(98), 97 (B, 100), 79 (40) 55 (40); calcd for $C_{14}H_{22}O$ *m/e* 206.1670, found *m/e* 206.1667.

1,9,9-Trimethyl-*cis*,*syn*,*cis*-tricyclo[6.3.0.0^{2,6}]undecan-2-one (30b). Hydrogenation of **28b** under the conditions described above gave a 96% yield of **30b**: IR (neat) 1739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.98 (s, 3 H), 1.05 (s, 3 H), 1.4–2.6 (m, 13 H); mass spectrum (70 eV), *m/e* (relative intensity) 206 (M^+, 15), 162 (15), 107 (50), 93 (60), 79 (65), 55 (80), 41 (B, 95); calcd for $C_{14}H_{22}O$ *m/e* 206.1670, found *m/e* 206.1676.

Isomerization of 28a and 28b. A mixture of **28a** and **28b** (40 mg) was refluxed for 12 h in 80% aqueous ethanol containing 5 mg of rhodium trichloride trihydrate. Filtration through alumina gave an oil [36 mg (90%); IR 1736 cm^{-1}] whose ^{1}H NMR spectrum lacked any olefinic absorption. Hydrogenation of this material over Pd/C (5%) gave 33 mg (81%) of ketone **30a**. The isomerization could also be effected in toluene (reflux, 16 h) containing *p*-toluenesulfonic acid, but lower yields were obtained at the expense of fragmentation products.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (11599-G1), and the Department of Chemistry at Illinois Institute of Technology for support of this work. We are further indebted to Dr. James Hudson of the University of Texas, Austin, for providing us with the mass spectral measurements.

Registry No. 1, 1001-93-0; 2, 922-65-6; 3, 50999-04-7; **4b**, 71779-51-6; **5**, 75283-35-1; **7**, 75283-36-2; **8**, 38312-94-6; **9**, 75283-37-3; **10a**, 75283-38-4; **10b**, 75283-39-5; **12**, 75283-40-8; **13**, 73522-96-0; **14**, 32405-38-2; **15**, 75283-41-9; **16**, 75283-42-0; **17**, 75283-43-1; **18**, 75299-07-9; **19**, 75283-44-2; **20**, 75283-45-3; **21**, 75283-46-4; **22a**, 75283-47-5; **22b**, 75283-48-6; **23**, 75283-49-7; **24**, 75283-50-0; **25a**, 75283-51-1; **25b**, 75331-62-3; **26**, 75283-52-2; **27**, 75283-53-3; **28a**, 75283-54-4; **28b**, 75331-63-4; **30a**, 75331-64-5; **30b**, 75331-65-6; 4,6-heptadienoyl chloride, 75283-55-5; 4,6-octadienoyl chloride, 75283-56-6; 5-(4,4-dimethylcyclopent-1-enyl)-4-pentenoyl chloride, 75283-57-7; 4,6-heptadienoic acid, 75283-35-1; 4,6-octadienoic acid, 75283-36-2; 5-(4,4-dimethylcyclopent-1-enyl)-4-pentenoic acid, 75283-39-5; dimethyl 2-(2,4-pentadien-1-yl)propanedioate, 75283-58-8; 2-(2,4-pentadien-1-yl)propanedioic acid, 75283-59-9; dimethyl 2-(2,4-hexadien-1-yl)propanedioate, 75283-60-2; 5,5-dimethyl-*cis*-2,3-epoxycyclohexanol, 38309-46-5; ethyl formate, 109-94-4; vinyl bromide, 593-60-2; triethyl orthoacetate, 78-39-7; dimethyl malonate, 108-59-8; oxalyl chloride, 79-37-8; diazomethane, 334-88-3; diazoethane, 1117-96-0; 2-chloro-7-(4,4-dimethylcyclopent-1-enyl)-6-hepten-3-one, 75283-61-3.

Stereochemistry of Addition of the Allyl Grignard Reagent to Hydroxybicyclo[2.2.1]hept-2-enes[1]

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Reactions of *syn*-bicyclo[2.2.1]hept-2-en-7-ol with an excess of allylmagnesium chloride in tetrahydrofuran or of allylmagnesium bromide in diethyl ether furnish an addition product shown to be 2-*exo*-allyl-*syn*-bicyclo[2.2.1]heptan-7-ol. Reactions of *endo*-bicyclo[2.2.1]hept-5-en-2-ol with the same reagents and with diallylmagnesium in ether furnish a compound shown to be 5-*endo*-allyl-*endo*-bicyclo[2.2.1]heptan-2-ol. A metalated hydroxyl group must play an active role in facilitating these additions since they proceed more rapidly than addition to the parent hydrocarbon, bicyclo[2.2.1]hept-2-ene, which furnishes 2-*exo*-allylbicyclo[2.2.1]heptane. They must also be considerably more rapid than additions to the epimeric alcohols (*anti*-bicyclo[2.2.1]hept-2-en-7-ol and *exo*-bicyclo[2.2.1]hept-5-en-2-ol) since no addition products were obtained from reactions with these alcohols. Attachment of the allyl group to the double bond of each bicycloheptenol from the side nearer the hydroxyl group suggests that at the time of addition the allyl is associated with the metalated hydroxyl group.

Eisch and Husk reported that allylmagnesium bromide (in excess) adds under mild conditions to the double bond of 1 (eq 1).[3] This addition was remarkable because under comparable conditions even the particularly reactive allyl Grignard reagent does not add to unstrained, nonconjugated alkenes. The hydroxyl group of 1 certainly reacts instantaneously with 1 mol of the Grignard reagent. The metalated hydroxyl group that results must in some manner facilitate the ready addition to the double bond.

$$\underset{\mathbf{1}}{CH_2{=}CHCH_2C(OH)Ph_2} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgBr} CH_2{=}CHCH_2CH_2CH_2CH_2C(OH)Ph_2 \quad (1)$$

A variety of additions of Grignard reagents to alkenols[4-8] have since been reported, as have similar additions to alkynols[6,9-11] and allenols.[12] Other functional groups, particularly amino and alkoxyl, have also been found to exert a promoting effect on Grignard reagent additions to carbon–carbon multiple bonds.[5,11,13] Hydroxyl and other

(1) Part of this work was described in a preliminary paper.[2a] Much of this work is taken from ref 2b.

(2) (a) Richey, H. G., Jr.; Wilkins, C. W., Jr.; Brown, B. S.; Moore, R. E. *Tetrahedron Lett.* **1976**, 723. (b) Wilkins, C. W., Jr. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1976.

(3) Eisch, J. J.; Husk, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 4194.

(4) Chérest, M.; Felkin, H.; Frajerman, C.; Lion, C.; Roussi, G.; Swierczewski, G. *Tetrahedron Lett.* **1966**, 875.

(5) Eisch, J. J.; Merkley, J. H. *J. Organomet. Chem.* **1969**, *20*, P27; *J. Am. Chem. Soc.* **1979**, *101*, 1148.

(6) Eisch, J. J.; Merkley, J. H.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 587.

(7) Felkin, H.; Kaeseberg, C. *Tetrahedron Lett.* **1970**, 4587.

(8) Richet, G.; Pecque, M. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1974**, *278*, 1519.

(9) Richey, H. G., Jr.; Von Rein, F. W. *J. Organomet. Chem.* **1969**, *20*, P32. Von Rein, F. W.; Richey, H. G., Jr. *Tetrahedron Lett.* **1971**, 3777.

(10) Miller, R. B.; Reichenbach, T. *Synth. Commun.* **1976**, 319. Bernadou, F.; Miginiac, L. *Tetrahedron Lett.* **1976**, 3083. Holm, T. *Acta Chem. Scand., Ser. B* **1976**, *30*, 985.

(11) Mornet, R.; Gouin, L. *Bull. Soc. Chim. Fr.* **1977**, 737.

(12) Richey, H. G., Jr.; Szucs, S. S. *Tetrahedron Lett.* **1971**, 3785.

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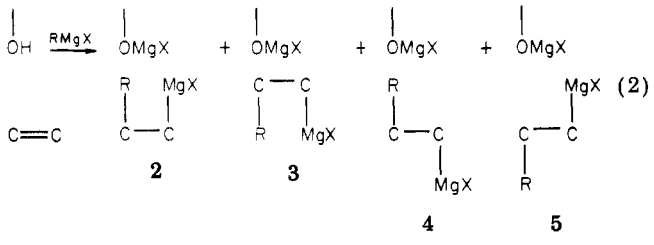
functional groups also facilitate additions to carbon–carbon multiple bonds by organolithium[14-16] and organozinc[17] compounds.

To define the role played by a hydroxyl group or other assisting function in such reactions, we thought it essential to determine definitively the stereochemical relationship at the time of addition between four groups: the alkene function, R and Mg from the Grignard reagent, and the metalated hydroxyl group. Do R and Mg add to the double bond of an alkenol in a syn or anti fashion? Is R attached to the face of the double bond near to or remote from the hydroxyl group? Possible stereochemistries of the resulting addition products are shown schematically in **2–5** (eq 2).[18]

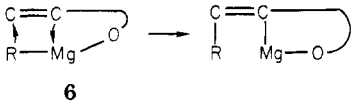


(2)

2 **3** **4** **5**

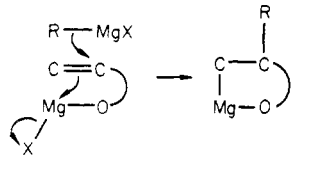
In **2** and **5**, both O and C might be linked to the same Mg. Although OMgX is indicated on these and some other structures in this paper, OMgR and OMgO are other possibilities.

Stereochemical information can rule out some mechanistic possibilities. For example, Eisch proposed[3] the mechanism illustrated in **6** (eq 3) and suggested that addition is favored by the intramolecularity of the process. This proposal predicts syn addition of R and Mg to the face of the double bond nearest to the metalated hydroxyl group (corresponding to formation of **2**). Felkin suggested[4] the mechanism shown in **7** (eq 4). R adds from an external molecule of an organomagnesium compound while OMgX acts simultaneously as an internal electrophile. This proposal predicts anti addition of R and Mg to the double bond and attachment of R to the face of the double bond furthest from the hydroxyl group (corresponding to formation of **5**).



(3)

6



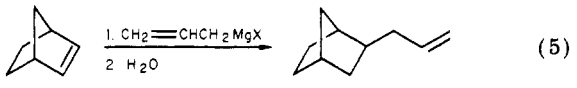
(4)

7

The investigation described in this paper was devoted to determining the relationship between R and OMgX. At the time that we first communicated our results,[2a] no other unambiguous information of this kind was available. The results of a related study[6] by Eisch and his co-workers that has since been published are compared to ours in the Discussion.

Results

Reactions of Allyl Grignard Reagents with Bicyclo[2.2.1]hept-2-ene (8). Additions to **8** were studied for comparison with those to hydroxy-substituted bicycloheptenes (eq 5). Compound **9** was isolated in 25% yield

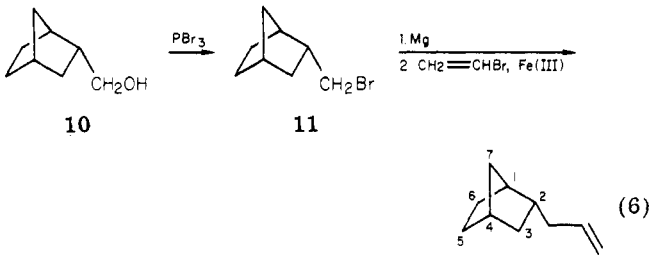


(5)

8 **9**

after a tetrahydrofuran (THF) solution of **8** and allylmagnesium chloride was heated for 120 h at 100 °C.[20] The same product was obtained by refluxing a diethyl ether solution of **8** and allylmagnesium bromide. These reactions, followed qualitatively by GC analysis of aliquots, slowed with time. This was probably due at least in part to disappearance of the Grignard reagent in other ways; considerably more reaction took place after addition of a fresh portion of Grignard solution to a reaction of **8** and allylmagnesium bromide that had almost stopped.

An exo configuration was assigned to the addition product on the basis of two types of evidence.[21] First, its ^1H and ^{13}C NMR spectra were different from those of the endo isomer (**12**), synthesized in an unambiguous fashion (eq 6). Second, its ^{13}C NMR spectrum is clearly that of the exo isomer. The highest field absorption of **9** is at 28.8 ppm (downfield from Me_4Si). The endo isomer should have an absorption for C-6 similar to that at 22.1 ppm for C-6 of *endo*-2-methylbicyclo[2.2.1]heptane.[19] In fact, **12** exhibits an absorption at 22.4 ppm that we assign to C-6.



(6)

10 **11** **12**

Reactions of Allyl Grignard Reagents with *syn*-(13) and *anti*-Bicyclo[2.2.1]hept-2-en-7-ol (16). Reactions of allylmagnesium chloride and **13** in THF at 100 °C gave two products (eq 7). The first was shown to be **14**.

(13) Richey, H. G., Jr.; Erickson, W. F.; Heyn, A. S. *Tetrahedron Lett.* **1971**, 2183. Nelson, D. J.; Miller, W. J. *J. Chem. Soc., Chem. Commun.* **1973**, 444. Mornet, R.; Gouin, L. *J. Organomet. Chem.* **1975**, *86*, 57, 297. Mornet, R.; Gouin, L. *Tetrahedron Lett.* **1977**, 167. Bouet, G.; Mornet, R.; Gouin, L. *J. Organomet. Chem.* **1977**, *135*, 151.

(14) Felkin, H.; Swierczewski, G.; Tambuté, A. *Tetrahedron Lett.* **1969**, 707.

(15) Crandall, J. K.; Clark, A. C. *Tetrahedron Lett.* **1969**, 325. Crandall, J. K.; Clark, A. C. *J. Org. Chem.* **1972**, *37*, 4236. Veefkind, A. H.; Bickelhaupt, F.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1058. Veefkind, A. H.; Schaaf, J. V. D.; Bickelhaupt, F.; Klumpp, G. W. *J. Chem. Soc., Chem. Commun.* **1971**, 722. Olsson, L.-I.; Claesson, A. *Tetrahedron Lett.* **1974**, 2161. Olsson, L.-I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1976**, *30*, 521. Dimmel, D. R.; O'Malley, J. P. *J. Org. Chem.* **1975**, *40*, 132.

(16) Dimmel, D. R.; Huang, S. *J. Org. Chem.* **1973**, *38*, 2756.

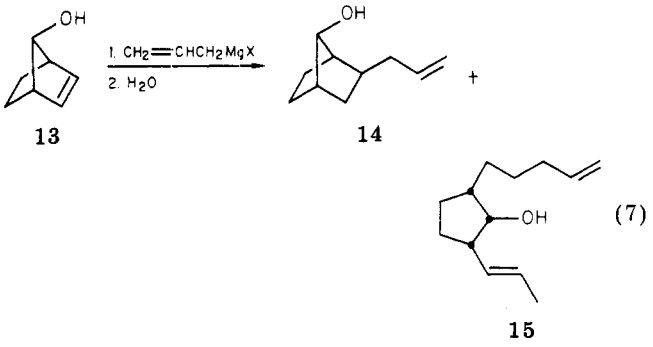
(17) Reviewed briefly in: Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. Also see: Frangin, Y.; Gaudemar, M. *Ibid.* **1977**, *142*, 9.

(18) If the hydroxyl group is located unsymmetrically with respect to the carbons of the alkene function, then two orientations of addition are possible. Stereochemical possibilities corresponding to **2–5** exist for each orientation.

(19) Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1973**, *51*, 2893.

(20) Reactions at 100 °C were invariably homogeneous, although precipitates were often present in reactions at lower temperatures.

(21) A product obtained recently from reaction of **8** and allylmagnesium bromide must also be **9** (Lehmkuhl, H.; Janssen, E. *Justus Liebigs Ann. Chem.* **1978**, 1854). Addition products isolated from reaction of **8** with several substituted allylic Grignard reagents are presumably also exo (the preceding reference and: Lehmkuhl, H.; Reinehr, D. *J. Organomet. Chem.* **1973**, *57*, 29; Lehmkuhl, H.; Reinehr, D.; Schomburg, G.; Henneberg, D.; Damen, H.; Schroth, G. *Justus Liebigs Ann. Chem.* **1975**, 103; Lehmkuhl, H.; Reinehr, D.; Henneberg, D.; Schomberg, G.; Schroth, G. *Ibid.* **1975**, 119).

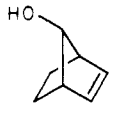


13 14 15 (7)

The second probably had the structure and configuration shown in **15**. GC analysis of aliquots showed that **15** formed at a slower rate than did **14** and apparently at the expense of **14**. For example, approximate amounts of **13**–**15** were 8%, 52%, and 7% after 1 h, and 0%, 16%, and 46% after 5 h. In a reaction of **13** and allylmagnesium bromide in refluxing diethyl ether, **14** was isolated in 42% yield after 5 h, and **15** was not detected.

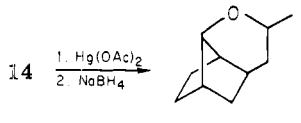
GC analysis of aliquots (see Experimental Section) suggested that addition to **13** is considerably more rapid than to **8**. However, comparisons are inexact because (a) somewhat different concentrations of reagents were used in different experiments, (b) kinetic orders of the reactions are unknown, and (c) reactions tended to slow and even to stop, presumably due at least in part to the disappearance of the Grignard reagent in other ways. Therefore, the reactivities of **8** and **13** were compared more directly by a competition experiment. Compound **14** was found but no **9** detected in a reaction at 100 °C in which **8** and (metalated) **13** were allowed to compete for a limited amount of allylmagnesium chloride in THF.[20] This result is consistent with addition to **13** being at least 20 times faster than to **8**.

Compound **16**, the epimer of **13**, gave no addition product when refluxed with allylmagnesium chloride in diethyl ether for 5 days. For consistency, this experiment should have been done with allylmagnesium bromide. However, in reactions with 4-hexyn-2-ol in diethyl ether, allylmagnesium chloride actually adds somewhat faster than allylmagnesium bromide.[22] If we assume that reactions of **16** with allylmagnesium chloride and bromide proceed at comparable rates, then addition to **13** is at least 10^3 times faster than to **16**.



16

Addition product **14** was converted to a compound whose spectral features are in accord with structure **17** (the configuration of the methyl group is not known; eq 8).

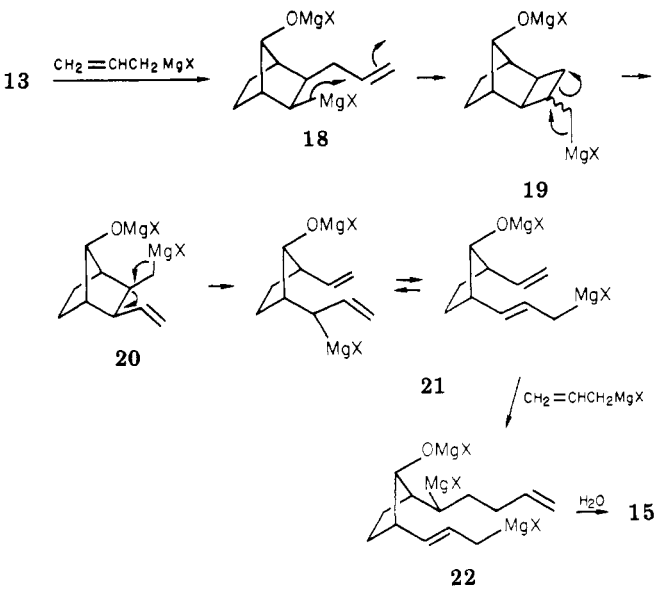


17 (8)

The ability of the hydroxyl group of **14** to add to the alkene function indicates that the allyl group is exo and that the hydroxyl group has not epimerized.

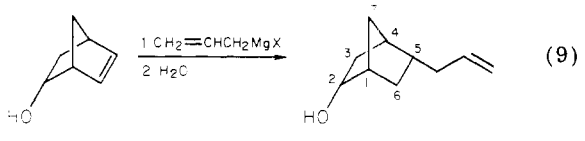
The configuration of **14** also is evident from its ^{13}C NMR spectrum. If it is assumed that a 2-*endo*-allyl group would cause the same shift at C-6 in bicyclo[2.2.1]heptan-7-ol as in bicyclo[2.2.1]heptane,[19] then C-6 in the *endo*-allyl isomer of **14** should absorb at 18.7 ppm.[23] Consistent with **14** having an exo configuration, the highest field absorption observed for the addition product is at 24.4 ppm.

Scheme I



We assume that **15** forms from further reaction of **18**,[24] the precursor of **14**. This is consistent with the decrease in **14** that accompanies the increase of **15**. Compound **15** was not formed when **14** was treated with allylmagnesium bromide in the same manner as was **13**. Therefore, it is likely that its formation requires the CMgX function present in **18**. A reasonable pathway for formation of **15** involves internal addition to form **19** followed by fragmentation to **20** and then to **21** (Scheme I). The configuration of **15** is assumed to be that resulting from this pathway. Similar processes have been noted in reactions of 2-methyl-2-propenyl and 2-butenyl Grignard reagents with **8**.[21] The final step is addition of the allyl Grignard reagent to **21**. Since the allyl Grignard reagent does not ordinarily add this readily to terminal alkenes, this addition must also be assisted by the metalated hydroxyl group.

Reactions of Allyl Organomagnesium Compounds with *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (23). Compound **24** was isolated in 20% yield from a reaction of **23** and allylmagnesium chloride in THF at 100 °C for 100 h. The same compound also formed in reactions of **23** in refluxing diethyl ether with allylmagnesium bromide or diallylmagnesium (eq 9). GC analysis of aliquots (see Experimental Section) suggested that addition to **23** relative to addition to **8** is considerably faster for allylmagnesium chloride in THF, though not significantly faster for allylmagnesium bromide in diethyl ether. The reactivities



23 24 (9)

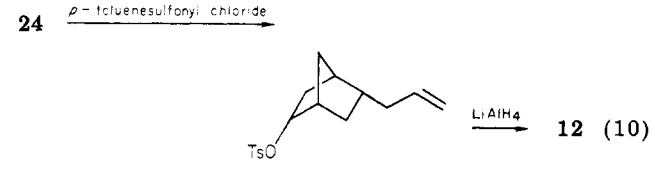
(22) Von Rein, F. W. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1972.

(23) The absorption due to all of the methylene carbons in bicyclo[2.2.1]heptan-7-ol is at about 25.9 ppm (estimated from the information in: Schneider, H.-J.; Bremser, W. *Tetrahedron Lett.* **1970**, 5197).

(24) In structures such as **20** in which both CMgX and OMgX are shown, the dominant species may actually have O and C linked to the same Mg.

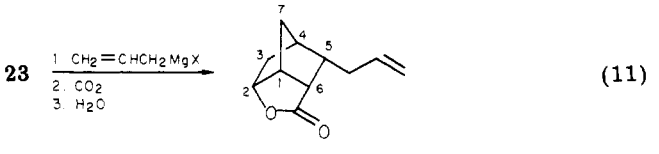
of 8 and (metalated) **23** toward allylmagnesium chloride in THF were compared more directly by a competition experiment. Compound **24** was found but no **9** detected in a reaction at 100 °C in which 8 and **23** were allowed to compete for a limited amount of the Grignard reagent.[20] This result is consistent with the addition to **23** being at least 20 times faster than that to 8.

The position (C-5 and C-6) and configuration (exo or endo) of the allyl group in the addition product were established by several chemical transformations. Conversion to a *p*-toluenesulfonate (**25**) followed by reduction produced **12** (eq 10), demonstrating that the allyl group was

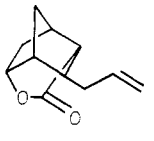


25

endo. Carbonation (instead of hydrolysis) of the solution obtained from the reaction of **23** and allylmagnesium chloride furnished a lactone (eq 11). Lactone formation



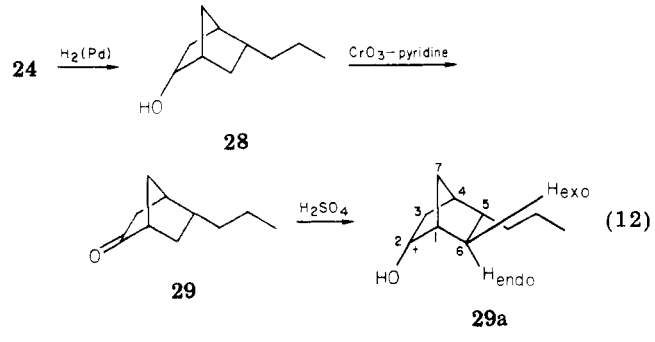
26



27

demonstrates that the hydroxyl group still is endo. The lactone is assumed to have the carbonyl group attached to C-6 rather than to C-5 since its IR and ^{1}H NMR spectral characteristics are similar to those of other γ-lactones related to **26**.[25] Presumably a lactone of structure **27** would exhibit quite different spectra. Since the lactone product indicates that Mg was at C-6, the allyl must be at C-5.

The addition compound was also converted to a ketone (**29**), whose ^{1}H NMR spectrum was an undecipherable smear (eq 12). However, when **29** was protonated (to form



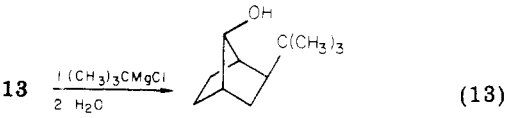
29 **29a**

29a), the absorption of the H at C-1 was shifted downfield, becoming readily observable. This absorption exhibited the coupling constant (about 4 Hz) usual for the C-1 H's of bicyclo[2.2.1]heptanes when an *exo*-H is present at C-6.[26]

Since this shows the exo position at C-6 to be occupied by a hydrogen, the alkyl group must be elsewhere.

Assignment of structure and configuration **24** to the addition product is also consistent with its NMR spectra. The chemical shift and splitting pattern of the absorption of the H at C-2 in the ^{1}H NMR spectrum is characteristic of an *endo*-bicyclo[2.2.1]heptan-2-ol.[27] Of the four possible attachments of the allyl (exo or endo at C-5 and C-6), the ^{13}C NMR spectrum is consistent only with the endo C-5 attachment shown in **24**.[28]

Other Reactions.[29,30] An addition product was present in about 10% yield after **13** was heated at 100 °C in a diethyl ether solution of *tert*-butylmagnesium chloride for 11 days (eq 13). Presumably the (metalated) hydroxyl



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group assisted the addition, since no addition product was obtained when 8 was treated similarly. The addition product, assumed to be **30**, was not investigated further since no addition product was noted in a similar reaction of **23**.

There was no evidence for significant formation of an addition product from prolonged heating at 100 °C of a THF solution of 1-propynylmagnesium chloride with **13** or a diethyl ether solution of *n*-propylmagnesium chloride with **23**. Only small amounts of new volatile compounds were detected upon prolonged reaction of **23** at 100 °C with a THF solution of benzylmagnesium chloride.

Discussion

A metalated hydroxyl group must play a direct role in additions of allyl Grignard reagents to alkenols **13** and **23** since these reactions are more rapid than additions to the parent alkene, 8. A hydroxyl group fixed in a position that

(25) For example, see: Ramey, K. C.; Lini, D. C.; Moriarty, R. M.; Gopal, H.; Welsh, H. G. *J. Am. Chem. Soc.* **1967**, *89*, 2401; Storm, D. R.; Koshland, D. E., Jr. *Ibid.* **1972**, *94*, 5808.

(26) For an example involving a protonated bicyclo[2.2.1]heptan-2-one, see: Farnum, D. G.; Mehta, G. *J. Am. Chem. Soc.* **1969**, *91*, 3256.

(27) For example, see: Musher, J. J. *Mol. Phys.* **1963**, *6*, 93.

(28) The ^{13}C NMR spectra of the four allyl compounds can be predicted from the known spectra (Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1976**, *54*, 1211) of the four corresponding methyl-substituted bicyclo[2.2.1]heptan-2-ols by adding the amounts for the effects of new α, β, and γ carbons when methyl is replaced by allyl. The same conclusions are reached for any reasonable set of values, though below we specifically assume 9.1, 9.4, and −2.5 ppm for the effects of the α, β, and γ carbons (Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984). Some of the obvious discrepancies between the observed spectrum and predictions for other isomers are noted below. (1) For an *endo*-allyl group at C-6, the absorption of C-2 is predicted to be 76.4 ppm, but 72.7 ppm is observed. (2) For an *exo*-allyl group at C-6, the absorption of C-1 is predicted to be at 46.7 ppm; with the exception of the absorptions of the vinyl C's and of C-2, the lowest-field absorption is observed at 43.1 ppm. (3) For an *exo*-allyl group at C-5, the highest field absorptions are predicted to be at 27.7 (C-6) and 34.1 (C-7) ppm; however, absorptions are observed at 25.7, 31.4, and 35.6 ppm. By contrast, when absorptions are arranged in order of chemical shifts, no absorption of the addition product is more than 0.8 ppm from the corresponding absorption predicted for **24**.

(29) A sample containing **23** and its epimer, *exo*-bicyclo[2.2.1]hept-5-en-2-ol (**31**), in a ratio of about 3:1 was used in a reaction with the *tert*-butyl Grignard reagent. During the course of the reaction, this ratio gradually decreased, reaching 0.5:1 after 30 days. Since the total amount of **23** plus **31** remained approximately constant, this change was due to isomerization rather than to selective loss of one epimer. Metalated **23** and **31** may have equilibrated by slow ionization to the corresponding carbonium ion followed by recombination (R–OMgX $\rightleftarrows$ R^+ $^-$OMgX).

(30) No evidence for an addition product was obtained when 3-(hydroxymethyl)cyclohexene (**32**) was refluxed for 11 days with a diethyl ether solution of allylmagnesium chloride. A small amount (6% by GC analysis) of an addition product (**34**) formed when a mixture of *exo*- and *endo*-5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene (**33**) was heated for 5 days at 100 °C with a diethyl ether solution of allylmagnesium bromide. Its structure and configuration were not determined.

precludes its approaching the double bond probably exerts a rate-decreasing effect. Addition to alcohol **16** was not observed and therefore must be considerably slower than addition to its epimer (**13**) and probably somewhat slower than addition to the corresponding hydrocarbon (**8**). It is possible that a retarding effect of a metalated hydroxyl group is operative even in hydroxyl-assisted reactions. The additions to **13** and **23** might be faster if it were not for a general rate-suppressing effect of a metalated hydroxyl group.[31]

The endo configuration of the allyl group in the product of addition to **23** also indicates that the hydroxyl group is involved. If the hydroxyl group of **23** played no direct role, then exo (rather than the observed endo) attachment of the allyl group should result, as in the addition to **8**. The hydroxyl group in *exo*-bicyclo[2.2.1]hept-5-en-2-ol (**31**), the epimer of **23**, cannot approach the double bond, and addition to **31** presumably would also be exo. In reactions of the allyl Grignard reagents with mixtures of **23** and **31**, no product of addition to **31** was detected. Therefore, addition leading either to exo or endo attachment to **31** must be considerably slower than the endo addition observed to **23**.

That assistance by the hydroxyl group is associated with a particular stereochemical pathway is shown by the different attachments of the allyl group in additions to **13** and **23**. The exo attachment of allyl in **13** might result from an inherent preference for this attachment in additions to bicyclo[2.2.1]hept-2-enes. However, that cannot be the explanation for endo attachment in the addition to **23**. In fact, in the absence of a hydroxyl-assisted pathway, an adverse steric effect of the *endo*-hydroxyl group of **23** would probably accentuate the usual preference for exo attachment. We conclude that the configuration of the allyl group in **23** results from involvement of the metalated hydroxyl group in the addition mechanism in a manner that leads to attachment of an allyl group to the face of the double bond nearest to the hydroxyl group.

In other work, we have found that additions to 3-(hydroxymethyl)cyclopropenes result in attachment of allyl to the side (cis) of the double bond nearest to the hydroxyl group.[32] Eisch and his co-workers have also recently reported concordant observations.[6] In the addition products from reactions of allylmagnesium bromide with 2-cyclohexenyldiphenylmethanol and of diallylmagnesium with 3-cyclopentenol, the allyl and hydroxyl groups were cis. The major product obtained from addition of allylmagnesium bromide to 3-cyclopentenol also was cis. Some trans product was observed, but the authors suggested that this may have arisen from isomerization of the cis product during the course of the slow reaction. It could also have resulted from a competing addition process not involving hydroxyl assistance.

All studies mentioned above involved homoallylic alcohols ($C_\delta{=}C_\gamma C_\beta C_\alpha OH$) and led to attachment of an allyl group to the face of the double bond nearest to the hydroxyl group. These observations are consistent with a mechanism in which the allyl group (R) is associated with the Mg attached to oxygen. This could reasonably be the mechanism shown in **6** that was first proposed by Eisch.[3]

It would be valuable to know the stereochemistry with which Mg becomes attached to a vinyl carbon during an addition to an alkenol. However, at present, this is not known with certainty for any addition to an alkenol. Of course, the position of Mg at the time of quenching can be determined. For example, since carbonation of Grignard reagents proceeds with retention of configuration, **26** must come from an intermediate with an endo Mg. However, we cannot be absolutely certain that the position of Mg at the time of quenching is the same as that immediately following addition. Saturated carbons bonded to Mg generally lose configuration rapidly in solution. Epimerization of 2-bicyclo[2.2.1]heptyl organomagnesium compounds is known to be slower than that of many organomagnesium compounds.[34] However, the available evidence does not indicate if these compounds would retain configuration under the particular reaction conditions used in our study. Moreover, the presence of the metalated hydroxyl group could accelerate epimerization. In the absence of control experiments demonstrating that the relevant exo and endo organomagnesium compounds are configurationally stable under the reaction conditions that were used, we are unwilling to draw conclusions.

Some stereochemical results of additions of allylmagnesium compounds to homopropargylic alcohols ($C_\delta{\equiv}C_\gamma C_\beta C_\alpha OH$) have been cited to support particular reaction pathways for addition to alkenols. Since we have been responsible for many of these results, we would like to caution that if *all* examples are considered,[5,6,9-11] then the results of additions to homopropargylic alcohols are more varied than those of additions to homoallylic alcohols. Products of attachment of the allyl group to both C_γ and C_δ have been obtained. Products in which the allyl group is attached to C_γ have resulted exclusively from cis attachment of allyl and Mg.[35] However, products in which the allyl group is attached to C_δ have in different examples resulted only from trans attachment, from both cis and trans attachment, and (in one instance[6]) from only cis attachment. The amounts of trans-γ, cis-δ, and trans-δ products are sensitive to small structural and solvent changes. A hydroxyl group must play a role in all of these additions, since they are faster than additions to alkynes lacking hydroxyl groups. However, assisted pathways leading to different addition products must be similar in energy. The different results found for alkynols and alkenols may reside in geometric differences between pathways involving these systems. For example, transition states for additions following a pathway such as that shown in **6** should be more strained for homopropargylic alcohols than for homoallylic alcohols. Other pathways, not observed for additions to alkenols, may become important in additions to alkynols.

Two significant limitations to the generality of the stereochemical conclusion reached in this paper should be noted. The first is that the conclusion may be valid only for allylic organomagnesium compounds, since all additions to alkenols that have provided stereochemical information have involved only these compounds. For a number of reasons, allylic compounds may be atypical in their reactions. For example, as shown in **35**, reactions of the allyl group can take place at the γ carbon, a possibility that does not exist for most other groups. In only one of the efforts to add other (*tert*-butyl, 1-propynyl, and benzyl) Grignard reagents to some of the substrates used in this study was

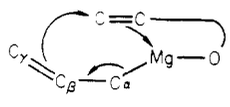
(31) The situation could resemble that observed for neighboring-group participation in nucleophilic substitution at saturated carbon (Capon, B. *Q. Rev., Chem. Soc.* **1964**, *18*, 45). The rates of some reactions involving participation would be greater were it not for an adverse inductive effect of the substituent.

(32) Richey, H. G., Jr.; Bension, R. M. *J. Org. Chem.*, following paper in this issue.

(33) Such cyclizations have been comprehensively reviewed: Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123; *Adv. Organomet. Chem.* **1977**, *16*, 131.

(34) Bergbreiter, D. E.; Reichert, O. M. *J. Organomet, Chem.* **1977**, *125*, 119 and references cited therein.

(35) We assume that in addition to alkynols, the position of Mg at the time of quenching is the same as that immediately following additon.



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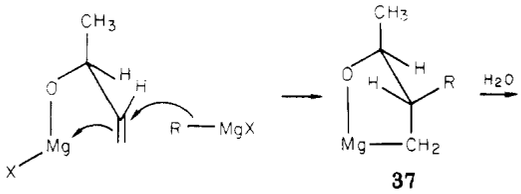
even an isolable amount of an addition product noted.[36]

The second limitation is that the conclusion may apply only to homoallylic alkenols, since all studies cited above involved such systems. In fact, there are indications that additions to allylic systems (C_γ=$C_\beta C_\alpha$OH) may proceed differently. In the additions that have been reported, attachment of R to both C_β and to C_γ has been noted, the latter accompanied by elimination to produce alkenes. Only one addition has given stereochemical information. Felkin and his co-workers observed that *erythro*-3-methyl-5-hexen-2-ol (**38**) predominated in the erythro–threo mixture obtained from addition of allylmagnesium bromide to 3-buten-1-ol (eq 14).[4] Of course, due to ro-



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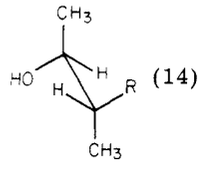

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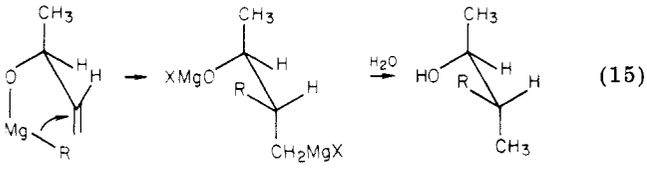
R = CH_2=$CHCH_2$ (14)

tation around single bonds, the relative positions of OMgX and R at the time of addition do not persist in the product. However, Felkin proposed that the stereochemistry was consistent with intermolecular mechanism **7**, the erythro isomer arising from a pathway (**36** → **37**) in which R and CH_3 are as far apart as possible.[39]

A mechanism in which R is donated by OMgR would probably furnish predominantly the threo isomer **41** (eq 15), since pathway **39** → **40** leading to that isomer keeps



39 40 41 (15)

the bulky groups, in this instance CH_3 and CH_2, as far apart as possible. In fact, addition of allyllithium and *n*-propyllithium led preferentially to formation of threo isomers.[14,40] Felkin proposed that their formation proceeded by a pathway resembling **39** → **40**.

Felkin's interpretation seems reasonable. Moreover, additions to propargylic alcohols (C_γ≡$C_\beta C_\alpha$OH) have been in accord with Felkin's proposal. Products in which R is attached to C_β have always resulted from trans addition of R and Mg.[35] Therefore, we conclude that the preferred addition pathway for homoallylic alkenols may not be that for other alkenols.

Experimental Section

^{1}H NMR spectra were taken at 60 MHz with Me_4Si as an internal standard. Absorptions are reported with the following notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions. Proton-decoupled ^{13}C NMR spectra were obtained with $CDCl_3$ as an internal lock; absorptions are reported relative to Me_4Si. IR and low-resolution mass spectra, though not generally reported in this paper, were taken for many compounds and are described in ref 2b. High-resolution mass spectra were obtained with an AEI Model MS 902 spectrometer. Melting points were taken in capillary tubes and are uncorrected. Compounds for which elemental analyses or high-resolution mass spectra are given have not been previously reported. Microanalyses were performed by Midwest Microlab, Ltd.

Most analytical and preparative GC separations were performed with thermal conductivity instruments using helium as the carrier gas and the following columns constructed of aluminum tubing: A, 30% diethylene glycol succinate on Gas Chrom P (60–80 mesh), 0.25 in. × 12 ft; B, 15% Carbowax 20M on Gas Chrom P (60–80 mesh), 0.25 in. × 6 ft; C, 20% SE-30 on Gas Chrom Q (60–80 mesh), 0.25 in. × 6 ft; D, 15% Carbowax 20M on Gas Chrom P (60–80 mesh), 0.38 in. × 9 ft; F, 20% Carbowax 20M on Gas Chrom P (40–80 mesh), 0.25 in. × 12 ft; H, 20% SE-30 on Gas Chrom Q (80–100 mesh), 0.25 in. × 12 ft. Peak areas were determined by using a planimeter or by cutting out and weighing the peak tracings. A few GC analyses were performed by using an instrument having a flame-ionization detector with helium as the carrier gas and the following U-shaped glass column: G, 20% SE-30 on Gas Chrom P (60–80 mesh), 2 mm (i.d.) × 6 ft. Peak areas were determined by using a Disc integrator. When amounts of components of a crude (undistilled) reaction mixture were determined by GC analysis, a weighed amount of a normal alkane was added as a standard. An alkane was chosen whose GC peak was known from preliminary work not to overlap with those of components of the reaction mixture. The amount of a component was determined from the area of its GC peak relative to the peak due to the internal standard, assuming that the response of the detector to different compounds was proportional to their molecular weights (the errors introduced by this assumption probably resulted in underestimating the yields of most components in this work). In the GC analysis of a distillation fraction, it was assumed that all of the material appeared in one of the observed peaks (a reasonable assumption since materials having little volatility had been removed).

Materials. (a) Substrates for Reactions with Organomagnesium Compounds. Bicyclo[2.2.1]hept-2-ene (**8**) and 3-(hydroxymethyl)cyclohexene were commercial samples (Aldrich Chemical Co.). *syn*-Bicyclo[2.2.1]hept-2-en-7-ol (**13**) was prepared from bicyclo[2.2.1]hept-2-ene as previously reported;[41] mp 87 °C (lit.[41] mp 88.5–89.5 °C). *anti*-Bicyclo[2.2.1]hept-2-en-7-ol (**16**) was prepared from 7-*tert*-butoxybicyclo[2.2.1]hept-2,5-diene as previously reported[42] and purified by sublimation [80 °C (100 torr)]; mp 115–116 °C (lit.[42] mp 117–118 °C). *endo*-Bicyclo-[2.2.1]hept-5-en-2-ol (**23**) was obtained (Aldrich Chemical Co.) as a liquid containing some of the exo isomer (**31**). Sublimation gave a solid, mp 103–109 °C (lit.[43a] mp 108–109 °C). The com-

(36) These Grignard reagents have groups that in addition products would be located rigidly with respect to the hydroxyl group and would have ^{1}H NMR absorptions readily distinguishable in complex NMR spectra. These features would facilitate determining their positions of attachment by interpretation of lanthanide-induced shifts in NMR spectra. The vinyl H absorptions of allyl groups are also easily distinguished in ^{1}H NMR spectra. However, due to rotation around the CH_2–CH bond of the allyl group, it is difficult to estimate the average position of the vinyl H's relative to the hydroxyl group in the possible isomers. Along with severe loss of resolution as shift reagents were added, this made unpromising some efforts to determine in this manner the positions of attachment of allyl in the addition products formed from **13**[37] and **23**.[38]

(37) These experiments were done by Robert E. Moore.

(38) These experiments were done by Barry S. Brown.

(39) This pathway was also supported by the conclusion (requiring some assumptions) that the rate of addition of allylmagnesium bromide to cinnamyl alcohol was proportional to [PhCH=$CHCH_2$OMgBr][CH_2=$CHCH_2$MgBr][$MgBr_2$].[7]

(40) See ref 16 for a related example.

(41) Baird, W. C., Jr. *J. Org. Chem.* **1966**, *31*, 2411.

(42) Story, P. R. *J. Org. Chem.* **1961**, *26*, 287.

position of the material (not greatly altered by sublimation) was determined from ratios of the ^1H NMR absorptions[43b] of the C-2 H's to be approximately 75% **23** and 25% **31**. For the competition experiment, a sample containing approximately 99% of **23** was obtained by GC separation (column F, 140 °C, retention time of 0.88 for **23** relative to **31**). 5-(Hydroxymethyl)bicyclo[2.2.1]-hept-2-ene (**33**, Eastman Organic Chemicals) was determined from ratios of the NMR absorptions[44] due to the hydroxymethyl group to be approximately 60% endo and 40% exo.

(b) Organomagnesium Compounds. The concentrations (typical values given in parentheses) of organomagnesium compounds generally were determined before use by a double-titration procedure.[45] *n*-Propylmagnesium chloride in diethyl ether (1.8 M) and benzylmagnesium chloride in THF (1.0 M) were commercial samples (Ventron Corp.). Commercial samples (Ventron Corp.) of allylmagnesium chloride in THF (1.5 M) and of allylmagnesium bromide in diethyl ether (1.2 M) were used for some reactions. However, where specifically indicated, these Grignard solutions and also allylmagnesium chloride in diethyl ether (2.5 M) were prepared immediately before use from the corresponding halides (distilled and stored over 4A molecular sieves) by using procedures similar to one already described.[46] Diallylmagnesium was prepared by addition of dioxane (52.9 g, 0.60 mol, distilled from sodium) over 2 h to a solution of allylmagnesium bromide prepared from magnesium (16.9 g, 0.70 mol), allyl bromide (72.6 g, 0.60 mol), and diethyl ether (275 mL). The mixture was centrifuged for 0.5 h at 1500 revolutions/min, and then the supernatant liquid carefully removed. The solvent was removed at reduced pressure, leaving a white solid. Diethyl ether (80 mL) was added to this solid, giving a white suspension; the suspension was stirred and representative samples were found to be 0.46 M. Hydrolysis of an aliquot followed by treatment with dilute nitric acid and silver nitrate solutions led to only a slight cloudiness, showing that the concentration of chloride was neglible. *tert*-Butylmagnesium chloride in diethyl ether (3.2 M) was prepared as already described.[47] 1-propynylmagnesium chloride in THF (1.5 M) was prepared, as already described,[48] by addition of 1-propyne to freshly prepared allylmagnesium chloride; the concentration is based on the concentration of allylmagnesium chloride from which it was prepared (the absence of any significant amount of allylmagnesium chloride was shown by the absence of allyl groups in the materials obtained from the reactions in which the propynylmagnesium chloride was used). Grignard reagents were prepared from magnesium turnings (Fisher Scientific Co.) with diethyl ether and THF that were distilled from lithium aluminum hydride or dried over sodium.

Procedure for Reactions with Organomagnesium Compounds. The reactions were carried out in standard-taper, three-necked, round-bottomed flasks containing a magnetic stirring bar and fitted with a condenser having a gas-inlet tube at the top, a pressure-equalizing addition funnel, and a rubber septum. Glassware was stored at 120 °C prior to assembly; after assembly (and addition of magnesium if the Grignard reagent was to be prepared), the apparatus was heated gently with a Bunsen burner while nitrogen was flowing rapidly through it. During the course of a reaction, a positive pressure of nitrogen was maintained in the closed reaction system.

Either a Grignard reagent was prepared in this assembly, by using one of the procedures already described, or a solution of commercial Grignard reagent or of diallylmagnesium was added through the serum stopper. Gas-tight syringes were used for all transfers of solutions of organomagnesium compounds and anhydrous solvents. A solution of the substrate (and, if used, the internal standard) dissolved in approximately one-third of the amount of solvent containing the organomagnesium compound was added slowly (about 15 min) from the dropping funnel to the stirred solution of the organomagnesium compound which was cooled in an ice bath. The molar ratio of organomagnesium compound to substrate is indicated for each reaction in the following sections.

Some reaction mixtures were left in this assembly at ambient or reflux temperature. Others were heated at 100 °C in ampules. A series of glass ampules, stored at 120 °C prior to use, were attached with Tygon tubing to a manifold which then was evacuated and filled with nitrogen several times. The manifold had an opening covered with a rubber serum stopper above the open end of each ampule. A gas-tight syringe with a long needle was used to fill each ampule through the serum stopper. The ampules were partially evacuated and cooled in liquid nitrogen prior to being sealed. Then the ampules were allowed to thaw and placed in a constant-temperature bath maintained at 100.0 °C.

After the desired reaction time, the flask or the contents of several ampules were cooled in an ice bath. A saturated ammonium chloride solution was added, the organic layer was separated, the aqueous layer was extracted several times with diethyl ether, and the combined organic extracts were dried (Na_2SO_4 or $MgSO_4$). Most of the solvent was removed at reduced pressure or by distillation, and then the residue was subjected to distillation at reduced pressure or to GC analysis.

The progress with time of some reactions was followed. An ampule was removed from the constant-temperature bath, cooled, opened, and fitted with a rubber septum. A saturated ammonium chloride solution was added by use of a syringe, and the organic layer was subjected to GC analysis. Alternatively, an aliquot was removed from the reaction flask by using a gas-tight syringe and then treated in a similar fashion.

In preliminary reactions, the crude reaction mixture was usually subjected to GC analysis. Components present in 2% yield would generally have been detected. Small samples of each significant component were collected for spectral analysis by using glass U-shaped tubes inserted into the exit port of the gas chromatograph and cooled in liquid nitrogen. In subsequent reactions, an internal standard was added if the progress of the reaction was to be followed by GC analysis.

Reactions of Bicyclo[2.2.1]hept-2-ene (8) with Grignard Reagents. (a) With Allylmagnesium Chloride in THF. Isolation of 9. The reaction (approximately 1:1) at 100 °C used freshly prepared Grignard reagent. Distillation of the material isolated from ampules that had been heated for 120 h gave **9**: 25% yield; bp 50 °C (3 torr); ^1H NMR (CCl_4) τ 3.85–4.62 (m, 1, =CH), 4.89–5.32 (c, 2, $=CH_2$), 7.65–9.17 (c, 13, all other H's); ^{13}C NMR ($CDCl_3$) δ 28.8, 30.0, 35.1, 36.6, 37.7, 40.6, 41.0, 41.6, 114.7, 137.9. Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.33; H, 11.76.

GC analysis (column H, 130 °C, retention times of 0.43 for **8** and 1.90 for **9** relative to nonane, the internal standard) of another reaction (6:1) with commercial Grignard reagent gave the following compositions: 5 h, 90% **8** and 9% **9**; 24 h, 56% and 24%; 48 h, 40% and 28%; 72 h, 36% and 37%.

(b) With Allylmagnesium Bromide in Diethyl Ether. The reaction (3:1) was at reflux temperature. GC analysis (as in part a) gave the following compositions: immediately after mixing, 85% **8** and 0% **9**; 27 h, 58% and 13%; 50 h, 43% and 35%; 96 h, 33% and 59%. More Grignard reagent (1:1) was added after 96 h, and the following compositions were then observed: 122 h, 19% **8** and 72% **9**; 144 h, 4% and 86%.

(c) With *tert*-Butylmagnesium Chloride. The reaction (10:1) was at 100 °C in diethyl ether. After 5 days, the only major peak observed upon GC analysis (column A, 170 °C) was due to **8**.

Preparation of 2-*endo*-Allylbicyclo[2.2.1]heptane (12). (a) *endo*-2-(Bromomethyl)bicyclo[2.2.1]heptane (11). A mixture of *endo*- and *exo*-5-carboxybicyclo[2.2.1]hept-2-ene, obtained as a liquid (Frinton Laboratories), was recrystallized repeatedly from pentane[49] at dry ice temperature to concentrate the endo isomer, mp 40–40.5 °C (lit.[49,50] mp 44.1–45.0 and 39 °C). This sample

(43) (a) Alder, K.; Rickert, H. F. *Justus Liebigs Ann. Chem.* **1940**, *543*, 1. (b) Wong, E. W. C.; Lee, C. C. *Can. J. Chem.* **1964**, *42*, 1245.
(44) Pretsch, E.; Immer, H.; Pascual, C.; Schaffner, K.; Simon, W. *Helv. Chim. Acta* **1967**, *50*, 105.
(45) Vlismas, T.; Parker, R. D. *J. Organomet. Chem.* **1967**, *10*, 193.
(46) Kharasch, M. S.; Fuchs, C. F. *J. Org. Chem.* **1944**, *9*, 359.
(47) Whitmore, F. C.; Badertscher, D. E. *J. Am. Chem. Soc.* **1933**, *55*, 1559.
(48) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: New York, 1971; p 26.
(49) Roberts, J. D.; Trumbull, E. R., Jr.; Bennett, W.; Armstrong, R. *J. Am. Chem. Soc.* **1950**, *72*, 3116.
(50) Alder, K.; Stein, G.; Liebmann, M.; Rolland, E. *Justus Liebigs Ann. Chem.* **1934**, *514*, 197.

was reduced as previously reported[51] to 5-*endo*-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene: 49% yield; bp 81 °C (7.0 torr) [lit.[51] bp 97–98 °C (20 torr)]. NMR analysis ($CDCl_3$) using the CH_2O absorptions[44] indicated that the product contained about 93% of the endo isomer and 7% of the exo isomer. By use of a procedure[51] that had been used to reduce the exo isomer, this sample was reduced to **10**: 89% yield; bp 85–86 °C (6.0 torr) [lit.[52] bp 93–95 °C (14 torr)].

The conversion of **11** to **12** was accomplished by using a procedure[53] that has been used to convert cyclopropylmethanol to cyclopropylmethyl bromide. A solution of **11** (4.1 g, 32 mmol) and anhydrous diethyl ether (25 mL) was cooled in a dry ice–acetone bath, and phosphorous tribromide (3.24 g, 12 mmol) was added slowly. The flask was permitted to slowly warm to room temperature overnight. Water (25 mL) was added slowly, and the mixture was extracted with diethyl ether. The ether solution was washed with a saturated sodium bicarbonate solution and dried (Drierite). Distillation gave **11**: 1.51 g (8.0 mmol, 25%); bp 35 °C (0.15 torr) [lit.[54] bp 83–84 °C (13 torr)]; ^1H NMR (CCl_4) τ 6.31–6.98 (c, 2, CH_2Br), 7.34–9.52 (c, 11, all other H's).

A large, undistillable residue remained.

(b) 2-*endo*-Allylbicyclo[2.2.1]heptane (12). The conversion of **11** to **12** was patterned after a procedure[55] that had been used with other compounds. Magnesium (triply sublimed, 0.292 g, 12 mmol) and THF (20 mL) were added to a carefully dried assembly (similar to that already described for the preparation of the organomagnesium compounds) in which an argon atmosphere was maintained. A solution of **11** (1.41 g, 7.5 mmol) and THF (12 mL) was added slowly. After the addition was completed, the flask was left at ambient temperature for 30 min and then refluxed for 1 h. The concentration of the Grignard reagent was 0.19 M.[45] The flask containing the Grignard reagent solution (ca. 30 mL, ca. 6 mmol) was cooled in an ice bath, and a solution of tris(dibenzoylmethano)iron(III) (0.014 g, 0.04 mmol), prepared as already described,[55] in THF (3 mL) was added. Five minutes later, vinyl bromide (0.17 g, 1.6 mmol) was added. After the flask had remained at ice-bath temperature for 1 h, dilute sulfuric acid (5 mL, 0.25 M) was added, the organic layer was removed, and the aqueous layer was extracted with diethyl ether. The organic extracts were washed with water and dried ($MgSO_4$). Most of the solvent was removed by distillation through a Vigreux column. GC analysis (column C, 165 °C) of the remainder showed two significant peaks (retention times 0.19 and 0.45 relative to dodecane, the internal standard). The first peak was relatively small and was not investigated. The material responsible for the second peak was **12**: yield 21% based on **11**, ca. 100% based on vinyl bromide (by mistake, an insufficient amount of vinyl bromide had been used); ^1H NMR (CCl_4) τ 3.91–4.80 (m, 1, =CH), 4.93–5.37 (c, 2, $=CH_2$), 7.72–9.57 (c, 11, all other H's); ^{13}C NMR ($CDCl_3$) δ 22.4, 30.1, 36.8, 37.2 (2 C's), 39.9 (3 C's), 114.2, 138.6; mass spectrum, m/z 136.1244 (M^+, calcd for $C_{10}H_{16}$ 136.1251).

Isomers **9** and **12** are readily distinguished by the appearance of their ^1H NMR spectra. The spectrum of isomer **12** has an absorption appearing roughly like a doublet centered at τ 9.45; isomer **9** has no absorption at that high a field. In the vinyl hydrogen absorption region, the spectrum of **12** has clusters of absorption at τ 5.03, 5.12, and 5.30, but that of **9** has absorptions at τ 5.00 and 5.22. The retention times of **9** and **12** relative to dodecane are 0.41 and 0.45 (column C, 165 °C).

Reactions of *syn*-Bicyclo[2.2.1]hept-2-en-7-ol (13) with Grignard Reagents. (a) With Allylmagnesium Chloride in THF. Isolation of 14 and 15. The reaction (approximately 4:1) for 48 h at 100 °C used freshly prepared Grignard reagent. Distillation gave a fraction [bp 50–85 °C (1 torr)] that was indicated by GC analysis (column C, 195 °C) to consist of two major components (retention times relative to tridecane of 0.59 and 2.64).

The first peak was due to **14**: ^1H NMR (CCl_4) τ 3.80–4.60 (m, 1, =CH), 4.79–5.28 (c, 2, $=CH_2$), 6.08 (m, 1, CHOH), 7.35 (s, 1, OH), 7.50–9.08 (c, 11, all other H's); ^{13}C NMR ($CDCl_3$) δ 24.4, 26.4, 33.7, 39.6, 39.8, 40.4, 42.9, 79.1, 113.1, 137.3. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.65; H, 10.53.

The second peak was due to a compound that is tentatively assigned structure and stereochemistry **15**: ^1H NMR (CCl_4) τ 3.92–4.67 (c, 3, =CH), 4.85–5.28 (c, 2, $=CH_2$), 6.14 (m, 1, CHOH), 7.05–7.66 (m, 1, CHCH=), 7.73–9.23 (c, 15, all remaining H's); mass spectrum, m/z 194.1687 (M^+, calcd for $C_{13}H_{22}O$ 194.1670).

GC analysis (column G, 125 °C; retention times relative to tridecane, the internal standard, of 0.11 for **13**, 0.59 for **14**, and 2.64 for **15**) of a similar reaction (approximately 10:1) with freshly prepared Grignard reagent gave the following compositions: before heating, 38% **13**, 2% **14**, and 0% **15**; 1 h, 8%, 52%, and 7%; 2 h, 0%, 35%, and 19%; 3 h, 0%, 20%, and 23%; 4 h, 0%, 18%, and 39%; 5 h, 0%, 16%, and 46%.

(b) With Allylmagnesium Bromide in Diethyl Ether. Isolation of 14. The reaction (approximately 6:1) at reflux temperature used freshly prepared Grignard reagent. GC analysis (column C, 150 °C, retention times relative to tridecane, the internal standard, of 0.17 for **13** and 0.71 for **14**) gave the following compositions: before refluxing, 64% of **13** and 0% of **14**; 1 h, 54% and 15%; 2 h, 36% and 30%; 3 h, 26% and 36%; 5 h, 20% and 47%. A peak due to **15** would certainly have been noted if this compound had been present in more than 2% yield. Distillation of the material remaining after 5 h gave **13**: 42% yield; bp 60–63 °C (0.09 torr).

(c) With *tert*-Butylmagnesium Chloride. Isolation of 30. The reaction (approximately 20:1) was at 100 °C in diethyl ether. GC analysis (column A, 145 °C) of aliquots showed the appearance of a new peak (retention times relative to tetradecane, the internal standard, of 3.25 for **13** and 5.37 for the new peak, which had a small trailing shoulder). A sample of the material responsible for this peak was collected and tentatively assigned structure **30**: ^1H NMR (CCl_4) τ 6.20 (m, 1 CHOH), 8.04–9.12 (c, 10, all other H's), 9.15 (s, 9, CH_3).

After 11 days, GC analysis indicated the presence of 10% of **30** and 80% of **13**.

(d) With 1-Propynylmagnesium Chloride. The reaction (approximately 25:1) was at 100 °C in THF. Even after 7 days, the only major peak observed upon GC analysis (column A, 170 °C) was due to **13**.

Conversion of Addition Product 14 to Cyclic Ether 17. The reaction was patterned after a procedure that has been used with another compound.[56] Mercuric acetate (1.01 g, 3.2 mmol) was added to a solution of **14** (0.484 g, 3.2 mmol), THF (15 mL), and water (15 mL), and the reaction was stirred for 25 min at ambient temperature. Then an aqueous solution of sodium borohydride (0.5 M, 35 mL) containing sodium hydroxide (0.1 g) was added slowly. The reaction mixture was extracted several times with diethyl ether and the extracts were dried ($MgSO_4$). The material left after removal of most of the solvent at reduced pressure afforded one major GC peak (column C, 180 °C, retention time of 0.79 relative to **14**) in addition to that due to **14**. The material affording this peak was collected and assigned structure **17**: ^1H NMR (CCl_4) τ 5.83–6.42 (c, 2, CHOH), 7.65–9.08 (c, 14, all other H's), includes 8.97 (d, J = 6 Hz, 3, CH_3); mass spectrum, m/z 152.1179 (M^+, calcd for $C_{10}H_{16}O$ 152.1200).

Assuming that all of the crude product was volatile, the GC analysis indicated a yield of 45% of **17**; an NMR spectrum of the crude product was consistent with this yield.

Reaction of Addition Product 14 with Allylmagnesium Bromide. The reaction (60:1, only 0.1 mmol of **14** was used) was for 72 h at 100 °C in THF. GC analysis (column C, 195 °C) revealed no material with a retention time greater than that of tridecane, the internal standard (**15** had a retention time of 2.64 relative to that of tridecane).

Reaction of *anti*-Bicyclo[2.2.1]hept-2-en-7-ol (16) with Allylmagnesium Chloride. The reaction (approximately 4:1) was for 5 days in diethyl ether at reflux temperature. A ^1H NMR spectrum indicated that the crude product contained only **16**.

Reactions of *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (23) with Organomagnesium Compounds. (a) With Allylmagnesium

(51) Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986.
(52) Alder, K.; Stein, G.; Rolland, E. *Justus Liebigs Ann. Chem.* **1936**, *525*, 247.
(53) Meek, J. S.; Rowe, J. W. *J. Am. Chem. Soc.* **1955**, *77*, 6675.
(54) Alder, K.; Windemuth, E. *Chem. Ber.* **1938**, *71*, 1939.
(55) Neumann, S. M.; Kochi, J. K. *J. Org. Chem.* **1975**, *40*, 559.
(56) Bindra, J. S.; Grodski, A.; Schaaf, T. K.; Corey, E. J. *J. Am. Chem. Soc.* **1973**, *95*, 7522.

Chloride in THF. Isolation of 24. The reaction (approximately 3:1) for 100 h at 100 °C used freshly prepared Grignard reagent. Distillation gave **24**: 20% yield; bp 84 °C (4 torr); ^{1}H NMR (CCl_4) τ 3.82–4.67 (m, 1, =CH), 4.76–5.22 (c, 2, $=CH_2$), 5.79 (m, 1, CHOH), 7.60–9.17 (c, 12, all other H's); ^{13}C NMR ($CDCl_3$) δ 25.7, 31.4, 35.6, 39.7, 39.8, 40.6, 43.1, 72.7, 114.3, 138.3. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.77; H, 10.51.

GC analysis (column H, 180 °C, retention times relative to undecane, the internal standard, of 0.54 for **23** and 1.82 for **24**) of a reaction (5:1) at 100 °C with commercial Grignard reagent gave the following compositions: before heating, 75% **23** and 0% **24**; 1 h, 46% and 24%; 2 h, 34% and 45%; 3 h, 20% and 50%; 4 h, 16% and 54%.

(b) With Allylmagnesium Chloride in THF Followed by Carbonation. Isolation of Lactone 26. The reaction (approximately 10:1) at reflux temperature for 7 days used freshly prepared Grignard reagent. The reaction flask was placed in an ice bath and the reaction mixture stirred rapidly while carbon dioxide was passed through the flask for 2 h. After hydrolysis by the slow addition of saturated ammonium chloride solution, the reaction mixture was acidified with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic extracts were combined and dried ($MgSO_4$). GC analysis (column C, 170 °C) revealed the presence of a new peak (retention times relative to tridecane, the internal standard, of 0.128 for **23**, 0.80 for **24**, and 2.57 for the new peak). The compound responsible for the new peak was assigned structure **26**: IR (CCl_4) 1770 cm^{-1} (C=O); ^{1}H NMR (CCl_4) τ 3.75–4.70 (m, 1, =CH), 4.73–5.32 (c, 2, $=CH_2$), 5.37 (m, 1, CHO), 6.86 (m, 1, H at C-1), 7.37–9.11 (c, 9, all other H's); mass spectrum, m/z 178.0987 (M^+, calcd for $C_{11}H_{14}O_2$ 178.0993).

The GC analysis indicated that the crude product contained 46% of **23**, 14% of **24**, and 12% of **26**.

(c) With Allylmagnesium Bromide in Diethyl Ether. The reaction (6:1) was at reflux temperature. GC analysis (column C, 170 °C, retention times relative to tridecane, the internal standard, of 0.25 for **23** and 0.80 for **24**) gave the following compositions: before refluxing, 61% **23** and 0% **24**; 10 h, 52% and 6%; 24 h, 66% and 13%; 48 h, 42% and 22%; 72 h, 34% and 30%; 96 h, 30% and 38%. GC analysis (column A, 180 °C) of **24** collected from column C showed only one peak.

(d) With Diallylmagnesium. The reaction (R_2Mg/ROH ratio was 7:1) was at reflux temperature. GC analysis (column C, 180 °C, retention times relative to dodecane, the internal standard, of 0.42 for **23** and 1.25 for **24**) gave the following compositions: before refluxing, 58% of **23** and 0% of **24**; 24 h, 47% and 4%; 48 h, 44% and 6%; 72 h, 41% and 10%; 96 h, 38% and 12%. A sample of **24** collected from column C exhibited the same infrared spectrum and GC retention time (column A) as that obtained from the reactions with allylmagnesium halides.

(e) With *tert*-Butylmagnesium Chloride. The reaction (approximately 20:1) was at 100 °C in diethyl ether. Over a period of 30 days, ampules were subjected to GC analysis (column B, 160 and 200 °C), but no significant new peaks were observed. The analysis (160 °C, retention times relative to tetradecane, the internal standard, of 0.7 for **23** and 1.2 for **31**) indicated that the ratio of **23** to **31**, about 3.0 in the reactant, decreased during the reaction (although the total amount of **23** plus **31** did not decrease greatly): 24 h, 2.3; 84 h, 0.7; 30 days, 0.5.

(f) With *n*-Propylmagnesium Chloride. The reaction (7:1) was in diethyl ether at 100 °C. Aliquots were subjected to GC analysis (column G, 120 °C) for 10 days, but no significant new peaks were seen. The crude material isolated after 12 days was almost completely the reactant.

(g) With Benzylmagnesium Chloride. The reaction (2:1) was at 100 °C in THF. Ampules were subjected to GC analysis (column D, 180 °C) over a period of 8 days. Even at the end of that time, the only major peaks were due to **23** and **31**, although several small peaks of longer retention time were present.

Reduction of Addition Product 24 to 2-*endo*-Allylbicyclo[2.2.1]heptane (12). A solution of freshly purified[57] *p*-toluenesulfonyl chloride (2.04 g, 10.7 mmol) in pyridine (15 mL, distilled from barium oxide) was added over 30 min to a solution of **24** (1.5 g, 9.8 mmol) in pyridine (10 mL) that was cooled in an ice bath. The solution was left under a nitrogen atmosphere in the ice bath for 48 h. Then the reaction mixture was poured into ice water (300 mL), stirred for 15 min, and extracted several times with diethyl ether. The ether extracts were washed with a hydrochloric acid solution (3 M), a saturated sodium bicarbonate solution, and a saturated sodium chloride solution and then dried ($MgSO_4$). Removal of the solvent at reduced pressure left material (2.6 g) whose spectra were in accord with structure **25**: ^{1}H NMR (CCl_4) τ 2.29 and 2.73 (A_2B_2 q, J_{AB} = 8 Hz, 4, aryl H's), 3.92–4.67 (m, 1, =CH), 4.85–5.52 (c, 3, $=CH_2$ and CHO), 7.56 (s, 3, CH_3), 7.60–9.32 (c, 11, all remaining H's); mass spectrum, m/z (M^+ too weak for high-resolution mass determination), 172.0190 (calcd for $C_7H_8O_3S$ 172.0194), 135.1165 (calcd for $C_{10}H_{15}$ 135.1173).

Attempts to crystallize this oil failed, and elemental analyses gave low values for S.

The procedure used to reduce **25** followed closely a procedure used with related *p*-toluenesulfonates.[58] A solution of **25** (2.5 g, ca. 8 mmol) in diethyl ether (20 mL) was added to a solution of lithium aluminum hydride (0.57 g, 13.5 mmol) in diethyl ether (5 mL). The solution was refluxed for 3 h under a nitrogen atmosphere. The mixture was cooled in an ice bath and hydrolyzed by addition first of wet ether and then of water. Aqueous sodium hydroxide (1 M, 150 mL) was added, the solution was extracted several times with diethyl ether, and the extracts were dried (K_2CO_3). Removal of the solvent at reduced pressure left a crude product shown by its ^{1}H NMR spectrum to consist mainly of **12**. GC analysis (column G, 110 °C) gave a yield of 80% (based upon **24** and calculated from the area of the peak due to **12** divided by the areas of all peaks). A sample purified by GC (column C, 150 °C) had IR and ^{1}H NMR spectra identical with those of the authentic sample of **12** whose preparation was described above.

Conversion of Addition Product 24 to Ketone 29. (a) Reduction of 24 to 28.[38] A sample of **24** (0.89 g, 5.8 mmol) was dissolved in absolute ethanol (200 mL) and a Pd on carbon catalyst (20 mg) added. The mixture was hydrogenated (3 atm of H_2) for 1 h in a Parr hydrogenator. The catalyst was removed by filtration and the solvent by distillation to give a crude product which on GC analysis (column B) showed only one significant peak and was assigned structure **28**: NMR (CCl_4) δ 5.87 (m, 1, CHOH), 7.70 (s, 1, OH), 7.77–9.30 (c, 16, all other H's). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.64; H, 11.72.

(b) Oxidation of 28 to Ketone 29.[38] Chromic anhydride (2.18 g, 21.8 mmol) was added slowly to dry pyridine (22 mL) with stirring. This mixture was added to a sample of **28** (0.85 g, 5.51 mmol) and pyridine (5 mL) and the mixture stirred for 1 h. The mixture was poured into water and extracted repeatedly with diethyl ether. The extracts were dried ($MgSO_4$), and the solvent was then removed to leave an oil which on GC analysis (column B) showed only one significant peak and was assigned structure **29**: IR (CCl_4) 1748 cm^{-1} (C=O); ^{1}H NMR (CCl_4) τ 7.37–9.32 (c, 16, all H's, strong absorptions were at 7.54, 8.08, 8.13, 8.32, 8.70, 8.99, and 9.07); ^{1}H NMR (H_2SO_4, tetramethylammonium fluoroborate, τ 6.87,[26] used as an internal standard) τ 6.43 (d, J = 6 Hz, H at C-1).

Reaction of 3-(Hydroxymethyl)cyclohexene (32) with Allylmagnesium Chloride. The reaction (approximately 3:1) was for 11 days in diethyl ether at reflux temperature. The ^{1}H NMR spectrum of the crude product showed it to contain only **32**. GC analysis (column C, 170 °C) showed only a peak due to **32**.

Reaction of 5-(Hydroxymethyl)bicyclo[2.2.1]hept-2-ene (33) with Allylmagnesium Bromide. Isolation of 34. The reaction (5:1) was in diethyl ether at 100 °C for 5 days. Distillation gave a fraction [bp 90–102 °C (0.35 torr)] that was indicated by GC analysis (column C, 220 °C) to contain a new component (retention times relative to tridecane, the internal standard, of 0.31 for **33** and 1.43 for the new component). The spectral properties of the new component were consistent with its being an allyl-substituted 2-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene (**34**): ^{1}H NMR (CCl_4) τ 3.85–4.78 (m, 1, =CH), 4.87–5.31 (c, 2, $=CH_2$), 6.60 (m, 2, CH_2OH), 6.85 (s, 1, OH), 7.59–9.68 (c, 13, all

(57) Pelletier, S. W. *Chem. Ind. (London)* **1953**, 1034.

(58) Hirsjärvi, P.; Kiviranta, A.; Tenhunen, E.; Varjovaara, M.-L. *Suom. Kemistil. B* **1971**, *44*, 391.

other H's); mass spectrum (70 eV), m/z 166.1345 (M^+, calcd for $C_{11}H_{18}O$ 166.1357).

The GC analysis indicated that the yield of **34** was 6%. Most of the remainder of this fraction was **33**, as was most of an earlier fraction (0.71 g) collected at 60–90 °C (0.30 torr).

Competition for a Limited Amount of Allylmagnesium Chloride. The relative amounts of Grignard reagent in THF, the alkenol, and 8 were 1.5:1.0:1.0, and the reactions were for 4 h at 100 °C.

(a) 13 and 8. GC analysis (column H, 170 °C, retention times relative to 8 of 2.16 for **13**, 2.92 for **9**, and 9.48 for **14**) indicated the relative molar amounts of 8, **13**, **9**, and **14** to be 3.5:2.9:0:1.0.

(b) 23 and 8. GC analysis (column H, 170 °C, retention times relative to 8 of 2.40 for **23**, 2.96 for **9**, and 9.3 for **24**) indicated the relative molar amounts of 8, **23**, **9**, and **24** to be 2.0:2.4:0:1.0.

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Registry No. 8, 498-66-8; 9, 60166-78-1; 10, 13137-31-0; 11, 16002-27-0; 12, 60166-77-0; 13, 13118-70-2; 14, 60166-73-6; 15, 75347-68-1; 16, 694-70-2; 17, 60166-74-7; 23, 694-97-3; 24, 60166-75-8; 25, 75347-69-2; 26, 60166-76-9; 28, 75347-70-5; 29, 75347-71-6; 30, 75347-72-7; 31, 2890-98-4; 32, 3309-97-5; 33, 95-12-5; 34, 75347-73-8; allyl chloride, 107-05-1; allyl bromide, 106-95-6; *tert*-butyl chloride, 507-20-0; *endo*-5-carboxybicyclo[2.2.1]hept-2-ene, 1195-12-6; *exo*-5-carboxybicyclo[2.2.1]hept-2-ene, 934-30-5; 5-*endo*-(hydroxymethyl)-bicyclo[2.2.1]hept-2-ene, 15507-06-9; vinyl bromide, 593-60-2; 1-propynyl chloride, 624-65-7; diallylmagnesium, 6928-75-2; *n*-propyl chloride, 540-54-5; benzyl chloride, 100-44-7.

Stereochemistry of Addition of Allylic Grignard Reagents to 3-(Hydroxymethyl)cyclopropenes[1]

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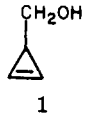
Allylic Grignard reagents add to the double bonds of alkyl-substituted 3-(hydroxymethyl)cyclopropenes. In the products, both the allyl group and the group (H or CO_2H) replacing magnesium are cis to the hydroxymethyl group. The new carbon–carbon bond is formed preferentially at the more substituted allylic carbon of the allyl group and at the more substituted carbon of the cyclopropene double bond.

Additions of Grignard reagents to unsaturated alcohols are often faster than those to equivalent substrates lacking hydroxyl functions.[2] In at least one of the metalated forms which it has in a reaction solution, the hydroxyl group can facilitate addition to a carbon–carbon multiple bond.

In another paper, we described the results of a study of stereochemical aspects of Grignard reagent addition to alkenols.[3] In reactions with homoallylic hydroxybicyclo-[2.2.1]hept-2-enes, an allyl group became attached to the face of the double bond over which the hydroxyl group was constrained.

This prior study had significant limitations. (1) Only allylic Grignard reagents added to the substrates. Since allylic Grignard reagents may add by pathways (for example, involving a γ-carbon) not available to most other Grignard reagents, results obtained with allylic reagents may not be typical. (2) The stereochemistry of initial attachment of magnesium was uncertain. Magnesium could have been replaced by some group (e.g., D, CO_2H) that would indicate its location. However, since inversion of configuration at a saturated carbon bonded to magnesium can be rapid, the stereochemistry of magnesium at the time of quenching may be different than that immediately following addition.

In this paper we describe additions to another group of substrates, alkyl derivatives of 3-(hydroxymethyl)cyclopropene (1). In these alkenols, as in the previously studied



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hydroxybicycloheptenes, the hydroxyl group has a homoallylic relationship to the double bond and is constrained over one of its faces. By using 3-(hydroxymethyl)cyclopropenes, we hoped to overcome the two limitations of the preceding study. (1) Since cyclopropenes are highly strained and unusually reactive toward many addition reactions, we hoped that a wide variety of Grignard reagents would add readily to (hydroxymethyl)cyclopropenes. In fact, several simple Grignard reagents are known to add to alkyl-substituted cyclopropenes under routine conditions.[4-10] (2) Since cis–trans interconversion

(1) Most of this work is taken from: Bension, R. M. Ph.D. Dissertation, The Pennsylvania State University, University, Park, PA, 1978.

(2) Reviewed briefly in ref 3 and the following: Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123; Courtois, G.; Miginiac, L. *Ibid.*, **1974**, *69*, 1.

(3) Richey, H. G., Jr.; Wilkins, C. W., Jr. *J. Org. Chem.*, preceding paper in this issue.

(4) Lukina, M. Y.; Ruavshevskaya, T. Y.; Nesmeyanova, O. A. *Dokl. Chem. (Engl. Transl.)* **1970**, *190*, 133; *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1970**, *190*, 1109.

(5) Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Kazanskii, B. A. *Dokl. Chem. (Engl. Transl.)* **1972**, *207*, 999; *Dokl. Akad Nauk SSSR, Ser. Khim.* **1972**, *207*, 1362.

(6) Avezov, I. B.; Bolesov, I. G.; Levina, R. Y. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 2129; *Zh. Org. Khim.* **1974**, *10*, 2114. Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Grinberg, V. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1977**, 2399; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 2590. Nesmeyanova, O. A.; Rudashevskaya, T. Y. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1978**, 1364; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 1562.

(7) Shell Internationale Research, Mattschappip B. V. *Netherlands Appl.* 74 02 879; *Chem. Abstr.* **1975**, *83*, 27684.

(8) Watkins, E. K. The Pennsylvania State University, unpublished observations.

0022-3263/80/1945-5036$01.00/0