	Temp, °C	$10^6 k$, s^{-1} [a]	k_{rel} (100 °C)
12 → 13	0.16	87.6	4.68 ± 0.09	0.059 [b]
		102.7	29.9 ± 0.7	
		114.6	104 ± 4	
	0.23	79.6	1.9	
		91.8	16	
		106.6	53	
	0.65	112	~50	
12 → 14	0.16	87.6	0.45	5×10^{-3} [c]
		102.7	2.4	
		114.6	7.3	
14 → 13	0.16	114.6	~2	$\sim 10^{-3}$
	~1	110	~0.3	
		125	~3.5	
exo-**31b → 32 + 33**	0.4	80	~80	~2
endo-**31a → 32 + 33**	0.4	76	>800	>40
25 → 26	~1	**110**	~1	$\sim 10^{-3}$
16a	0.145	66–80		1.68[d]
16b	0.06	66–94		(1.00)[d,e]

[a] Error limits where given are standard deviations from a least-squares correlation. Errors in other rates are probably about ±10%, unless otherwise indicated as approximate. [b] $\Delta H^{\ddagger} = 31.6 \pm 0.9$ kcal/mol; $\Delta S^{\ddagger} = 4.3 \pm 1.5$ eu. [c] $\Delta H^{\ddagger} = 28$ kcal/mol, $\Delta S^{\ddagger} = -10$ eu. [d] Reference 17. [e] $\Delta H^{\ddagger} = 31.9 \pm 0.7$ kcal/mol, $\Delta S^{\ddagger} = 11 \pm 1$ eu.

that would have to be involved in a rearrangement to a norbornyl skeleton is no longer situated anti to the departing OH function. In NMR spectra of Grignard reagents prepared in this study, H-2 gave a poorly resolved multiplet, probably consistent with the anticipated mixture of exo and endo configurations of the magnesium halide function.

The configuration at C_6 (or C_7) is less satisfactorily established on the basis of coupling patterns of H-6n and H-6x. There are differences in coupling constants apparent in the spectra of unsaturated and more highly substituted compounds,[13] but the multiplets for compounds in eq 2 are complex and poorly resolved, precluding any really definitive distinction from coupling patterns. On the other hand, there does appear to be a consistent chemical shift difference, with either a hydrogen or methyl appearing at higher field when in the endo position.[13,14] Interestingly, exo and endo methoxy groups appear to have the same shift.[15] In the present work, the isomers with endo methoxy or ethoxy groups had shorter GC retention times. The methoxy derivatives had more easily interpreted spectra.

The conformation of cycloheptenes has been discussed by a number of workers.[16] Although there is some disagreement, it appears that both chair (**11a**) and boat (**11b**) forms may be reasonably accessible energetically. The boat form may undergo pseudorotation through the apparently high-

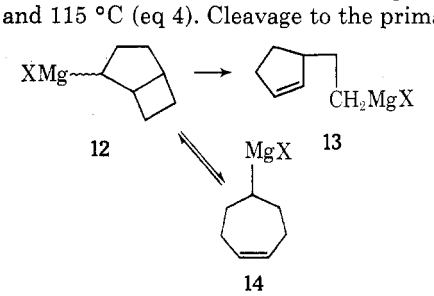


11a **11b** **11c**

er energy twist-boat (**11c**), but the chair form is more rigid. NMR spectra of the 5-substituted cycloheptenes prepared in the present work are of some interest. The C_5 proton of both the alcohol and its acetate appear as well-resolved multiplets, showing coupling to two sets of two protons, probably those cis and trans at C_4 and C_6 (apparent J = 3.8, 8.6 Hz in the alcohol; 4.0, 8.0 Hz in the acetate). However, the bromide has only an unresolved multiplet of comparable width. The difference is probably a consequence of virtual coupling to other ring hydrogens, rather than a difference in conformation; a two-proton multiplet (probably at C_4 and C_6), which appears at high field in the alcohol and acetate, is deshielded in the bromide so as to fall within the multiplet of other ring hydrogens. In the Grignard reagent, the C_5 proton is a pentuplet resulting from apparently equal coupling to four protons ($J \sim 5.5$ Hz). The difference could be attributed either to conformational difference, or to a "deceptively simple" situation. Unfortunately, the coupling patterns do not allow a clear choice among conformations. Examination of models suggests that an axial C_5 hydrogen in either the chair or boat conformation should have one large and one quite small coupling constant, while an equatorial C_5 hydrogen in either conformation should have two rather small coupling constants.

Preparation and Rearrangement of Grignard Reagents. Grignard reagents, prepared in ether or THF solution from halides **2, 3, 6,** and **9,** were heated in sealed tubes. Products of reaction were determined by hydrolysis of the reagent, followed by their separation with gas chromatography. In some instances, NMR spectra of the intact Grignard reagent provided evidence of the reaction. By analyzing products as a function of time, a measure of the rate of reaction could be obtained. Kinetics results are listed in Table I. This table also includes rough rate estimates made by analysis of only one to three samples of heated Grignard rather than the minimum of six to eight tubes used for the better kinetics runs.

The 2-Bicyclo[3.2.0]heptyl Grignard. Rearrangement of the unsubstituted 2-bicyclo[3.2.0]heptyl Grignard reagent **12** in ether solution was studied at temperatures between 80 and 115 °C (eq 4). Cleavage to the primary cyclo-

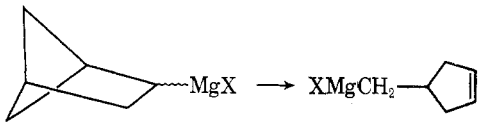


(4)

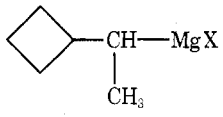
pentenylethyl Grignard **13** as the major pathway was indicated by the appearance of a high-field CH_2Mg triplet in the NMR spectrum of the heated Grignard. Gas chromatographic analysis of the hydrocarbons formed by hydrolysis showed that the secondary cycloheptenyl Grignard **14** was a minor rearrangement product (6.7% at 114.6 °C to 9.6% at

87.6 °C). At much longer heating times, it appeared that **14** was slowly converted to **13**. This was confirmed by independent preparation and rearrangement of **14**. The conversion of **14** to **13** presumably occurred via cyclization to **12**, although this intermediate did not reach sufficient concentration to allow the detection of any bicyclo[3.2.0]heptane on hydrolysis. Norbornane, resulting from minor amounts of 7-bromonorbornane present in both starting bromides, comprised a constant fraction of the hydrolysis products.

In a previous publication,[17] it was pointed out that 2-bicyclo[2.1.1]hexyl Grignard reagents **15** undergo ring cleavage reactions considerably more slowly than the monocyclic analogue **16**, despite a somewhat greater relief of ring strain



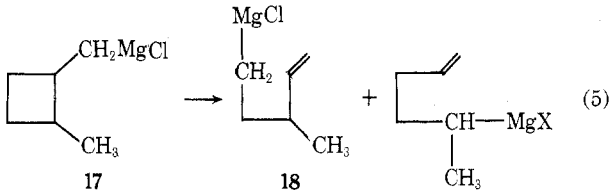
15



16a, X = Cl
b, X = Br

during cleavage of the bicyclic organomagnesium. The difference was attributed to the inability of the more rigid bicyclic Grignard to attain optimum transition state geometry without energetically costly distortion.

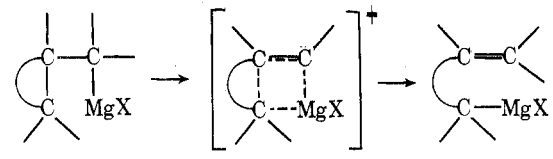
The cleavage reaction of **12** to **13** may be retarded in a similar fashion. As shown in Table I, **12** rearranges more slowly than **16b** by a factor of 0.059. A correction should be made to allow for the fact that the bicyclic Grignard has a cis 2-alkyl substituent on the cyclobutane ring. Since *cis*-**17** cleaves to **18**, with a rate about 0.3 that of cyclobutylmeth-



17 **18** **19** (5)

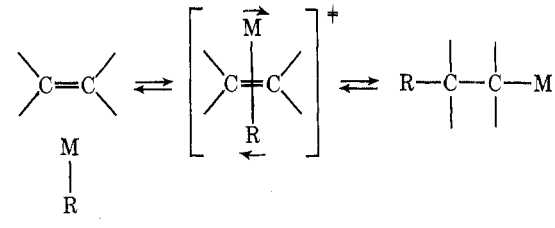
ylmagnesium chloride,[18] a corrected relative rate for the rearrangement **12** → **13** would be about 0.2. This decrease in rate is found despite a probable increase in thermodynamic driving force for the reaction (by release of ring strain). Unfortunately, heat of formation information is not available for the bicyclo[3.2.0]heptyl ring system, so this conclusion must be based on estimates of the strain energy.[19,20]

Formation of the minor cycloheptenyl Grignard product **14** in significant amount warrants comment. In terms of product stability alone, this is anticipated to be the lesser of the two products, since a secondary Grignard is about 3–5 kcal/mol less stable than a primary one,[25-27] and the strain energies of cyclopentene and cycloheptene are similar.[21] In the simpler cleavage reaction of eq 5, where the choice is also between formation of primary (**18**) and secondary (**19**) Grignards, the primary predominates by a factor of close to 100. In the absence of additional factors, then, a comparable ratio of ca. 100:1 might have been expected for **13**:**14** also. Such an additional factor may indeed exist. The most obvious model for the previously supported four-center transition state[2,3] is one in which the four atoms involved are arranged in an approximately coplanar and rectangular array:

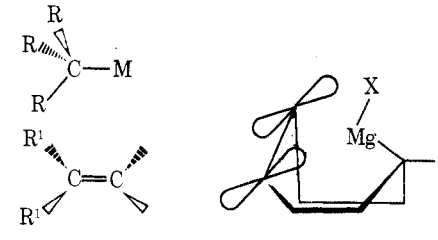


Examination of models shows that such a configuration can be attained for the cleavage to the cyclopentenylethyl Grignard **13** with minimal bond bending, though probably some increase in torsional strain. However, the distortion necessary to pass through such a transition state en route to **14** should be prohibitive. Yet, the rearrangement path to secondary Grignard (**12** → **14**) competes more favorably in the constrained bicycloheptyl Grignard than in the more flexible case of **17** → **19**. Furthermore, it appears that the absolute rates of these two rearrangements yielding secondary Grignard are similar.[28] We must therefore conclude that the reaction coordinate leading to **14** more closely resembles the ideal geometry for this reaction than the one leading to **13**, and that the "coplanar rectangular" model is a poor one for this transition state.

Additional insight into the reaction coordinate may be drawn by viewing it in the reverse direction—as an intramolecular addition. The "coplanar-rectangular" transition state corresponds to a parallel approach of the C–Mg bond to one lobe of the C=C π orbital. In an alternative reaction coordinate, the approach might be in perpendicular fashion:



A similar reaction coordinate has been proposed on other grounds by Eisch for the addition of triphenylaluminum to alkynes.[29a] This reaction path may have the additional virtue of avoiding the unfavorable steric interactions illustrated in **20**, which are present in any coplanar approach. In the present instance, we might note that a substituent in the axial 5 position of a boat cycloheptene (**21**) is held in a location over the double bond, probably ideal for a "perpendicular" approach to the addition.[29b]

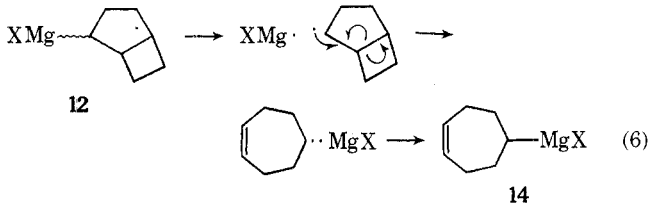


20 **21**

A reaction coordinate involving this perpendicular approach would also fit well with the notion of a π-complex intermediate in the addition. Intramolecular interaction of the metal of an organometallic with olefinic π electrons has been demonstrated for organolithium, -aluminum, and -zinc compounds,[30] and π-complex intermediates are widely considered in additions of organometallics to alkenes or alkynes.[31] Such a mechanism has been suggested for the Grignard cyclization–cleavage process, though without firm experimental support.[2-4]

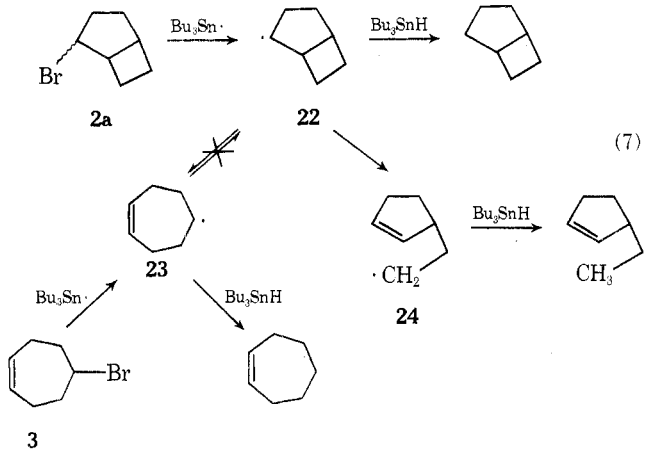
A possible alternative to the logic above is that the reaction proceeds by two concurrent mechanisms—a coplanar

four-center cleavage to the cyclopentenylethyl Grignard **13**, and a competing *radical* cleavage to the cycloheptenyl Grignard (eq 6). However, additional experiments render this



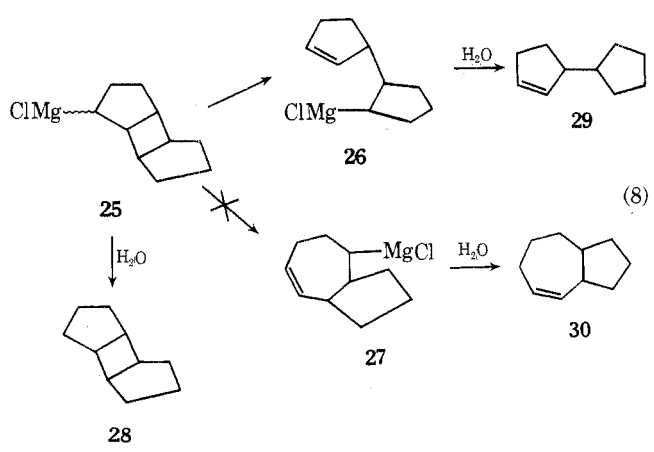
12 14 (6)

explanation untenable. Reduction of either **2a** or **3** with tri-*n*-butyltin hydride in the absence of solvent led to the corresponding hydrocarbon as essentially the only product. In 0.02 M hydride solution, reduction of excess **2a** gave sizable amounts of 3-ethylcyclopentene, resulting from partial rearrangement of the intermediate radical **22**. The absence of cycloheptene in the product, and of significant amounts of 3-ethylcyclopentene from reduction of **3**, indicate that interconversion of radicals **22** and **23** is much slower than rearrangement of **22** to **24**. Therefore, a radical mechanism cannot explain the formation of **14**.



(7)

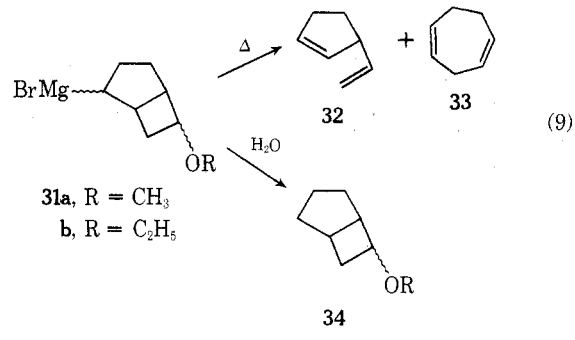
The 3-Tricyclo[5.3.0.0^{2,6}]decyl Grignard (25). With the tricyclic Grignard reagent **25**, rearrangement by either of the two available bond cleavages would produce a secondary Grignard reagent (eq 8). Since cleavage to the (secondary) cycloheptene was unexpectedly favorable in rearrangement of the bicyclic Grignard **12**, it might have been anticipated to compete even more strongly here. It was found that **25** does rearrange slowly, but that hydrolysis yielded only the hydrocarbons **28** and **29**, corresponding to unrearranged and the rearranged Grignard **26**, respectively. There was no evidence for the presence of **30**, so cleavage to **27** must be unimportant. Examination of models suggests



(8)

that the rigidity imposed by the additional fused ring may destabilize **27** relative to **26**. The conformation with a chair cycloheptene should be badly strained—the dihedral angle between bonds in the cyclopentane ring would have to be nearly 90°—and interconversion between boat conformations should also be quite hindered. It may be that the added strain is severe enough to decrease the rate of cleavage by this pathway to a very small value. Alternatively, recyclization of **27** to **25** may occur rapidly enough that the concentration of the former never reaches a significant level.

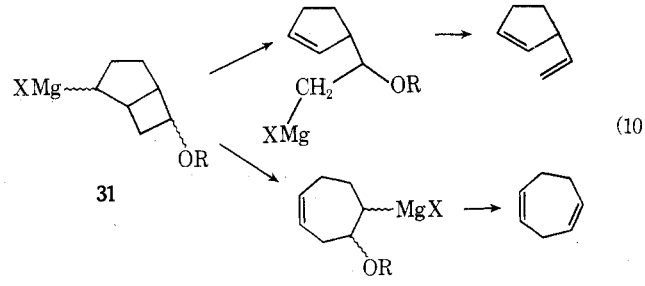
The 6-Alkoxybicyclo[3.2.0]hept-2-yl Grignard Reagents. A study of the alkoxy-substituted Grignard reagents **31** was initiated to investigate the possibility of concerted fragmentation processes, in which breaking of the C_6–alkoxy bond occurs in the same step as C_2–Mg cleavage.



(9)

Such processes would have as driving force the conversion of a magnesium alkyl to a magnesium alkoxide. Examination of models suggests that in the transition states **35** and **36** for a concerted fragmentation, twisting and puckering of the rings allows the cleaving bonds to *approach* an electronically favorable anti-coplanar orientation about each of the forming double bonds (though all *three* bonds undergoing cleavage cannot be mutually coplanar). Similarly in **37**, the two eliminations are syn and anti copolanar. Coordination between the departing magnesium and alkoxy functions would provide further assistance to cleavage, as shown in **38**. However, close approach of the ether oxygen to the magnesium requires twisting away from an anti-coplanar orientation. In transition state **39**, both eliminations would be anti, but the product would be *trans,trans*-1,4-cycloheptadiene. It is important to note that **35**–**38** are all specific to elimination of an endo alkoxy group, but that the exo epimer probably does not have a reasonable concerted pathway.

Alternatively, cleavage to yield the same products might occur in stepwise fashion, as shown in eq 10.

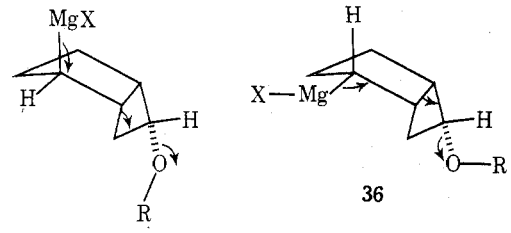


(10)

On heating, Grignard reagents **31** did cleave to yield the dienes 3-vinylcyclopentene (**32**) and 1,4-cycloheptadiene (**33**) as major and minor product, respectively. The Grignard solutions studied were mixtures of the epimers with exo and endo alkoxy groups. It was apparent, from analysis of solutions heated for different periods of time before hydrolysis, that the epimers showed quantitative differences

in their behavior. The epimer with endo alkoxy decomposed substantially more rapidly. For example, although *endo*-**31b** had rearranged nearly completely after 1 h at 80°, the *exo*-**31b** in the same solution disappeared with a half-life of 2–3 h. Compared with the cleavage rearrangement of Grignard reagent **12**, the approximate relative rates of *endo*- and *exo*-**31** were about 10^3 and 30, respectively. The products from the two epimers also differed. Product formed in the later stages of the reaction, when only *exo*-**31** was reacting, had about 15–20% of the minor cycloheptadiene product **33**. Early in the reaction it was present in smaller amounts, consistent with its formation as 5–10% of the product from *endo*-**31**. A more accurate comparison between epimers was precluded by sizable amounts of disproportionation during formation of the Grignard.

The increased cleavage rates of both epimers are consistent with the operation of an electron-withdrawing inductive effect of the alkoxy group, which stabilizes the intermediate structures in the stepwise mechanism of eq 10.[32] The greater rate with endo alkoxy could be a consequence of relief of steric repulsions present in the starting material. Alternatively, it may be evidence for the importance of concerted fragmentations such as **35–38**, which are specific



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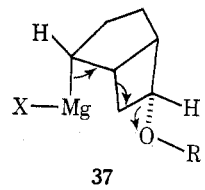

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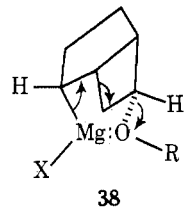

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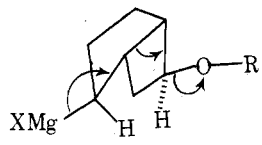

39

to this epimer. The product mixture observed may be more difficult to rationalize with the concerted mechanism. The relative amounts of cleavage to the seven-membered ring products for both exo and endo alkoxy (15–20 and 5–10%, respectively) are similar to that found in the cleavage of **12** (7–10%). It requires a rather remarkable coincidence for *endo*-**31**, reacting by two or more concerted fragmentation pathways which are specific to a single product, to yield nearly the same mixture of five- and seven-membered ring products as *exo*-**31** and **12**.

Experimental Section

Spectra were run on Varian Associates A-60, T-60, and HA-100 NMR spectrometers, and Beckman IR-5 and IR-8 ir spectrophotometers. Gas chromatography was on Varian Aerograph A-90-P chromatographs, using the following columns: A, 0.25 in. × 10 ft, 20% Carbowax 20M on Chromosorb P; B, 0.25 in. × 10 ft, 25% Ucon polar on firebrick; C, 0.25 in. × 10 ft, 20% poly-*m*-phenyl ether on Chromosorb P; D, 0.25 in. × 5 ft, Tide.

Preparation and Handling of Grignard Reagents. Grignard reagents were prepared in a flask sealed to a condenser, with a side arm above the condenser for attachment to a nitrogen source or vacuum line. The solvents used were distilled from lithium aluminum hydride under a slow stream of nitrogen and transferred by syringe. Magnesium was a sublimed grade.[34] When necessary, a small crystal of I_2 or a very small amount of methyl iodide, ethyl bromide, or ethylene chloride was used to help initiate the reaction. Reactions were run under a slight positive pressure of dry nitrogen. In instances where hydrolysis or disproportionation products were sufficiently volatile, the solvent and any volatile components were pumped to a cold trap under high vacuum, and replaced by fresh solvent. Samples of Grignard (ca. 0.5–1 ml) were sealed in ampules, and sometimes in an NMR tube. After heating, the ampules were opened in an inert atmosphere "glove bag", and either hydrolyzed immediately or fitted to an adapter which allowed volatiles to be pumped to a trap before hydrolysis. Hydrocarbon products were analyzed by gas chromatography, on the assumption of equal sensitivity of isomeric hydrocarbons. Rearrangement rates were determined from a plot of log ([unrearranged]/[unrearranged] + [rearranged]) vs. time.

2-Halobicyclo[3.2.0]heptanes (2). *exo*-2-Bicyclo[3.2.0]heptanol was prepared as reported by Winstein and Stafford:[5] bp 85–86 °C (20 mm); n^{25}D 1.4850; NMR (CCl_4) δ 3.88 (d, 2, J = 3.0 Hz), 3.62 (s, 1, OH), and 1.0–3.0 ppm (m, 10). Reaction of 1.0 g (8.9 mmol) of the alcohol with thionyl chloride (1.06 g, 8.9 mmol) and pyridine (0.70 g, 8.9 mmol) yielded 0.30 g (26%) of product: bp 60 °C (20 mm); n^{24}D 1.4857; NMR (CCl_4) δ 1.0–3.0 (m, 10), 3.89 (s, broad, ca. ⅔ H), and 4.12 ppm (d, ca. ⅓ H, J = 3.7 Hz). This mixture was not studied further.

To a stirred solution of the alcohol (10.0 g, 0.089 mol) and triphenylphosphine (24.5 g, 0.0935 mol) in dry dimethylformamide (50 ml) at 50–57 °C, bromine (14.5 g, 0.089 mol) was added over a period of 45 min. After an additional 1 h of heating at this temperature, the mixture was distilled under vacuum (up to 80 °C at 1 mm). The distillate was diluted with 50 ml of saturated aqueous sodium chloride and extracted with petroleum ether. The extract was washed with aqueous sodium chloride solution, distilled twice, and chromatographed on alumina to yield 4.5 g (30%) of product: bp 69° (10 mm); n^{27}D 1.5092; NMR (neat) δ 3.9–4.45 (m, 1, CHBr) and 1.0–3.2 ppm (m, 10).

Anal. Calcd for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 48.29; H, 6.43.

Gas chromatography on column A showed the presence of three components in relative amounts (in order of increasing elution time) of 12.5, 21.5, and 66%.

Grignard Reagent from 2-Bromobicyclo[3.2.0]heptane. Grignard reagents were prepared from the bromide and an excess of sublimed magnesium in ether or tetrahydrofuran solution.

After completion of the reaction, the solvent and any volatile materials present were pumped to a cold trap (at ca. 5 μ pressure), and fresh solvent was added. Gas chromatographic examination (column B) of either the volatiles from the Grignard preparation or the product of hydrolysis of the Grignard (with cold 3 N HCl) showed two hydrocarbons. The first of these, present to the extent of 10% in the volatiles from the Grignard preparation and 13–14% in the hydrolysis product, had retention time and infrared and NMR spectra identical with those of authentic norbornane. The major component of the Grignard hydrolysis was identified as bicyclo[3.2.0]heptane on the following basis: (a) mode of formation, as major hydrolysis product from the starting halide; (b) ir spectrum, with major peaks coinciding in position with those in an authentic dilute solution spectrum kindly furnished to us by Professor W. G. Dauben; (c) NMR spectrum, which had complex absorption from δ 1.0 to 2.4 ppm and a broadened singlet at 2.75 ppm in a ratio of 10:2, but no olefinic proton absorption. The NMR spectrum of the Grignard in THF (ca. 0.8 M) had a broad, ill-defined multiplet from about δ 0.1 to −0.6 ppm, and no olefinic absorption.

When the Grignard solutions were heated for a number of hours in sealed tubes in the vicinity of 100 °C, changes occurred both in the NMR spectrum and in the hydrolysis products. In the NMR, there appeared a prominent triplet at δ −0.5 ppm (J = 8.5 Hz, CH_2Mg) and olefinic absorption at 5.66 ppm (apparent AB quartet, $J_{AB} \simeq$ 5.5 Hz, with probable further triplet splitting of ca. 2 Hz). Hydrolysis yielded two new components, formed initially in a ratio of about 10:1. The first of these was identified as 3-ethylcyclopentene: NMR (CCl_4) δ 0.91 (t, 3, J = 7 Hz, CH_3), 1.0–2.8 (m, 7), and 5.63 ppm (s, 2, olefinic); ir identical with published spectrum.[35] The second (minor) component was cycloheptene: NMR (CCl_4) δ 1.65 (m, 6), 2.13 (m, 4, allylic), and 5.72 ppm (apparent triplet, 2, J = 3.5 Hz, olefinic) and identical with an authentic sample; ir identical with published spectrum[36] and authentic sam-

ple. At long heating time, the cycloheptene in the Grignard hydrolysis product decreased relative to the 3-ethylcyclopentene.

At least two minor components having retention times similar to bicyclo[3.2.0]heptane were detected, but not identified. First, the NMR spectrum of the bicyclo[3.2.0]heptane in the volatiles pumped from the Grignard preparation indicated the presence of unsaturation (δ 5.78 ppm, s). Integration of the spectrum would be consistent with an approximately 1:1 mixture of bicyclo[3.2.0]heptane and bicyclo[3.2.0]hept-2-ene. Second, at long heating times, the GC peak corresponding in retention time to bicyclo[3.2.0]heptane remained constant at about 5% of the total product. Unsaturation was indicated by NMR (δ 5.78 and 4.71 ppm) and infrared spectra (3060 and 802 cm^{-1}). A saturated component (NMR singlets at δ 0.99 and 1.20 ppm) also appeared to be present. The olefinic NMR signals were not present in the hydrolysis product of the unheated Grignard reagent.

In determining the kinetics of the rearrangement, the concentration of unrearranged hydrocarbon was decreased to allow for the 5% of nonrearranging material. The total rate of disappearance of starting material was determined, and apportioned between the two rearrangement paths according to the average ratio of ethylcyclopentene to cycloheptene.

5-Bromocycloheptene. 4-Cycloheptenol was prepared by the method of Cope:[6] bp 68.5–70.7 °C (8 mm) [lit.[6] bp 83–84 °C (11 mm)]; NMR (CCl_4) δ 1.46 (m, 2), 1.7–2.5 (m, 6), 3.73 (triplet of triplets, 1, J = 3.8, 8.6 Hz, CHOH), 4.30 (s, 1, OH), 5.69 ppm (m, 2, olefinic).

Phosphorus tribromide (7.08 g, 26 mmol) was added dropwise to a mixture of 4-cycloheptenol (7.9 g, 69 mmol) and pyridine (1.45 g, 18 mmol) in 15 ml of anhydrous ether cooled to 0 °C. The mixture was allowed to warm to room temperature and stand overnight. The ether was distilled at atmospheric pressure, and then the residue was slowly heated under vacuum (~8 mm) to a maximum temperature of 105 °C. Product distilled to a receiver. Redistillation yielded 5.8 g: bp 62–64 °C (8 mm); NMR (CCl_4) δ 1.7–2.5 (m, 8), 4.39 (s, b, 1, CHBr), 5.76 ppm (m, 2, olefinic). Gas chromatography (column B) showed the presence of a minor component (ca. 10%) eluted just ahead of the major bromide.

Anal. Calcd for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 47.85; H, 6.28.

Grignard Reagent from 5-Bromocycloheptene. A Grignard reagent was prepared from 5-bromocycloheptene and magnesium in dried ether. Hydrolysis of the Grignard reagent yielded a mixture of hydrocarbons consisting principally of cycloheptene (86%) and norbornane (9%), as shown by GC analysis (column B). Two minor components of longer retention time, both unsaturated, were present. The solvent pumped from the Grignard preparation had the same components, with the norbornane and cycloheptene comprising about 50% of the total. The ir and NMR spectra of the major longer retention time component were identical with those of 1,4-cycloheptadiene (see below).

An NMR spectrum of the Grignard solution in ether showed olefinic absorption at δ 5.7 ppm as an unsymmetrical complex multiplet, about 15 Hz wide. The CHMg resonance was obscured by the solvent side bands in ether, but appeared at δ 0.5 ppm in THF solution. It was an apparent pentuplet, with J = 5.5 Hz. A weak broad doublet absorption at δ −0.4 ppm was not identified.

The Grignard solution in ether was heated for 92 h at 130 °C. Volatiles were removed under vacuum and the residual Grignard was hydrolyzed. As before, the product contained cycloheptene and norbornane, but the major component was identified as 3-ethylcyclopentene. About 72% of the cycloheptenyl component had undergone rearrangement. The volatiles pumped from the Grignard before hydrolysis contained the same components as previously, with cycloheptene comprising the major portion. The norbornane appeared to have remained as a constant 8–10% of the total products. A sample heated for 120 h at 110 °C showed a smaller fraction of rearrangement (6–7%).

The NMR spectrum of the heated Grignard reagent showed additional rather ill-defined olefinic absorption at δ 5.45–5.65, and a sharp singlet at 5.33 ppm attributed to ethylene formed by attack of Grignard on the ether solvent. A high-field CH_2Mg triplet appeared at −0.50 ppm, with J = 8.5 Hz.

6-Alkoxybicyclo[3.2.0]heptan-2-ones (4a and 4b). An excess of methyl vinyl ether (3–4 ml) was condensed into Pyrex ampules of 1-cm diameter. 2-Cyclopenten-1-one (2 g) was added to each, and the ampules were sealed under vacuum. The ampules were exposed for 24 h to the output of a Hanovia 450-W mercury arc lamp, while immersed in a bath of water at about 10 °C. After irradiation, the ampules were opened and combined, and the mixture distilled to yield 71% of **4a:** bp 216, 110–112 °C (20 mm); ir (CCl_4) 1748, 1124 cm^{-1}; NMR (CCl_4) δ 4.1–3.4 (m, 1, CHO), 3.17 (s, 3, OCH_3), and 3.1–1.4 ppm (m, 8). Gas chromatography (columns C and D) showed that the product was a mixture of two incompletely separated components present in roughly equal amount.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.57, H, 8.57. Found: C, 68.28; H, 8.49.

A similar reaction of cyclopentenone (25 g, 0.30 ml) and ethyl vinyl ether (50 ml) yielded a mixture of **4b:** bp 62–65 °C (1 mm); ir (CCl_4) 1742, 1120 cm^{-1}; NMR (CCl_4) δ 4.25–3.6 (m, 1, CHO), 3.32 (q, 2, J = 7 Hz, CH_2O), 3.1–1.35 (m, 8), 1.4 ppm (t, 3, J = 7 Hz, CH_3). Gas chromatography (column C) again showed a mixture of two partially separated components in approximately a 1:1 ratio.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.02; H, 8.83.

6-Alkoxybicyclo[3.2.0]heptanes (34a and 34b). A mixture of methoxy ketone **4a** (2.52 g, 0.018 mol), 85% hydrazine hydrate (20 ml), and diethylene glycol (20 ml) was heated at reflux for 45 min. The mixture was cooled, potassium hydroxide (6.7 g, 0.12 mol) was added, and the mixture was distilled slowly up to a pot temperature of 190 °C. The distillate was extracted with pentane, dried (Na_2SO_4), and distilled to yield 1.15 g (45%) of **34a,** ir (CCl_4) 1123 cm^{-1}. The product was a mixture of two components present in equal amount, which were separated by preparative GC (column C, in order of increasing retention time): (1) endo methoxy, NMR (CCl_4) δ 4.1–3.3 (m, 1, CHO), 3.10 (s, 3, OCH_3), and 3.0–1.25 (m, 10); and (2) exo methoxy, NMR (CCl_4) δ 3.6–3.15 (m, 1, CHO), 3.10 (s, 3, OCH_3), 2.6 (s, b, 2, bridgehead), and 2.35–1.15 ppm (m, 8).

Anal. Calcd for $C_8H_{14}O$: C, 76.14, H, 11.18. Found: C, 76.23; H, 10.95.

A similar mixture was produced by reaction of bromide **6a** (1 g) with an equimolar quantity of tri-*n*-butyltin hydride in refluxing benzene. Reduction of **6a** (1 g) by addition as a solution in 2 ml of ethanol to 0.25 g of molten sodium yielded a mixture of products shown by NMR to contain some unsaturation. On GC column D, the product was separated into two portions. The first of these (18%) had ir (CCl_4) 1640 (C=C) and 1078 cm^{-1}; NMR (CCl_4) δ 5.7 (b, 2, =CH), 3.75–3.25 (m, 1, CHO), 3.15 (s, 3.0 CH_3), and 3.1–1.9 ppm (m, 6), and was tentatively identified as *endo*-6-methoxybicyclo[3.2.0]hept-2-ene. The second appeared to contain mostly the expected saturated reduction product, along with about 15–20% of an olefinic component.

Wolff-Kishner reduction of the ethoxy ketone **4b** was carried out in similar fashion: ir (CCl_4) 1133 and 1108 cm^{-1}. The components were separated by preparative gas chromatography on column C: (1) endo ethoxy, NMR (CCl_4) δ 3.82 (q, b, 1, J = 7.5 Hz, CHO), 3.27 (q, 2, J = 6.8 Hz, CH_2O), 3.0–1.3 (m, 10), and 1.11 ppm (t, 3, J = 6.8 Hz, CH_3); (2) exo ethoxy, NMR (CCl_4) δ 3.3 (q, superimposed on an unresolved multiplet, 3, $J_{quartet}$ = 6.8 Hz, CHO and CH_2O), 2.6 (s, b, 2, bridgehead), 2.4–1.3 (m, 8), 1.11 (t, 3, J = 6.8, CH_3).

6-Alkoxybicyclo[3.2.0]-heptan-*endo*-2-ols (5a and 5b). A suspension of methoxy ketone **4a** (10.9 g, 0.072 mol) in 50 ml of 2 N sodium hydroxide was added in portions to a solution of sodium borohydride (2.0 g, 0.072 mol) in 15 ml of 2 N sodium hydroxide. The mixture was stirred and maintained at 35–40 °C by cooling during the addition, then heated gradually to 90 °C over 2 h and maintained at that temperature for 1.5 h. Anhydrous potassium carbonate (9.6 g) was added, the organic layer was separated, and the aqueous phase was extracted with ether. The organic solutions were dried (Na_2SO_4) and distilled to yield 7.5 g (68.5%) of **5a:** bp 127–130° (20 mm); ir (CCl_4) 3457, 1207, 1120, and 1072 cm^{-1}. The product was found by GC to consist of two components which were preparatively separated (column D) for spectroscopic characterization: (1) endo methoxy, NMR (CCl_4) δ 4.1–3.4 (m, 3, OH and CHO), 3.13 (s, 3, OCH_3), and 2.9–1.2 ppm (m, 8); (2) exo methoxy, NMR (CCl_4) δ 4.2–3.7 (m, 2, OH and C_2HO), 3.25 (m, 1, C_6HO), 3.13 (s, 3, OCH_3), 2.5 (s, b, 2, bridgehead), and 2.5–1.3 (m, 6).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.60; H, 9.86. Found: C, 67.57; H, 9.88.

The ethoxy ketone **4b** was reduced to **5b** by addition of sodium borohydride (2.5 g, 0.066 mol) in small portions to a solution of ketone (20.9 g, 0.135 mol) in 100 ml of absolute ethanol. The mixture was refluxed for 3 h, 100 g of 25% aqueous sodium hydroxide was added, reflux was continued for 1 h, and 100 ml of water was added. The product was extracted into ether, washed, dried, and distilled to yield 18.7 g (90%): bp 77–81 °C (1 mm); ir (CCl_4) 3454, 1192, 1120, and 1070 cm^{-1}. The mixture had NMR absorption for the ethoxy group at 3.28 and 1.13 ppm (J = 7 Hz) and multiplet absorption in the region 4.4–3.5 ppm attributable to the CHO pro-

tons. Partial resolution could be obtained by gas chromatography (column C), but spectra of the separated fractions were relatively uninformative.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 69.15; H, 10.49.

***exo*-2-Bromo-6-alkoxybicyclo[3.2.0]heptanes (6a and 6b).** Bromine (7.2 g, 0.045 mol) was added dropwise over a period of 30 min to a stirred solution of **5a** (6.4 g, 0.045 mol) and triphenylphosphine (11.8 g, 0.045 mol) in 80 ml of dry dimethylformamide, maintained at 55 °C. After 2.5 h of additional heating at 55 °C, the reaction mixture was distilled, up to a pot temperature of 90 °C (1 mm). The distillate was extracted with 30–60 °C petroleum ether. The extract was washed (aqueous NaCl), dried ($CaCl_2$), and distilled to give a 61% yield of **6a:** bp 69–70 °C (1 mm); ir (CCl_4) 1207, 1120, and 1072 cm^{-1}. Analysis by gas chromatography (columns C and D) showed the presence of two components, which were preparatively separated for spectroscopic characterization: (1) endo methoxy, NMR (CCl_4) δ 4.25 (d, 1, $J \sim 3$ Hz, CHBr), 4.0–3.5 (m, 1, CHO), 3.14 (s, 3, OCH_3), and 3.1–1.0 ppm (m, 8); (2) exo methoxy, NMR (CCl_4) δ 4.25 (d, 1, $J \sim 3$ Hz, CHBr), 3.3 (m, 1, CHO), 3.14 (s, 3, OCH_3), and 3.1–1.0 ppm (m, 8).

Anal. Calcd for $C_8H_{13}BrO$: C, 46.85; H, 6.34. Found: C, 46.88; H, 6.45.

In analogous fashion, **5b** was converted to **6b** in 53% yield: bp 90° (1 mm); ir (CCl_4) 2999, 1291, 1229, 1199, 1133, 1119, 898, 734, and 711 cm^{-1}. The NMR spectrum had a total of four hydrogens at low field (4.4–3.0 ppm), including a one-proton doublet at 4.20 ppm ($J \sim 3$ Hz, CHBr), a two-proton quartet at 3.27 ppm ($J = 7$ Hz, CH_2O), and additional absorption totaling about one hydrogen, partially obscured by the ethoxy quartet, and partially appearing as an apparent quartet at 3.84 ppm ($J \sim 7$ Hz). Along with complex absorption from 3.0 to 1.3 ppm, the methyl triplet appeared at 1.12 ppm ($J = 7$ Hz). Gas chromatography (column C) indicated a mixture of two components, present in approximately equal amounts.

Grignard Reagents from 6a and 6b. Grignard reagents were prepared from 0.5–2-g samples of **6a** or **6b** and an excess of sublimed magnesium in ether, following the general procedure. Concentrations were determined by acid titration and, in some cases, by complexiometric titration for magnesium. In either case, hydrolysis yielded a similar mixture which was partially resolved by gas chromatography (columns C and D). The major GC fraction was a broadened peak which included both exo and endo isomers of the appropriate 6-alkoxybicyclo[3.2.0]heptane, along with small amounts of an unsaturated component tentatively assigned as the *exo*-6-alkoxybicyclo[3.2.0]hept-2-ene. The probable endo isomer of the latter was eluted shortly before the major peak. This portion of the product closely resembled the product of sodium–ethanol reduction of **6a** (see above). The unsaturated components, which are presumed to have originated in a side reaction during Grignard reagent formation, comprised about 25–30% of the total product. On heating for a period of hours in the vicinity of 80 °C two new components appeared, which increased with time at the expense of the major fraction. These were identified by comparison of ir and NMR spectra and GC retention times with authentic samples of 3-vinylcyclopentene (**32**) and 1,4-cycloheptadiene (**33**) (in order of retention time). In some cases, the Grignard reagent appeared to have significant amounts of the former before heating. They were formed in a ratio of 5 to 10:1. In addition, both Grignard reagents contained a small amount (<1%) of an unidentified component eluted between **14** and **15**, which appeared saturated from its NMR spectrum, and which did not vary with heating time.

3-Vinylcyclopentene was prepared by the reaction of a Grignard reagent from 2.0 g (0.019 mol) of vinyl bromide in THF with 2.0 g (0.02 mol) of 3-chlorocyclopentene. The reaction mixture was hydrolyzed, dried (Na_2SO_4), and distilled to yield 0.8 g (40%) of product: bp 91–93 °C (lit.[37] bp 93 °C); ir (CCl_4) 3100 and 1620 cm^{-1} (C=C); NMR (CCl_4) δ 5.45–6.20 (m, 3, =CH), 4.70–5.20 (m, 2, $=CH_2$), 3.2 (m, 1), and 2.5–1.2 ppm (m, 4).

1,4-Cycloheptadiene was prepared by the method of Doering and Roth.[38] Components separated by GC and characterized by NMR were cycloheptene, 1,4-cycloheptadiene, and unreacted 1,3,5-cycloheptatriene. The diene had NMR (CCl_4) δ 5.8 (m, 4, olefinic), 3.0 (m, 2, doubly allylic), and 2.4 (m, 4, allylic).

Tricyclo[5.3.0.$0^{2,6}$]decan-3-ol (8) was prepared by addition of an ether solution of tricyclo[5.3.0.$0^{2,6}$]decan-3-one[7] (**7**, 5 g, 33 mmol) to lithium aluminum hydride (0.63 g, 16.6 mmol) in ether. Excess hydride was decomposed with ethyl acetate followed by water. The product was obtained in 80% yield by evaporation of the solvent and recrystallization from benzene and petroleum ether: mp 67–70 °C; NMR (CCl_4) δ 4.08 (broadened q, 1, $J \sim 7$ Hz, CHOH), 3.25 (s, 1, OH), 2.55 (broadened s, 1, bridgehead), and 2.2–1.3 ppm (m, 13); (pyridine) δ 5.57 (s, 1, OH), 4.32 (q, 1, $J = 7.5$ Hz, CHOH), 2.87 (broadened s, 1, bridgehead), and 2.3–1.3 ppm (m, 13).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.72; H, 10.66.

3-Chlorotricyclo[5.3.0.$0^{2,6}$]decane (9). To 5 g (33 mmol) of 8 and 2.60 g (33 mmol) of pyridine cooled to 0 °C, 4.3 g (36 mmol) of thionyl chloride was added dropwise. The temperature was raised over 2 h to about 95 °C, and maintained at that temperature for another 2 h. The reaction mixture was extracted with petroleum ether. The solvent was evaporated and the product distilled to yield 75% of product: bp 64–70 °C (0.45 mm); NMR (CCl_4) δ 4.15 (d, 1, $J = 3.2$ Hz, CHCl), 2.3–1.4 (m, 14).

Anal. Calcd for $C_{10}H_{15}Cl$: C, 70.36; H, 8.85. Found: C, 70.55; H, 9.18.

Tricyclo[5.3.0.$0^{2,6}$]decane (28). A mixture of 3.25 g of **7**, 15 ml of diethylene glycol, and 15 ml of hydrazine hydrate was refluxed for 15 min. Potassium hydroxide (5 g) was added, and product was distilled from the reaction mixture. The product was taken up in petroleum ether, dried, and distilled, bp 61 °C (25 mm) [lit.[39] bp 52–53 °C (10 mm)].

Grignard Reagent from 3-Chlorotricyclo[5.3.0.$0^{2,6}$]decane. A Grignard reagent was prepared from 1 g of the chloride and 0.172 g of sublimed magnesium in 5 ml of dry ether. Part of the solution was hydrolyzed. Gas chromatography (column B) showed two products in a ratio of 3.5:1. The first of these had GC retention time, ir, and NMR spectra identical with those of authentic tricyclo[5.3.0.$0^{2,5}$]decane. The minor component had retention time, ir, and NMR spectra identical with those of authentic 3-cyclopentylcyclopentene (see below). A Grignard reagent prepared in THF yielded much less of the latter.

The solution was heated for 540 h at 110 °C and hydrolyzed. The same two components were present, as shown by spectra of isolated samples. The ratio was now 1:4.

3-Cyclopentylcyclopentene was prepared by reaction of 3-chlorocyclopentene with cyclopentylmagnesium chloride.[40] Gas chromatography indicated a major component (ca. 80–85% of the total) and several minor components: bp 59–65 °C (10 mm) [lit.[40] bp 63 °C (9 mm)]; NMR (CCl_4) δ 5.9 (s, 2, olefinic) and 2.4–1.0 ppm (m, 14).

Reaction of 2a and 3 with Tri-*n*-butyltin Hydride. A solution was prepared containing tri-*n*-butyltin hydride (0.020 M) in *n*-decane which had been deoxygenated by passage of a stream of nitrogen. A 5-ml portion of this solution was heated to 80 °C with a trace of azobisisobutyronitrile, and 0.060 g (3.4×10^{-4} mol) of **2a** was added. The solution was heated for 1 h, and analyzed by gas chromatography (column B). The major hydrocarbon products, identified by GC retention times, were 3-ethylcyclopentene (29%) and bicyclo[3.2.0]heptane (61%). Minor amounts of norbornane and an unknown component were present. Cycloheptene was not detected (<1%). A reaction carried out in the absence of solvent gave only bicyclo[3.2.0]heptane. The total yield of hydrocarbon products was 50%.

A similar reaction with **3** led mainly to cycloheptene (78%) and several minor components, in a total yield of about 61%. Maximum amounts of 3-ethylcyclopentene, norbornane, and bicyclo[3.2.0]heptane, based upon the areas of GC peaks of similar retention time, were 2, 4.5, and 4.5%, respectively. It is possible that some of these may have resulted from reduction of the corresponding bromide present as an impurity in **3**.

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Registry No.—**1**, 41398-40-7; *exo*-**2a**, 57761-89-4; *endo*-**2a**, 57794-33-9; *exo*-**2b**, 57761-90-7; **3**, 54484-64-9; *endo*-**4a**, 57761-91-8; *exo*-**4a**, 57794-34-0; *endo*-**4b**, 57761-92-9; *exo*-**4b**, 57794-35-1; *endo*-**5a**, 57761-93-0; *exo*-**5a**, 57794-36-2; *endo*-**5b**, 57761-94-1; *exo*-**5b**, 57794-37-3; *endo*-**6a**, 57761-95-2; *exo*-**6a**, 57794-38-4; *endo*-**6b**, 57761-96-3; *exo*-**6b**, 57794-39-5; **7**, 57794-40-8; **8**, 57761-97-4; **9**, 57761-98-5; **28**, 5650-12-4; **29**, 2690-17-7; **33**, 7161-35-5;

endo-**34a**, 54594-95-5; *exo*-**34a**, 54561-40-9; *endo*-**34b**, 57761-99-6; *exo*-**34b**, 57794-41-9; 7-chloronorbornane, 765-80-0; 7-bromonorbornane, 13237-88-2; 4-cycloheptenol, 6925-17-3; 2-cyclopenten-1-one, 930-30-3; methyl vinyl ether, 107-25-5; ethyl vinyl ether, 109-92-2; *endo*-6-methoxybicyclo[3.2.0]hept-2-ene, 54594-94-4; 3-vinylcyclopentene, 26727-45-7; vinyl bromide, 593-60-2; 3-chlorocyclopentene, 96-40-2; (1-chloroethyl)cyclobutane, 57762-00-2; (1-bromoethyl)cyclobutane, 20826-75-9.

References and Notes

(1) This work was taken from the PH/D. Theses of R. J. Theissen, University of Minnesota, 1966, and C. E. Cannon, University of Wisconsin—Milwaukee, 1974, and from the M.S. Thesis of A. T. Chen, University of Wisconsin—Milwaukee, 1969.

(2) For a review of such organomagnesium rearrangements, see E. A. Hill, *J. Organomet. Chem.*, **91**, 123 (1975).

(3) E. A. Hill and J. A. Davidson, *J. Am. Chem. Soc.*, **86**, 4663 (1964).

(4) E. A. Hill and G. E.-M. Shih, *J. Am. Chem. Soc.*, **95**, 7764 (1973).

(5) S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1967).

(6) A. C. Cope, C. H. Park, and P. Scheiner, *J. Am. Chem. Soc.*, **84**, 4862 (1962).

(7) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(8) (a) T. N. Margulis, *Acta Crystallogr.*, **18**, 742 (1965); (b) P. R. Brook, A. J. Duke, and J. R. C. Duke, *Chem. Commun.*, 574 (1970); (c) F. P. Boer and P. P. North, *J. Chem. Soc., Perkin Trans. 2*, 416 (1972).

(9) J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **88**, 420 (1966).

(10) (a) R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **35**, 1627 (1970); (b) T. Svensson, *Chem. Scr.*, **3**, 171 (1973).

(11) (a) S. C. Lewis and G. H. Whitham, *J. Chem. Soc. C*, 274 (1967); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (c) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962); (d) R. K. Lustgarten, M. Brookhard, and S. Winstein, *ibid.*, **94**, 2347 (1972).

(12) (a) T. Matsumoto, H. Shirahama, A. Ichihara, S. Kagawa, and S. Matsumoto, *Tetrahedron Lett.*, 4103 (1969); (b) R. L. Cargill and D. M. Pond, *J. Org. Chem.*, **31**, 2414 (1966); (c) R. M. Coates and K. Yano, *J. Am. Chem. Soc.*, **95**, 2203 (1973).

(13) (a) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Am. Chem. Soc.*, **92**, 1399 (1970); (b) B. M. Jacobson and P. D. Bartlett, *J. Org. Chem.*, **38**, 1030 (1973); (c) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970).

(14) (a) K. B. Wiberg and W.-F. Chen, *J. Org. Chem.*, **37**, 3235 (1972); (b) T. Winkler and W. von Philipsborn, *Helv. Chim. Acta*, **51**, 183 (1968); (c) B. D. Kramer and P. D. Bartlett, *J. Am. Chem. Soc.*, **94**, 3934 (1972); (d) W. T. Brady, F. H. Parry III, and J. D. Stockton, *J. Org. Chem.*, **36**, 1486 (1971); (e) K. Doerffel, R. Ehrig, H. G. Hauthal, H. Kasper, and G. Zimmermann, *J. Prakt. Chem.*, **314**, 385 (1972); (f) P. R. Brook and A. J. Duke, *J. Chem. Soc., Perkin Trans. 1*, 1013 (1973).

(15) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

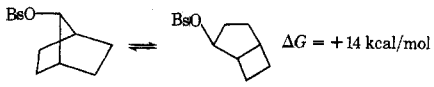
(16) (a) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Am. Chem. Soc.*, **90**, 5773 (1968); (b) R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960); (c) G. Favini, G. Buemi, and M. Raimondi, *J. Mol. Struct.*, **2**, 137 (1968); (d) N. Neto, C. di Lauro, and S. Califano, *Spectrochim. Acta, Part A*, **26**, 1489 (1970); (e) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 722 (1962); (f) G. L. Buchanan and J. M. McCrae, *Tetrahedron*, **23**, 279 (1967); (g) S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965); (h) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **87**, 3139 (1965); (i) M. St.-Jacques and C. Vaziri, *Can. J. Chem.*, **49**, 1256 (1971); (j) E. S. Glazer, R. Knorr, C. Ganter, and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 6026 (1972).

(17) E. A. Hill, R. J. Theissen, and K. Taucher, *J. Org. Chem.*, **34**, 3061 (1969).

(18) E. A. Hill, A. T. Chen, and A. Doughty, *J. Am. Chem. Soc.*, **98**, 167 (1976).

(19) The ring strain might be approximated by the sum of strain energies of the component rings. Since the strain energy of the cyclopentene ring of the product is slightly less than that of cyclopentane,[21] the cleavage of **12** would be slightly more exothermic than that of **16**.

(20) The stabilities of the [3.2.0] and [2.2.1] systems have been compared from solvolysis-derived data:[22]



Greater flexibility and the existence of enantiomers in the [3.2.0] system should combine to give it more entropy. Ignoring any other steric interactions of the brosylate group, the ring strain of the [3.2.0] system should then be *at least* 14 kcal/mol greater than the 18.5 kcal of strain of norbornane.[23] Various estimates of the additional entropy[24] suggest that the ring strain is probably 33.5–35 kcal/mol. Taken with the strain of the cyclopentene ring in the product (5.9 kcal/mol),[21] the relief of strain should be in the range of 27.5–29 kcal. In the cleavage of **16**, relief of the ring strain of cyclobutane (26.2 kcal)[21] provides the driving force.

(21) Strain energies are taken as equivalent to empirical ring corrections to heat of formation estimates, as tabulated by S. W. Benson, F. R. Cruickshank, D. M. Golden, R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(22) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Kleindinst, Jr., *J. Am. Chem. Soc.*, **80**, 5895 (1958).

(23) A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(24) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, **15**, 266 (1970).

(25) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 460 (1966).

(26) A. Maercker and R. Geuss, *Chem. Ber.*, **106**, 773 (1973).

(27) D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

(28) The rearrangement of **17**[18] has a rate relative to cyclobutylmethyl chloride of 0.3 in THF solution at 60 °C. Approximately 1% of the rearrangement leads to **19**, so the relative rate of **17** → **19** is about 3×10^{-3}. From Table I, the rate of **12** → **14** is approximately 5×10^{-3} relative to **16b** in ether solution. Since the rates of cyclobutylmethyl chloride and **16a** are the same within a factor of 2, the rates of **12** → **14** and **17** → **19** must be quite similar.

(29) (a) J. J. Eisch and R. Amtmann, *J. Org. Chem.*, **37**, 3410 (1972). (b) A referee has noted that the planar rectangular, four-center process should be disallowed on symmetry grounds. This question is discussed elsewhere,[2] and it has been pointed out that use of an additional electrophilic metal orbital removes such restrictions. Orbital symmetry constraints on the perpendicular transition state are similar to the coplanar, unless the addition is antarafacial with respect to the double bond, or occurs with inversion at one end of the adding single bond.

(30) J. B. Smart, R. Hogan, P. A. Scherr, M. T. Emerson, and J. P. Oliver, *J. Organomet. Chem.*, **64**, 1 (1974); G. Hata, *Chem. Commun.*, 7 (1968); J. St. Denis, J. P. Oliver, T. W. Dolzine, and J. B. Smart, *J. Organomet. Chem.*, **71**, 315 (1974).

(31) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967); P. D. Bartlett, C. V. Gobel, and W. P. Weber, *J. Am. Chem. Soc.*, **91**, 7425 (1969).

(32) The magnitude of the inductive effect might be considered in the context of the Taft σ^* correlation.[33] If σ^* for β-OR is taken as +0.52 (equal to that for CH_2OCH_3 vs. CH_3), a rate increase of 30 corresponds to $\rho^* \sim +2.8$. This value is slightly smaller in absolute magnitude than those observed in most acid dissociation equilibria (2.6–4.3), or in some carbonium ion forming reactions (~ -3.5). Since the Grignard cleavage reaction leads to formation of a polar C–Mg bond rather than a carbanion, a reduced substituent effect might be expected. It is possible that the nonpolar ether solvent may significantly influence the magnitude of ρ^*.

(33) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 556; P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, N.Y., 1968, pp 35–45; J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, pp 219–227.

(34) We are indebted to the Dow Metal Products Co. for a gift of sublimed magnesium.

(35) Infrared Spectral Data, American Petroleum Institute, Research Project 44, spectrum no. 1938.

(36) Reference 34, spectrum no. 2109.

(37) G. Wittig and G. Klumpp, *Tetrahedron Lett.*, 607 (1963).

(38) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(39) H. D. Scharf and F. Korte, *Chem. Ber.*, **97**, 2425 (1964); G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(40) G. E. Goheen, *J. Am. Chem. Soc.*, **63**, 744 (1941); J. T. Braunn, E. Kamp, and J. Kopp, *Chem. Ber.*, **70B**, 1750 (1937).