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.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers and the high-resolution mass spectrometer that were used. C.W. thanks the National Fellowships Fund for fellowship support. We thank Dr. Robert D. Minard for obtaining the mass spectra and Barry S. Brown and Robert E. Moore for some preliminary work on this project.

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]

Herman G. Richey, Jr.,* and Rouvain M. Bension

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

Received April 23, 1980

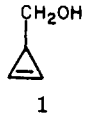
Allylic Grignard reagents add to the double bonds of alkyl-substituted 3-(hydroxymethyl)cyclopropenes. In the products, both the allyl group and the group (H or CO_2H) replacing magnesium are cis to the hydroxymethyl group. The new carbon–carbon bond is formed preferentially at the more substituted allylic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



1

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.

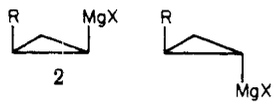
(6) Avezov, I. B.; Bolesov, I. G.; Levina, R. Y. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 2129; *Zh. Org. Khim.* **1974**, *10*, 2114. Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Grinberg, V. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1977**, 2399; *Izv. Akad. Nauk SSSR,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

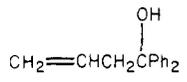
of cyclopropyl Grignard reagents (**2** ⇌ **3**) is not significant



2 **3**

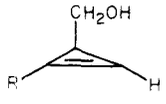
under ordinary reaction conditions,[11,12] it seemed more probable that the stereochemistry of magnesium would be preserved in additions to (hydroxymethyl)cyclopropenes than to hydroxybicycloheptenes. Of course, the metalated hydroxyl group might somehow accelerate cis–trans isomerization.

We also wanted to determine the effect of different degrees of substitution of the two double bond carbons on the orientation of addition. Although the double bond carbons in acyclic substrates such as **4**[13] differ in substi-



4

tution, they also differ in distance from the hydroxyl group. Except for effects of conformational preferences involving the cyclopropyl–CH_2OH bond, the two carbons of the double bond of **5** are equidistant from the hydroxyl function. Therefore, **5** is more suitable than acylic substrates for determining the effect of substitution on orientation.



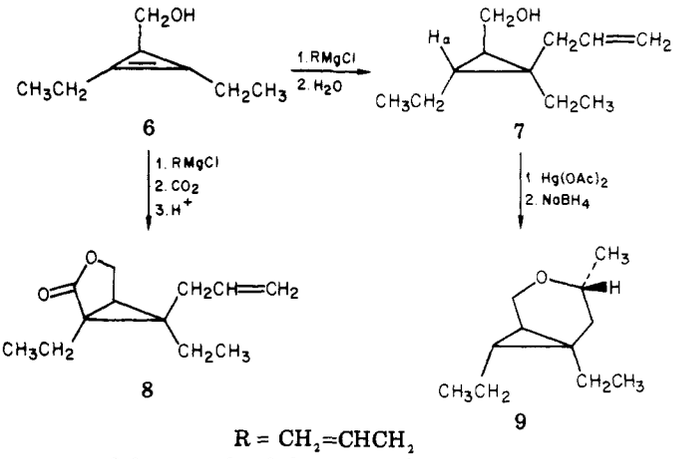
5

Results

Additions to three substrates (**6**, **11**, and **14**) were investigated. Reaction of **6** and an excess of allylmagnesium chloride in diethyl ether at ambient temperature overnight followed by hydrolysis gave **7** (54% yield)[14] as the only significant product (Scheme I). Carbonation followed by hydrolysis of a similar reaction solution gave lactone **8** (59%). By oxymercuration–demercuration, alcohol **7** was converted to cyclic ether **9** (50%). Structures **7**–**9** are consistent with the ^1H NMR spectra. Stereochemical assignments are considered in the Discussion.

No addition products were found in similar reactions of **6** with diethyl ether solutions of phenylmagnesium bromide, *tert*-butylmagnesium chloride, and methylmagnesium iodide or with a tetrahydrofuran (THF) solution of vinylmagnesium bromide.[15] Substantial amounts of **6** were

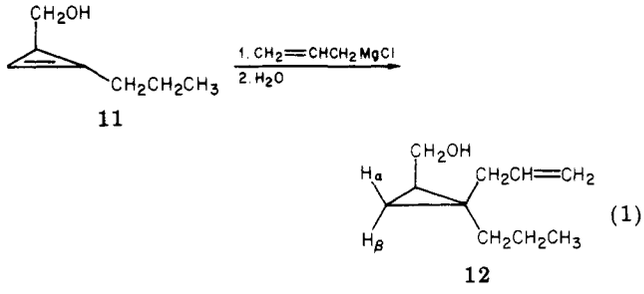
Scheme I



R = CH_2=$CHCH_2$

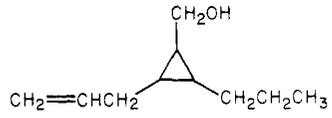
recovered from each of these reactions.

Reaction of **11** and an excess of allylmagnesium chloride in diethyl ether at ambient temperature overnight gave **12** (64%)[14] as the only product (eq 1). The ^1H NMR spec-



11 **12** (1)

trum is completely consistent with the proposed structure and specifically excludes structure **13** resulting from the

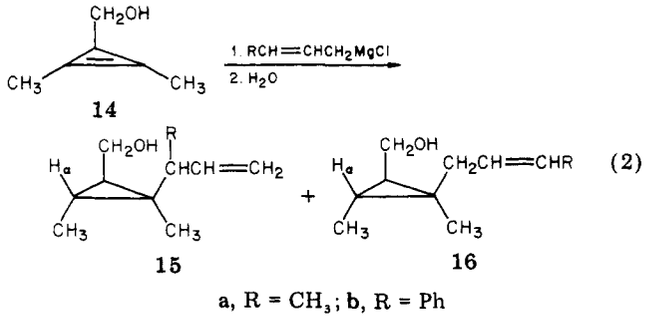


13

other possible orientation of addition. Assignment of stereochemistry is considered in the Discussion.

No evidence for significant amounts of addition products was found in similar reactions of **11** with diethyl ether solutions of benzylmagnesium chloride, *tert*-butylmagnesium chloride, or methylmagnesium iodide. Although no **11** was recovered from the reaction with benzylmagnesium chloride, substantial amounts were isolated from the other reactions.

Reaction of **14** and an excess of crotylmagnesium chloride in diethyl ether at ambient temperature overnight gave **15a** (40%)[14] and **16a** (6%) as the only significant products (eq 2). A similar reaction with cinnamyl-



14 **15** **16** (2)

a, R = CH_3; b, R = Ph

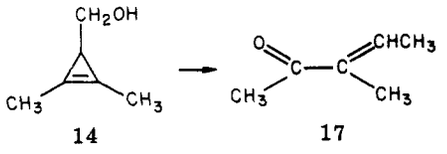
magnesium chloride gave **15b** (48%) as the only significant product. No **16b** was detected. The ^1H NMR spectra are

(9) Lehmkuhl, H.; Mehler, K. *Justus Liebigs Ann. Chem.* **1978**, 1841.
(10) Wilkins, C. W., Jr. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1976.
(11) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter 3.
(12) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288.
(13) Eisch, J. J.; Merkley, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 1148.
(14) See the Experimental Section for a description of the procedure and assumptions used in determining yields by GC analysis.
(15) Similar reactions using commercial (instead of freshly prepared) vinylmagnesium bromide gave a product tentatively identified from its ^1H NMR spectrum as 1,2-diethyl-3-(hydroxymethyl)cyclopropane (**10**, stereochemistry uncertain). The nature of the component in the commercial Grignard reagent solution that was responsible for this product was not investigated. The presence in the commercial sample of some species with a Mg–H bond is one possibility. Magnesium hydrides have been observed to add to alkenes (Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* **1977**, *99*, 310) and, because of the strain of cyclopropenes, might be expected to add particularly rapidly to **6**. The reduction of alkenes by magnesium hydrides is catalyzed by transition metals (Ashby, E. C.; Smith, T. *J. Chem. Soc., Chem. Commun.* **1978**, 30) which also are possible impurities in the commercial sample.

in accord with the structural assignments. Configurational assignments are considered in the Discussion.

No addition products were found in similar reactions of **14** with diethyl ether solutions of benzylmagnesium chloride, *tert*-butylmagnesium chloride, or cyclopropylmagnesium bromide. Substantial amounts of **14** were recovered from all but the benzylmagnesium chloride reaction.

No addition products were obtained nor was **14** recovered from reactions of **14** with THF solutions of allylzinc bromide for 10 h at 0 °C or at −78 °C, followed by hydrolysis. The reaction at 0 °C furnished a complex mixture of compounds and the reaction at −78 °C a substantial amount (43%)[14] of 3-methyl-3-penten-2-one (**17**), an isomer of **14** (eq 3). The isomerization was not investigated, but it could reasonably have been initiated by the action of protonic or Lewis acids on the reactant.[16]



(3)

Discussion

Stereochemistry of the Addition Products. The relative cis–trans stereochemistry of the groups attached to the cyclopropyl ring of each addition product can be established by the effects of a lanthanide shift reagent on its ^{1}H NMR spectrum.[17] The shifts of individual absorptions per equivalent of added europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) [Eu(fod)$_3$] are shown in Figure 1.

As an example of the shift reagent method, consider the observations with **7**. The CH_2 hydrogen absorption of the allyl group shifts 3.6 ppm per mole of added shift reagent. This is considerably greater than the shift (2.3 ppm) of the CH_2 hydrogen absorptions of the two ethyl substituents. The hydroxyl group, to which the shift reagent complexes, must be nearer to the allyl group than to the ethyl groups. With respect to hydroxymethyl, the allyl group is cis, and the ethyl groups are trans. Therefore, the hydroxymethyl group is cis to a ring hydrogen (H_α). This stereochemical assignment for H_α also seems likely since the absorption of H_α shifts about twice as much as that of the CH_2 hydrogens of allyl. Note that the shift of the H_α absorption of **12** is considerably greater than that of the CH_2 hydrogens of the allyl group, but that of H_β (trans to hydroxymethyl) is less.

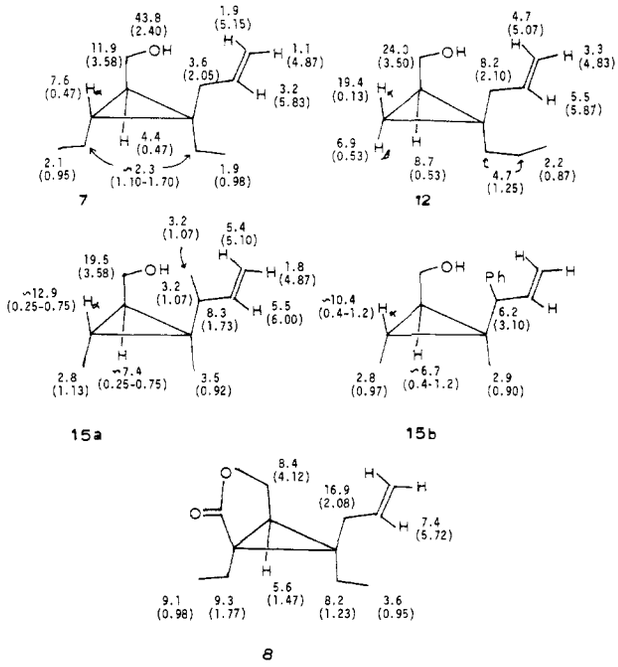


Figure 1. Downfield shifts (parts per million) of ^{1}H NMR absorptions of CCl_4 solutions of addition products per equivalent of added Eu(fod)$_3$.[18] The numbers in parentheses are the chemical shifts (δ) in the absence of the shift reagent.[19]

The effects of shift reagents on ^{1}H NMR spectra also are consistent with hydroxymethyl being cis to allyl in **12**, **15a**, and **15b** and to the H in **15a** and **15b** that had replaced Mg. We assume that the relative stereochemistry of ring substituents in minor product **16a** is the same as that in the other addition products. The configuration of the double bond of **16a** was not rigorously established. However, the chemical shifts of absorptions of the CH_2 and CH_3 hydrogens of the crotyl side chain and the degree of splitting of the CH_3 absorption are more characteristic of a cis configuration.[20] We can make no assignment of the configuration of the chiral carbon of the allylic side chain of **15a** or of **15b** relative to the remainder of the molecule.

The stereochemistry of **7** deduced from the shift reagent studies was confirmed by chemical transformations. Conversion of **7** to a cyclic ether (**9**) indicates that the allyl and hydroxymethyl groups are cis. The stereochemistry at the chiral carbon generated on formation of **9** from **7** is assigned on the basis of the chemical shift (δ 2.95) of the tertiary hydrogen at this carbon. The unusually small δ value suggests that this hydrogen is shielded significantly by the cyclopropyl ring and hence lies over that ring.[21]

Isolation of a lactone (**8**) when the solution from reaction of **6** and allylmagnesium chloride is carbonated rather than hydrolyzed also is consistent with a cis relationship in **7** between H_α and the hydroxymethyl group. Since no free hydroxy acid was noted, carbonation apparently resulted

(16) A comparable α,β-unsaturated ketone was obtained by hydrolysis of the *p*-toluenesulfonate ester of 3-(hydroxymethyl)-1,2-diphenylcyclopropene to furnish a cyclobutenol which underwent a facile thermal isomerization (Breslow, R.; Lockhart, J.; Small, A. *J. Am. Chem. Soc.* **1962**, *84*, 2793). There are other reports of rearrangements of (hydroxymethyl)cyclopropenes to cyclobutene derivatives: Vincens, M.; Vidal, M.; Arnaud, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *271*, 1190; Gensler, W. J.; Langone, J. J.; Floyd, M. B. *J. Am. Chem. Soc.* **1971**, *93*, 3828; Shleider, I. A.; Isaev, I. S.; Koptyug, V. A. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 1357; *Zh. Org. Khim.* **1972**, *8*, 1337.

(17) Effects of lanthanide shift reagents on spectra of other (hydroxylmethyl)cyclopropanes have been reported: Tomić, L.; Majereski, Z.; Tomić, M.; Sunko, D. E. *J. Chem. Soc., Chem. Commun.* **1971**, 719; Mariano, P. S.; McElroy, R. *Tetrahedron Lett.* **1972**, 5305; Crombie, L.; Findley, D. A. R.; Whiting, D. A. *Ibid.* **1972**, 4027; Campbell, R. V. M.; Crombie, L.; Findley, D. A. R.; King, R. W.; Pattenden, G.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 897.

(18) The stereochemical assignments are based on relative shifts within a given molecule rather than on the absolute values of the shifts per mole of added Eu(fod)$_3$. For that reason, we did not investigate further to determine if some significantly different absolute chemical shifts for structurally similar protons located in different molecules are indeed correct or are due to experimental error.

(19) Some of the chemical shifts in Figure 1 are extrapolated from those obtained in the presence of several concentrations of shift reagent and therefore are not precisely the same as those estimated from the conventional spectra that are recorded in the Experimental Section.

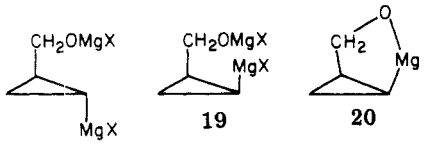
(20) This is apparent in the spectra of a number of *cis*- and *trans*-2-alkenes (with no substituents on the "crotyl" part): In "Selected Nuclear Magnetic Resonance Spectral Data, 40 MHz, 60 MHz, and 100 MHz Compilations, American Petroleum Institute Research Project 44"; Thermodynamics Research Center, Texas Engineering Experiment Station, Texas A&M University: College Station, TX, 1978.

(21) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; Chapter 2-2. The absorption at δ 2.95 is split too extensively to be due to one of the CH_2O hydrogens.

only in introduction of carbon dioxide cis to hydroxymethyl. Both carbonation[11,12,22] and protonation[5,11] of the cyclopropyl–Mg bond are expected to proceed with retention of configuration. Therefore, the observation that carbon dioxide is incorporated cis to hydroxymethyl indicates that H_α in 7 also is cis. Allyl must have the same stereochemistry in 8 as in 7. A cis relationship of allyl and the lactone ring is consistent with the effects of the lanthanide shift reagent on the ^1H NMR spectrum of 8.[23]

Conclusions. The results of this study show that in additions of allylic Grignard reagents to 3-(hydroxymethyl)cyclopropenes, the allyl group becomes attached to the side of the double bond nearest to the hydroxyl group. Similar conclusions were reached in our study[3] of additions of the allyl Grignard reagent to bicyclo[2.2.1]-heptenols and in a study recently reported by Eisch and his co-workers[24] of additions of the allyl Grignard reagent to some other substrates.

The group (H or CO_2H) that replaces magnesium is also found to be cis to hydroxymethyl. Therefore, magnesium and hydroxymethyl must have been cis when the reactions were quenched. Since cyclopropyl–Mg bonds do not ordinarily undergo cis–trans isomerization,[11,12] it is tempting to assume that hydroxymethyl and Mg also were cis immediately following addition. However, it is conceivable that the (metalated) hydroxymethyl group facilitates isomerization. Therefore, in the absence of a demonstration that a species of structure 18 would not isomerize readily to 19 (or 20), the stereochemistry of Mg is not definitely established.



18 19 20

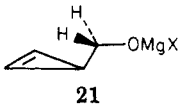
The positions of attachment were unexceptional when an unsymmetrical alkene function and unsymmetrical allylic groups were used. As is usually found in additions of Grignard reagents[4-6,8,10,25] and some other polar main-group organometallic compounds[26] to alkenes, addition to 11 resulted in attachment of magnesium to the less substituted double bond carbon. The predominant formation of the new bond at the γ-carbon of the crotyl and cinnamyl Grignard reagents is characteristic of other reactions of these Grignard reagents.[27-29]

Are the additions that we observed ones in which the hydroxyl group is directly involved? We think so. The side of the double bond nearest the hydroxyl group must be the most hindered. Preferential attachment of allylic groups to that face would seem unlikely unless the hydroxyl group in some manner directs the addition.

Since several Grignard reagents have been observed to add to cyclopropenes under mild conditions,[4-9] we had expected to observe addition of a variety of reagents to the (hydroxymethyl)cyclopropenes. Since the other reagents that we tried did not add, we do not know if the stereochemical results for allylic reagents are general.

Comparison with literature results suggests that a (metalated) 3-hydroxymethyl group may actually retard addition to a cyclopropene. One comparison involves reactions of two substrates that have one alkyl group attached to the cyclopropene double bond. Methylmagnesium iodide adds at 0 °C to 1,3,3-trimethylcyclopropene[4] but not at room temperature to 11. Of course, even a hydroxyl-assisted addition to a (hydroxymethyl)cyclopropene might be slower than addition to a comparable cyclopropene lacking a hydroxyl group. Evidence for a rate-retarding effect of a metalated hydroxyl group fixed in a location that precludes direct involvement in addition to the double bond was noted in the study with hydroxybicycloheptenes.[3] However, the rate-retarding factor may also be operative in substrates, such as the (hydroxymethyl)cyclopropenes, in which the hydroxyl group can be involved. The rate of the hydroxyl-assisted additions might be greater were it for a general rate-suppressing effect of a metalated hydroxyl group.

The geometry of the (hydroxymethyl)cyclopropenes must be far from optimal for involvement of hydroxyl in additions. At least in part, this could be due to a metalated (hydroxymethyl)cyclopropene being most stable in a conformation such as 21 in which OMgX is remote from the



21

cyclopropyl ring. Assumption of a geometry in which the metalated hydroxyl group is near the double bond would require an added input of energy not necessary in systems in which the hydroxyl group is permanently constrained to a position near the double bond.

Experimental Section

^1H 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. For determination of the effects on chemical shifts of added europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) [Eu(fod)$_3$] (Ventron Corp.), a weighed amount of a compound, purified by GC, was washed with CCl_4 into an NMR tube, which then was capped with a rubber septum. Small portions of a solution of known concentration of [Eu(fod)$_3$] in CCl_4 were added by using a syringe, and a spectrum was recorded after each addition. High-resolution mass spectra were obtained by using an AEI Model MS 902 spectrometer. Microanalyses were performed by Midwest Microlab, Ltd.

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, 20% SE-30 on Gas Chrom Q (80–100 mesh), 0.25 in. × 12 ft; B, 20% FFAP on Chromosorb W (60–80 mesh), 0.25 in. × 10 ft; C, Apiezon M on Gas Chrom P (60–80 mesh), 0.25 in. × 15 ft. Peak areas were determined by tracing the peaks on the chart paper with an electronic plotter and converting the resulting signal to digital values by using a computer program written by Hayden Clark of the Department of Chemistry at The Pennsylvania State University. To determine the yield of a compound in a reaction mixture by GC analysis, a weighed amount of 1-heptanol or 1-octanol was added as a standard to a weighed amount of the reaction mixture. The amount of a compound was determined from the area of its GC peak relative to the peak due to the

(22) Jensen, F. R.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1966**, *88*, 3437.
(23) The lanthanide shift reagent probably complexes to the carbonyl oxygen of 8: Hart, H.; Love, G. M. *Tetrahedron Lett.* **1971**, 625.
(24) Eisch, J. J.; Merkley, J. H.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 587.
(25) Lehmkuhl, H.; Reinehr, D.; Schomburg, G.; Henneberg, D.; Damen, H.; Schroth, G. *Justus Liebigs Ann. Chem.* **1975**, 103. Lehmkuhl, H.; Reinehr, D.; Henneberg, D.; Schomburg, G.; Schroth, G. *Ibid.* **1975**, 119. There are some apparent exceptions: Lehmkuhl, H.; Olbrysch, O.; Reinehr, D.; Schomburg, G.; Henneberg, D. *Ibid.* **1975**, 145; Lehmkuhl, H.; Bergstein, D.; Henneberg, D.; Janssen, E.; Olbrysch, O.; Reinehr, D.; Schomburg, G. *Ibid.* **1975**, 1176.
(26) Examples of organozinc compounds are in: Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1973**, *60*, 1.
(27) De Wolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 753.
(28) Benkeser, R. A. *Synthesis* **1971**, 347.
(29) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1.

standard by 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 somewhat underestimating the yields of most products in this work).

Substrates for Reactions with Grignard Reagents. 3-(Hydroxymethyl)-1,2-diethylcyclopropene (6). The reaction of 3-hexyne (49.2 g, 0.60 mol) and ethyl diazoacetate (22.8 g, 0.20 mol) followed the procedure used in the preparation of 11. Distillation yielded 3-(carboethoxy)-1,2-diethylcyclopropene: 12.4 g, (0.074 mol, 37%); bp 54 °C (0.3 torr) [lit.[30] bp 56 °C (1.3 torr)]; ^{1}H NMR (CCl_4) δ 1.17 (t, 6, J = 7 Hz, =CHCH$_2$CH$_3$), 1.22 (t, 3, J = 8 Hz, OCH$_2$CH$_3$), 1.98 (s, 1, CH), 2.48 (q, 4, J = 8 Hz, =CCH$_2$), 4.08 (q, 2, J = 8 Hz, OCH$_2$).

With a procedure[31] that has been used to reduce some other (carboethoxy)cyclopropenes, this ester was reduced to 6: 95% yield; ^{1}H NMR (CCl_4) δ 1.13 (t, 6, J = 7 Hz, CH$_3$), 1.52 (t, 1, J = 5 Hz, CH), 2.30 (q, 4, J = 7 Hz, =CCH$_2$), 2.67 (s, 1, OH), 3.38 (d, 2, J = 5 Hz, CH$_2$O) (this spectrum agrees with partial NMR data[32] that have been reported). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.97; H, 10.99.

3-(Hydroxymethyl)-1-propylcyclopropene (11). The reaction of 1-pentyne (170 mL, 1.72 mol) and ethyl diazoacetate (34.7 g, 0.30 mol) followed a procedure[33] used for an analogous reaction of 4-octyne. The solution was placed in a photochemical reaction vessel (Ace Glass 6523-03) containing a magnetic stirring bar and fitted with a thermometer and a water-cooled condenser connected to a liquid nitrogen cooled cold trap which in turn was connected to a nitrogen system which maintained the vessel under a slight positive pressure of nitrogen. The quartz immersion well (Ace Glass 6515-25) contained a quartz high-pressure mercury-vapor lamp (Hanovia 679A-36) attached to a power supply (Ace Glass 6515-50). The solution was irradiated until the IR absorption of ethyl diazoacetate at 2130 cm^{-1} was no longer evident (22 h). After removal of most of the unreacted alkyne by distillation at atmospheric pressure, the residue was distilled through a 6-in. Vigreux column. GC analysis (column B, 150 °C) of the only fraction [14.1 g; bp 35–39 °C (0.5 torr)] gave five significant peaks (relative retention times 0.59, 1.00, 1.68, 2.22, and 2.76). The peak assigned a retention time of 1.00 had 70% of the total area of all GC peaks. The ^{1}H NMR spectrum showed the compound responsible for this peak to be 3-(carboethoxy)-1-propylcyclopropene. On the assumption that some of the other peaks could be due to insertion products[30,33] and hence might be terminal alkynes, a portion (12.0 g) of the product was shaken with two 110-mL aliquots of a 0.46 M aqueous silver nitrate solution. The organic layer then was dried (Na_2SO_4). Removal of solvent at atmospheric pressure followed by distillation through a 6-in. Vigreux column gave one fraction (9.1 g, 0.059 mol, 23%) of 3-(carboethoxy)-1-propylcyclopropene shown by GC analysis to be more than 90% pure: bp 35–39 °C (0.5 torr) [lit.[30] bp 43–44 °C (0.6 torr)]; ^{1}H NMR (CCl_4) δ 1.12 (t, 3, J = 7 Hz, CH$_2$CH$_2$CH$_3$), 1.23 (t, 3, J = 7 Hz, OCH$_2$CH$_3$), 1.65 (m, 2, CH$_2$CH$_2$CH$_3$), 2.02 (d, 1, J = 1.5 Hz, CH), 2.48 (t, 2, J = 7 Hz, CH$_2$CH$_2$CH$_3$), 4.05 (q, 2, J = 7 Hz, CH$_2$O), 6.03 (m, 1, resembles a q with J = 1.5 Hz, =CH) (this spectrum agrees with partial NMR data[32] that have been reported).

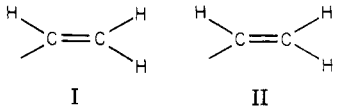
The ester was reduced to 11 by the procedure used to prepare 6. After removal of the solvent, distillation afforded only one fraction (34%) which was shown to be 11: bp 45 °C (0.45 torr); ^{1}H NMR (CCl_4) δ 0.98 (t, 3, J = 7 Hz, CH$_3$), 1.60 (m, 2, CH$_2$CH$_3$), 1.63 (dt, 1, J = 1.5, 4.5 Hz, CH), 2.47 (t, 2, J = 7 Hz, CH$_2$CH$_2$CH$_3$), 3.35 (s, 1, OH), 3.40 (d, 2, J = 4.5 Hz, CH$_2$O), 6.63 (m, 1, =CH).

3-(Hydroxymethyl)-1,2-dimethylcyclopropene (14). The reaction of 2-butyne (140 g, 2.6 mol) and ethyl diazoacetate (36.5 g, 0.32 mol) followed the procedure used in the preparation of 11. Distillation yielded only one fraction that was essentially pure 3-(carboethoxy)-1,2-dimethylcyclopropene: 11.0 g (0.078 mol, 25%); bp 34–38 °C (0.5 torr) [lit.[30] bp 47 °C (3.5 torr)]; ^{1}H NMR (CCl_4) δ 1.25 (t, 3, J = 7 Hz, CH$_2$CH$_3$), 1.93 (s, 1, CH), 2.08 (s, 6, =CCH$_3$), 4.15 (q, 2, J = 7 Hz, CH$_2$) (this spectrum agrees with partial NMR data[30] that have been reported).

With the procedure used to prepare 6, the ester was reduced to 14: 92% yield; bp 42–50 °C (2.5 torr); ^{1}H NMR (CCl_4) δ 1.53 (t, 1, J = 4 Hz, CH), 2.00 (s, 6, CH$_3$), 3.00 (s, 1, OH), 3.38 (d, 2, J = 4 Hz, CH$_2$O) (this spectrum agrees with partial NMR data[34] that have been reported).

Procedure for Reactions with Grignard Reagents. 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 press-equalizing addition funnel, and a rubber septum. Glassware was stored at 115 °C prior to assembly; after assembly (and addition of magnesium if the Grignard reagent was to be prepared in situ), the apparatus was heated gently with a Bunsen burner while nitrogen flowed rapidly through it. During the course of a reaction, a slight positive pressure of nitrogen was maintained in the closed reaction system. Grignard reagents were prepared by slow, dropwise addition of a solution of alkyl halide to magnesium turnings (Ventron Corp. or J. T. Baker Chemical Co.) in the ice-cooled reaction flask. Diethyl ether and tetrahydrofuran (THF) used as solvents were stored over sodium. The concentration of each Grignard reagent solution was determined by hydrolysis followed by titration with a standard hydrochloric acid solution. A solution of the alcohol was added to the ice-cooled solution of Grignard reagent. After 4 h, the ice bath was removed and the reaction mixture left standing overnight. Reaction mixtures were quenched by being poured into ice–water. The organic layer was separated and the aqueous layer extracted twice with 50-mL portions of ether. The organic extracts were dried (Na_2SO_4 or $MgSO_4$), and most of the solvent was removed by distillation at atmospheric pressure. The residue was 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 cooled in liquid nitrogen and inserted into the exit port of the gas chromatograph.

Reactions of 3-(Hydroxymethyl)-1,2-diethylcyclopropene (6) with Grignard Reagents. (a) With Allylmagnesium Chloride. Isolation of 7. The alcohol (1.00 g, 7.9 mmol) in diethyl ether (20 mL) was added to a solution of the Grignard reagent (23 mmol, 0.32 M) that had been prepared by addition of allyl chloride (3.1 g, 41 mmol) in diethyl ether (30 mL) to magnesium (1.00 g, 41 mmol) in diethyl ether (40 mL). GC analysis (column B, 185 °C) of the residue remaining after workup showed the only significant component (except for residual solvent) to be 7: 0.72 g (4.3 mmol, 54%); ^{1}H NMR (CCl_4) δ 0.2–0.8 (c, 2, CH), 1.00 (c, 6, CH$_3$), 1.1–1.7 (c, 4, CH$_2$CH$_3$), 2.05 (m, 2, =CHCH$_2$), 2.40 (s, 1, OH), 3.58 (c, 2, CH$_2$O), 4.87 (m, 1, I), 5.15 (m, 1, II), 5.5–6.2 (m, 1, =CH). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.26; H, 11.88.



I II

(b) With Allylmagnesium Chloride Followed by Carbonation. Isolation of Lactone 8. The procedure was similar to the preceding reaction except that (a) after being allowed to stand overnight, the reaction flask was placed in an ice bath, and carbon dioxide was passed through the flask for 2 h, and (b) after addition to ice–water, the reaction mixture was acidified with dilute hydrochloric acid before extraction. GC analysis (column A, 210 °C) showed the presence only of solvent and of 8: 0.91 g (4.7 mmol, 59%); ^{1}H NMR (CCl_4) δ 0.95 (t, 3, J = 6 Hz, CH$_2$CCH$_2$CH$_3$), 0.98 (t, 3, J = 6 Hz, COCCH$_2$CH$_3$), 1.23 (q, 2, J = 6 Hz, CH$_2$CCH$_2$CH$_3$), 1.47 (m, 1, CH), 1.77 (q, 2, J = 6 Hz, COCCH$_2$), 2.08 (d, 2, J = 7 Hz, =CHCH$_2$), 4.12 (m, 2, CH$_2$O), 4.90 (m, 1, I), 5.12 (m, 1, II), 5.72 (m, 1, =CH); IR (CCl_4) 1675 cm^{-1} (C=O); mass spectrum, m/z 194.1322 (M$^+$, calcd for $C_{12}H_{18}O_2$ 194.1306).

(c) With Vinylmagnesium Bromide. Isolation of 10. The alcohol (1.00 g, 7.9 mmol) in diethyl ether (5 mL) was added to

(30) Vidal, M.; Vincens, M.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1972**, 657.
(31) Vidal, M.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1972**, 675.
(32) Vidal, M.; Pierre, J.-L.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1969**, 2864.
(33) Lind, H.; Deutschmann, A. J., Jr. *J. Org. Chem.* **1967**, *32*, 326.
(34) Pierre, J. L.; Vincens, M.; Vidal, M. *Bull. Soc. Chim. Fr.* **1971**, 1775.

a solution of the Grignard reagent prepared from vinyl bromide (5.35 g, 50 mmol) and magnesium (1.20 g, 50 mmol) in THF (20 mL). GC analysis (column C, 175 °C) of the residue remaining after the workup showed the presence only of solvent and of **6**.

GC analysis (column C, 175 °C) of the residue from a similar reaction using commercial (Ventron Corp.) vinylmagnesium bromide (50 mL, 1.01 M, 50 mmol) gave a product tentatively identified as 1,2-diethyl-3-(hydroxymethyl)cyclopropane (**10**): 39% yield; ^{1}H NMR (CCl_4) δ 0.2–0.8 (c, 3, CH), 0.8–1.8 (c, 10, CH_2CH_3), 3.00 (s, 1, OH), 3.32 (d, 2, J = 6 Hz, CH_2O).

Repetition of the reactions with freshly prepared and with commercial Grignard reagents gave the same results as before.

(d) With Other Grignard Reagents. Reactions of **6** similar to that with allylmagnesium chloride were carried out with three other Grignard reagents. The ^{1}H NMR spectra (CCl_4) of the residues after workup of the reactions with phenylmagnesium bromide, *tert*-butylmagnesium chloride, and methylmagnesium iodide showed no evidence for addition products and indicated the presence of **6** (84%, 70%, and 80%, respectively).

Conversion of Addition Product 7 to Cyclic Ether 9. The reaction was patterned after a procedure that has been used with another compound.[35] Mercuric acetate (0.38 g, 1.19 mmol) was added to a solution of **7** (0.20 g, 1.19 mmol), THF (1 mL), and water (1 mL), and the reaction was stirred at ambient temperature for 25 min. Then a solution of sodium borohydride (0.95 g, 2.5 mmol) and sodium hydroxide (0.10 g, 2.5 mmol) in water (5 mL) was added slowly. The reaction was extracted with three 5-mL portions of diethyl ether, and the extracts were dried ($MgSO_4$). After removal of most of the solvent, GC analysis (column A, 185 °C) of the residue showed the presence only of solvent and of one other component, identified as **9**: 0.10 g (0.60 mmol, 50%); ^{1}H NMR (CCl_4) δ 0.17 (m, 1, CH_3CH_2CH), 0.57 (m, 1, OCH_2CH), 0.8–1.3 (c, 9, CH_3), 1.3–1.9 (c, 6, CH_2CH_3 and CCH_2CH), 2.95 (m, 1, CHO, the extensive splitting of this absorption precludes its being due to one of the CH_2O H's), 3.74 (c, 2, CH_2O); mass spectrum, m/z 168.1526 (M^+, calcd for $C_{11}H_{20}O$ 168.1514).

Reactions of 3-(Hydroxymethyl)-1-propylcyclopropene (11) with Grignard Reagents. (a) With Allylmagnesium Chloride. Isolation of 12. The alcohol (0.50 g, 4.5 mmol) in diethyl ether was added to a solution of the Grignard reagent (22 mmol, 0.55 M) that had been prepared by addition of allyl chloride (7.6 g, 100 mmol) in diethyl ether (20 mL) to magnesium (2.4 g, 100 mmol) in diethyl ether (20 mL). GC analysis (column A, 185 °C) of the residue remaining after the workup indicated the presence only of solvent, **11**, and one new component, shown to be **12**: 0.44 g (2.9 mmol, 64%); ^{1}H NMR (CCl_4) δ 0.0–0.7 (c, 3, CH), 0.87 (t, 3, J = 6 Hz, CH_3), 1.25 (c, 4, CH_2CH_2), 2.10 (d, 2, J = 6 Hz, $=CCH_2$), 3.13 (s, 1, OH), 3.50 (d, 2, J = 7 Hz, CH_2O), 4.88 (m, 1, I), 5.07 (m, 1, II), 5.87 (m, 1, =CH). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.66; H, 11.86.

(b) With Other Grignard Reagents. Reactions of **11** similar to that with allylmagnesium chloride were carried out with three other Grignard reagents. The ^{1}H NMR spectrum of the residue after workup of a reaction with benzylmagnesium chloride showed absorptions due to unknown components but no absorptions due to **11** and none expected for an addition product. The spectrum of the residue from a reaction with *tert*-butylmagnesium chloride showed no evidence for an addition product but indicated an 89% recovery of **11**. The ^{1}H NMR spectrum and GC analysis (column A, 150 °C, and several other columns) of the residue from a reaction with methylmagnesium iodide showed it to be mainly **11**, though some new components were present in small amounts.

Reactions of 3-(Hydroxymethyl)-1,2-dimethylcyclopropene (14) with Organometallic Compounds. (a) With Crotylmagnesium Chloride. Isolation of 15a and 16a. The alcohol (1.00 g, 10.2 mmol) in diethyl ether (20 mL) was added to a solution of the Grignard reagent (88 mmol, 0.59 M) that had been prepared by addition of crotyl chloride (9.0 g, 100 mmol) in diethyl ether (110 mL) to magnesium (7.2 g, 300 mmol) in diethyl ether (40 mL). GC analysis (column A, 200 °C) of the residue remaining after workup revealed the presence, in addition to solvent, of some **14** and of two new components (relative retention times 0.88 and 1.00).

The first component was identified as **15a**: 0.62 g (4.0 mmol, 40%); ^{1}H NMR (CCl_4) δ 0.3–0.8 (c, 2, cyclopropyl H's), 0.92 (s, 3, CCH_3), 1.07 (d, 3, J = 7 Hz, $=CHCHCH_3$), 1.13 (d, 3, J = 5 Hz, $CHCHCH_3$), 1.73 (q, 1, J = 7 Hz, CHCH=), 1.87 (s, 1, OH), 3.57 (d, 2, J = 7 Hz, CH_2O), 4.87 (m, 1, I), 5.10 (m, 1, II), 6.00 (m, 1, =CH). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.67; H, 11.96.

The second component was identified as **16a**: 0.10 g (0.65 mmol, 6%); ^{1}H NMR (CCl_4) δ 0.3–0.7 (c, 2, CH), 1.00 (s, 3, CCH_3), 1.08 (d, 3, J = 7 Hz, $CHCH_3$), 1.58 (d, 3, J = 5 Hz, $=CHCH_3$), 2.02 (d, 2, J = 5 Hz, $=CHCH_2$), 2.60 (s, 1, OH), 3.50 (c, 2, CH_2O), 5.43 (c, 2, =CH). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.62; H, 11.78.

(b) With Cinnamylmagnesium Chloride. Isolation of 15b. Freshly distilled cinnamyl chloride (7.63 g, 50 mmol) was added at ambient temperature to magnesium (1.22 g, 50 mmol) in diethyl ether (10 mL) until the reaction mixture turned cloudy. Then more diethyl ether (100 mL) was added directly to the reaction vessel which was cooled in an ice bath for the remainder of the addition. The alcohol (1.00 g, 10.2 mmol) was added to the resulting Grignard reagent solution (26 mmol, 0.16 M). GC analysis (column A, 220 °C) indicated the presence in addition to solvent of four components (relative retention times 0.13, 0.16, 1.00, and 2.28). By their ^{1}H NMR spectra (CCl_4), the first two components were identified as 3-phenyl-1-propene and 1-phenyl-1-propene (hydrolysis products of the Grignard reagent) and the last as 1,4-diphenyl-1,5-hexadiene[36] (presumably from coupling during the preparation of the Grignard reagent). The third component was shown to be **15b**: 1.05 g (4.9 mmol, 48%); ^{1}H NMR (CCl_4) δ 0.4–1.2 (c, 2, cyclopropyl H's), 0.90 (s, 3, CCH_3), 0.97 (d, 3, J = 8 Hz, $CHCH_3$), 2.03 (s, 1, OH), 3.10 (d, 1, J = 8 Hz, PhCH), 3.68 (d, 2, J = 7 Hz, CH_2O), 5.10 (m, 1, I), 5.33 (m, 1, II), 6.30 (m, 1, =CH), 7.28 (s, 5, Ph). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.33; H, 9.09.

(c) With Other Grignard Reagents. Reactions of **14** similar to those with allylic Grignard reagents were carried out with three other Grignard reagents. The ^{1}H NMR spectra (CCl_4) of the residues after workup of the reactions with benzylmagnesium chloride, *tert*-butylmagnesium chloride, and cyclopropylmagnesium chloride showed no evidence for addition products and indicated the presence of **14** (23%, 100%, and 100%, respectively).

(d) With Allylzinc Bromide. Allylzinc bromide was prepared by addition of allyl bromide (24.2 g, 200 mmol) in THF (50 mL) to powdered zinc (15.6 g, 240 mmol) in THF (90 mL). ^{1}H NMR analysis of the solution showed the presence only of THF and allylzinc bromide.[37] Half of this solution was transferred to another reaction vessel. A solution of the alcohol (1.00 g, 10.2 mmol) in diethyl ether (4 mL) was added to each portion of the allylzinc bromide solution, one portion cooled in an ice bath and the other in a dry ice bath. Each solution was cooled for 10 h and then hydrolyzed and worked up as were the Grignard reagent reactions. The ^{1}H NMR spectrum and GC analysis (column A, 140 °C) of the residue from hydrolysis of the reaction that had been cooled in ice showed it to be a complex mixture but not to contain **14** or a simple addition product. The residue from the reaction cooled in dry ice contained one major product indicated by its ^{1}H NMR and IR spectra[38] to be 3-methyl-3-penten-2-one (0.43 g, 4.4 mmol, 43%).

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers and the high-resolution mass spectrometer that were used. We thank Dr. Robert D. Minard for obtaining the mass spectra.

Registry No. **6**, 65016-07-1; **7**, 75299-25-1; **8**, 75311-35-2; **9**,

(35) Bindra, J. S.; Grodski, A.; Schaaf, T. K.; Corey, E. J. *J. Am. Chem. Soc.* **1973**, *95*, 7522.

(36) Koch, H. P. *J. Chem. Soc.* **1948**, 1111.

(37) Similar to the spectrum of diallylzinc in benzene: Thiele, K.-H.; Zdunneck, P. *J. Organomet. Chem.* **1965**, *4*, 10.

(38) Hasbrouck, R. W.; Kiessling, A. D. A. *J. Org. Chem.* **1973**, *38*, 2103.

75299-26-2; **10**, 75299-27-3; **11**, 75299-28-4; **12**, 75299-29-5; **14**, 33283-69-1; **15a**, 75299-30-8; **15b**, 75299-31-9; **16a**, 75299-32-0; **17**, 565-62-8; 3-hexyne, 928-49-4; ethyl diazoacetate, 623-73-4; 3-(carboethoxy)-1,2-diethylcyclopropene, 35920-11-7; 1-pentyne, 627-19-0; 3-(carboethoxy)-1-propylcyclopropene, 26347-06-8; 2-butyne, 503-17-3; 3-(carboethoxy)-1,2-dimethylcyclopropene, 5783-75-5; allyl chloride, 107-05-1; vinyl bromide, 593-60-2; crotyl chloride, 591-97-9; cinnamyl chloride, 2687-12-9.

Addition of *n*-Butyllithium to Hydroxybicyclo[2.2.1]hept-2-enes[1]

Herman G. Richey, Jr.,* Cletus W. Wilkins, Jr., and Rouvain M. Bension

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

Received April 23, 1980

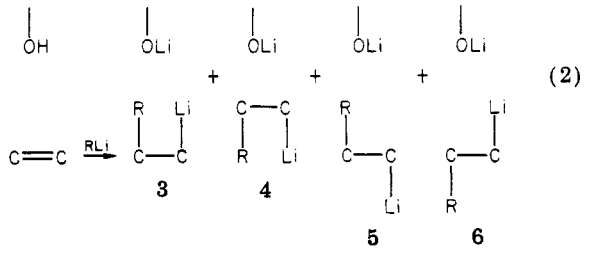
n-Butyllithium adds to the double bonds of bicyclo[2.2.1]hept-2-ene (**7**), *endo*-bicyclo[2.2.1]hept-5-en-2-ol (**9**), *exo*-bicyclo[2.2.1]hept-5-en-2-ol (**12**), *syn*-bicyclo[2.2.1]hept-2-en-7-ol (**14**), and *anti*-bicyclo[2.2.1]hept-2-en-7-ol (**18**). The *n*-butyl group was shown to be attached at an exo position and in the additions to **9** and **12** to be at C-5 rather than C-6. Competition experiments suggest that addition to **9** is somewhat faster than to **7** but that additions to **14** and **18** are slower. The role of a metalated hydroxyl group in assisting these reactions is considered. No addition products were obtained from reactions at ambient temperature of *n*-butyllithium with 3-(hydroxymethyl)-1,2-diethylcyclopropene (**20**), 3-(hydroxymethyl)-1,2-dimethylcyclopropene (**23**), or 3-(hydroxymethyl)-1-propylcyclopropene (**24**), but some 1-(hydroxymethyl)-2-ethylidene-3-deuterio-3-ethylcyclopropane (**21**) was obtained from a reaction with **20** at dry ice temperature followed by quenching with D_2O.

Crandall[4] and Felkin[5] and their co-workers were the first to report that organolithium compounds (in excess) add to allyl alcohol (**1** → **2**) and some other allylic alcohols. In

$$\underset{\mathbf{1}}{CH_2{=}CHCH_2OH} \xrightarrow[2.\ H_2O]{1.\ RLi} \underset{\mathbf{2}}{CH_3C(R)HCH_2OH} \quad (1)$$

these reactions the hydroxyl group certainly reacts immediately with 1 equiv of the organolithium compound. Since organolithium compounds do not add as readily to comparable hydrocarbons lacking a hydroxyl group,[6] the metalated hydroxyl group that results must facilitate addition. Additions to other allylic alcohols[7,8] and propargylic alcohols[9,10] have since been noted. Moreover, tertiary amino,[11,12] alkoxyl,[12-16] and alkylthio[12] groups have also been found to facilitate addition to allylic or homallylic alkene functions and to propargylic alkyne functions.

We hoped that an understanding of the role played by a hydroxyl group in assisting additions to alkenes would be advanced by defining the stereochemical relationship at the time of addition between four critical groups: the alkene function, R and Li from the organolithium compound, and the metalated hydroxyl group. Do R and Li add in a syn or anti fashion? What is their relationship to the metalated hydroxyl group? Possible configurations of the resulting addition products are shown schematically in **3**-**6** (eq 2). The problem is similar to that of the addition of organomagnesium compounds to alkenols that we have discussed recently.[17,18]



In this paper, we describe reactions of organolithium compounds with 2- and 7-hydroxybicyclo[2.2.1]hept-2-enes and with 3-(hydroxymethyl)cyclopropenes. The possible advantages of these substrates, the same chosen for our studies with organomagnesium compounds, have already been considered.[17,18]

Results

It was important in this study to be able to add the same organolithium compound to both **9** and **14**, a pair of hydroxyl-substituted bicyclo[2.2.1]hept-2-enes in which the

(1) Much of this work is taken from ref 2 and 3.
(2) Wilkins, C. W., Jr. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1976.
(3) Bension, R. M. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1978.
(4) Crandall, J. K.; Clark, A. C. *Tetrahedron Lett.* **1969**, 325. Crandall, J. K.; Clark, A. C. *J. Org. Chem.* **1972**, *37*, 4236.
(5) Felkin, H.; Swierczewski, G.; Tambuté, A. *Tetrahedron Lett.* **1969**, 707.
(6) For a summary, see: Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; Chapter 7.
(7) Dimmel, D. R.; Huang, S. *J. Org. Chem.* **1973**, *38*, 2756.
(8) Dimmel, D. R.; O'Malley, J. P. *J. Org. Chem.* **1975**, *40*, 132.
(9) Von Rein, F. W. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1972.
(10) Olsson, L.-I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1976**, *30*, 521.
(11) Richey, H. G., Jr.; Erickson, W. F.; Heyn, A. S. *Tetrahedron Lett.* **1971**, 2187.
(12) Veefkind, A. H.; Schaaf, J. V. D.; Bickelhaupt, F.; Klumpp, G. W. *J. Chem. Soc. D* **1971**, 722.
(13) Wittig, G.; Otten, J. *Tetrahedron Lett.* **1963**, 601.
(14) Klumpp, G. W.; Veefkind, A. H.; de Graaf, W. L.; Bickelhaupt, F. *Justus Liebigs Ann. Chem.* **1967**, *706*, 47.
(15) Veefkind, A. H.; Bickelhaupt, F.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1058.
(16) Kool, M.; Klumpp, G. W. *Tetrahedron Lett.* **1978**, 1873.
(17) Richey, H. G., Jr.; Wilkins, C. W., Jr. *J. Org. Chem.*, companion paper in this issue.
(18) Richey, H. G., Jr.; Bension, R. M. *J. Org. Chem.*, previous paper in this issue.

0022-3263/80/1945-5042$01.00/0