Stereochemical Factors in the Carbomagnesiation of Unsaturated Alcohols[1]

John J. Eisch,* [2] Joseph H. Merkley, and James E. Galle

Departments of Chemistry, The Catholic University of America, Washington, D.C. 20017, and The State University of New York at Binghamton, Binghamton, New York 13901

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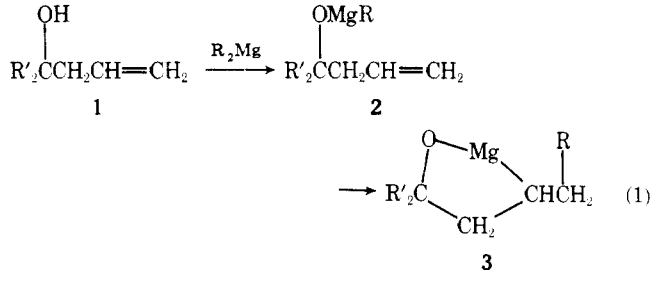
In order to ascertain the stereochemical course of carbomagnesiating unsaturated alcohols, allylmagnesium bromide in ether was allowed to react, in turn, with 2-cyclopentenol, 3-cyclopentenol, 1-(1-propynyl)cyclohexanol, 1-(2-butynyl)cyclohexanol, and (2-cyclohexenyl)diphenylcarbinol. 2-Cyclopentenol and 1-(1-propynyl)cyclohexanol underwent substitutive allylation to yield, respectively, allylcyclopentenes and (2-allyl-2-methylvinylidene)cyclohexane. 3-Cyclopentenol gave an 80:20 mixture of *cis*- and *trans*-3-allylcyclopentanol and some 3-(5-hexenyl)cyclopentanol and its dehydration product. In contrast, diallylmagnesium gave only *cis*-3-allylcyclopentanol and the hexenyl derivatives. 1-(2-Butynyl)cyclohexanol gave only 1-[(*E*)-3-methyl-2,5-hexadienyl]cyclohexanol, the product of cis carbomagnesiation; (2-cyclohexenyl)diphenylcarbinol gave the carbomagnesiated product, which had formed by syn addition to the olefinic bond from the side cis with respect to the hydroxydiphenylmethyl group. This last stereochemical relationship was shown by an NMR analysis on the lactone and the *tert*-butoxy derivatives formed from the Grignard adduct. In light of these findings, the fostering and orientating effect of the hydroxyl group on carbomagnesiation is ascribed to the formation and intramolecular rearrangement of an allylmagnesium alkoxide. The proximity of the allyl–magnesium bond to the carbon–carbon π bond brings about an electrophilic attack by the magnesium center and a net syn addition.

The ease with which various organomagnesium reagents add to the olefinic linkage of alkenols (in the form of their magnesium salts) has been the subject of a recent structural and mechanistic study.[1] An analysis of this facile carbomagnesiation in terms of substrate, magnesium reagent, and medium led to the suggestion that the reaction occurs via the intramolecular rearrangement of an (alkenoxy)alkylmagnesium (**2**), which in turn arises from the alcoholysis (**1**) of any R_2Mg component in the Grignard reagent (eq 1). Further-

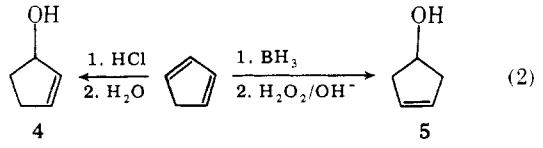


more, the regiospecificity of the carbon–magnesium bond addition (**2** → **3**) and the solvent effects indicate an electrophilic attack by the magnesium on the proximate carbon–carbon π bond.

In order to test such an electrophilic mechanistic hypothesis, the stereochemical course of these carbomagnesiations required scrutiny. Preliminary findings from the action of allylmagnesium bromide on alkynols[3] and on hydroxyl-bearing bicyclo[2.2.1]hept-2-ene derivatives[4] did support the conclusion that carbomagnesiation occurred syn to the carbon–carbon unsaturation and, in the bicycloheptene system, cis with respect to the appended hydroxyl group.[4] But to gain assurance that such a stereochemical outcome was not limited to such strained unsaturated systems, an examination of the response of a series of alkenols to carbomagnesiation has now been undertaken. Alkenols of the cyclopentenyl and cyclohexenyl systems proved to be most informative of the stereochemical course.

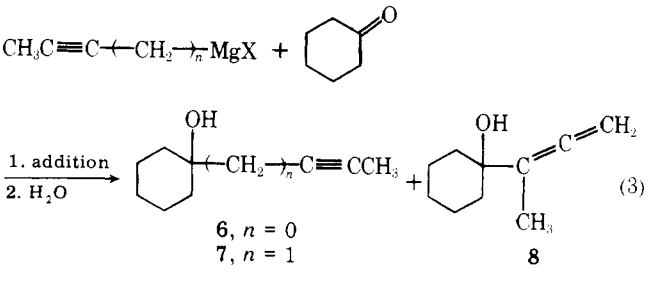
Results

Preparation of the Unsaturated Alcohols. 2-Cyclopentenol (**4**) and 3-cyclopentenol (**5**) were prepared from 1,3-cyclopentadiene by a hydrochlorination–hydrolysis sequence or a hydroboration–oxidation sequence, respectively



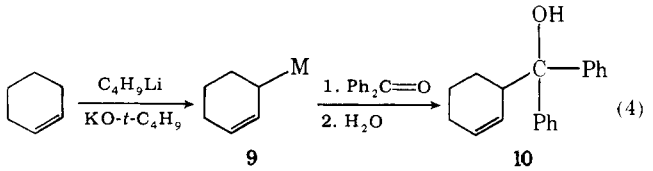
(eq 2). These cycloalkenols possessed the advantage of an endocyclic double bond responsive to electrophilic additions,[5] but a disadvantage lay in their secondary alcoholic character. As will be seen, however, magnesium salts of such alcohols are prone to epimerizations.

The 1-(1-propynyl)- and the 1-(2-butynyl)cyclohexanols (**6** and **7**) were readily accessible through the addition of the appropriate alkynylmagnesium reagent to cyclohexanone. In the preparation of **7**, the allenic isomer, 1-(1,2-butadien-3-yl)cyclohexanol (**8**), was also formed and had to be separated (eq 3). These alkynols were designed to reveal the stereo-



chemistry for the carbomagnesiation of propargylic or homopropargylic alcohols.

Finally, the synthesis of (2-cyclohexenyl)diphenylcarbinol (**10**) was achieved by the metalation of cyclohexene with a combination of butyllithium and potassium *tert*-butoxide to yield **9** and the reaction of **9** with benzophenone (eq 4). Being a tertiary carbinol, **9** lacked the drawbacks of **4** and **5**, since



hydride transfers could not intrude. Although the cyclohexene ring was less reactive to electrophilic addition than the cyclopentene ring,[5] dehydration of **10** under the reaction con-

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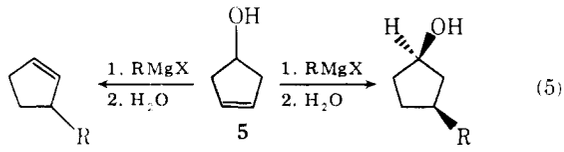
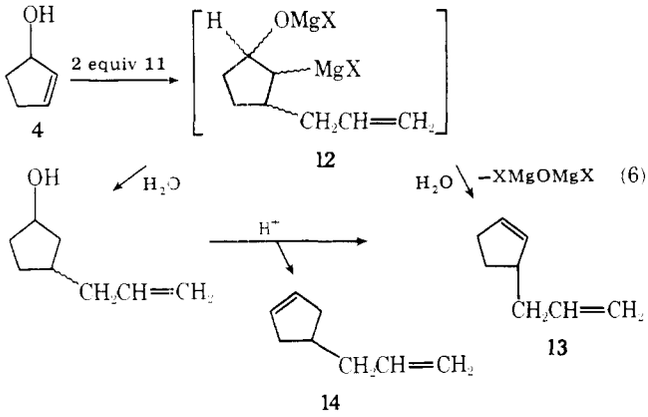
ditions for carbomagnesiation was also less serious, compared with the ready dehydration tendency of **4** and **5**. Naturally, any such dehydration would destroy the stereochemical reference point for the carbomagnesiation reaction (eq 5).



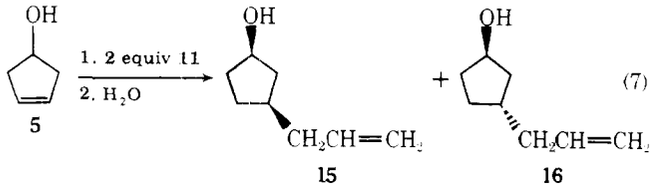
(5)

Reactions with Allylmagnesium Bromide (11). Cyclopentenols. 2-Cyclopentenol (**4**) proved unreactive toward **11**, even after prolonged heating in ether or in benzene. Finally, after 7 days in refluxing toluene over half of **4** was allylated, but then dehydration was complete (cf. eq 5). Due to the tendency of **4** itself and intermediates, such as **12**, to dehydrate and polymerize in the presence of Lewis acids,[6] an unstable mixture of hydrocarbons was isolated. Although not isolated in a highly pure state, the major products appeared to be positional isomers of allylcyclopentene (**13** and **14**, eq 6).



(6)

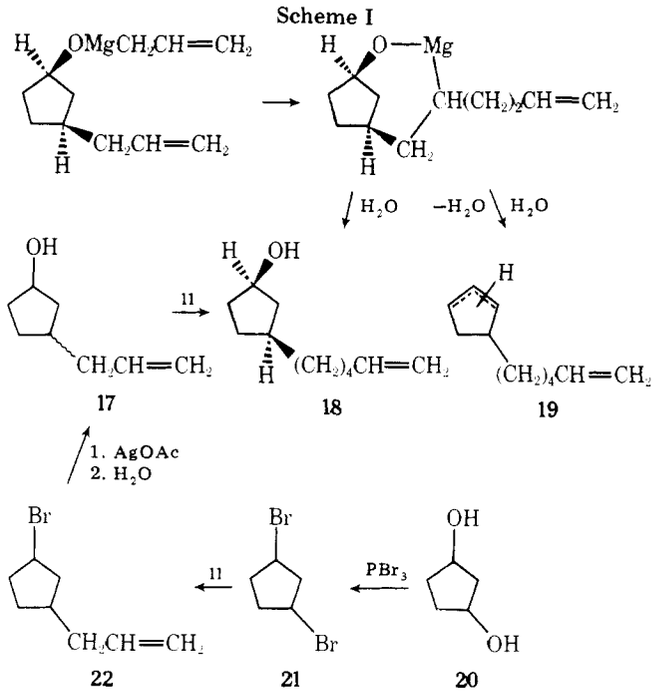
3-Cyclopentenol (**5**) reacted with **11** under less stringent conditions, and hence the allylated cyclopentanol could be isolated. Heating **5** and **11** for 2 days in benzene gave about 30% of allylcyclopentanols and ca. 10% of diallylated cyclopentenes and cyclopentanols. By fractional distillation the allylcyclopentanols were separated into a major product, *cis*-3-allylcyclopentanol (**15**, ca. 80%), and a minor product, *trans*-3-allylcyclopentanol (**16**, 20%). These stereochemistry assignments are based upon NMR correlations developed by others. Thus, the proton on the carbon of secondary alcohols (**CHOH**) in 2-phenylcyclohexanols occurs at a higher magnetic field in the trans isomer than that in the cis isomer;[7] likewise, a similar relationship is observed in the methylcyclohexanols.[8] In the present situation the 3-allylcyclopentanol termed the cis isomer (**15**) has its **CHOH** signal at δ 4.20 and the trans isomer (**16**) at δ 3.50 (eq 7). From spectral data it is concluded



(7)

that the higher boiling products are actually the (5-hexenyl)-cyclopentanol **18** and -cyclopentenes **19**, assumed to arise from an allylmagnesium salt of **15** (Scheme I). Support for this assumption was gained by observing that a synthetic sample of a cis,trans mixture of 3-allylcyclopentanols (**17**) did react with allylmagnesium bromide (**11**) to yield some **18** and **19**, although not efficiently. (Cf. infra for the reaction of **5** with diallylmagnesium.)

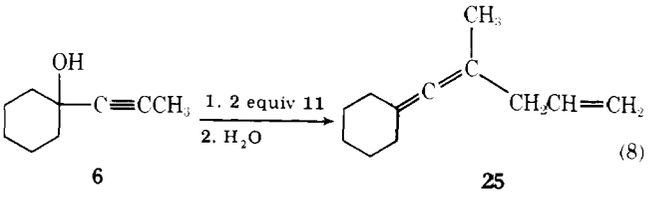
Scheme I



Finally, in Scheme I is depicted the synthetic route by which an authentic sample of **17** was synthesized, in order to remove any doubt about the skeletal structure of **15** and **16**. The synthetic sequence is reasonably satisfactory except for the conversion of **22** into **17**, where traces of the acetate were difficult to remove.

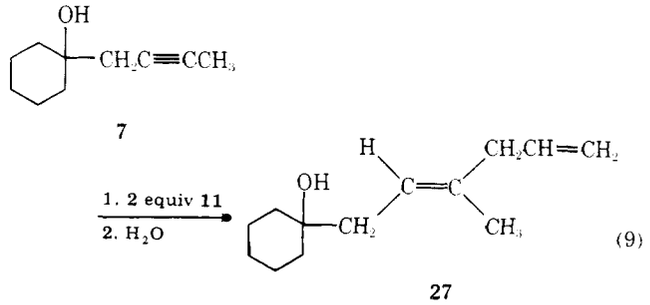
The reaction of 3-cyclopentenol (**5**) with diallylmagnesium (**23**) in refluxing benzene proceeded slowly but cleanly to yield only the *cis*-3-allylcyclopentanol (**15**) and no trans isomer. In addition, the 3-(5-hexenyl)cyclopentanol (**18**) and -cyclopentenes (**19**) were again found in the higher boiling fractions (cf. Scheme I).

1-Alkynylcyclohexanols. 1-(1-Propynyl)cyclohexanol (**6**) reacted with the Grignard reagent **11** in refluxing toluene to give 80% of (2-allyl-2-methylvinylidene)cyclohexane (**25**). The reaction could be made to proceed satisfactorily in refluxing ether by adding a catalytic amount of nickel(II) acetylacetonate,[1] but even under these milder conditions no intermediate alcohol could be detected (eq 8).



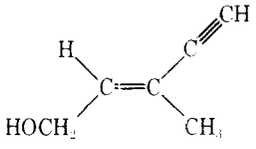
(8)

The 1-(2-butynyl)cyclohexanol substrate (**7**) proved more reactive, for refluxing in ether with **11** gave a good yield of 1-[(*E*)-3-methyl-2,5-hexadienyl]cyclohexanol (**27**), the product of a cis carbomagnesiation (eq 9). The stereochemical



(9)

assignment of **27** rests upon the 0.8-Hz splitting of the methyl group by the vinyl proton near the hydroxyl group. Others have shown that for the isomeric 3-methyl-2-penten-4-yn-1-ols the *E* isomer (**28**) has a methyl–vinyl coupling of 1.0 Hz, while the *Z* isomer (**29**) has a coupling of 1.5 Hz.[9]



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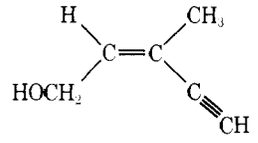
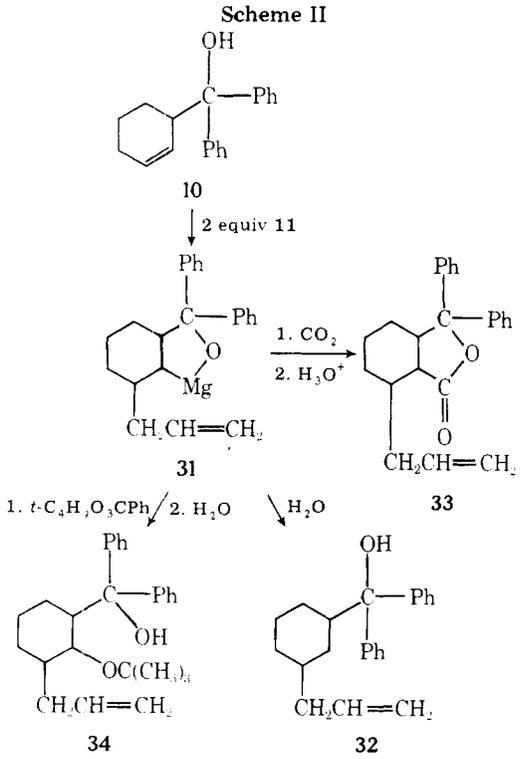


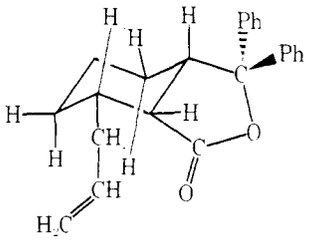
29

(2-Cyclohexenyl)diphenylcarbinol (10). This carbinol reacted slowly but smoothly with **11** in refluxing ether, without undergoing any dehydration. The resulting organomagnesium intermediate (**31**) could be hydrolyzed to give (3-allylcyclohexyl)diphenylcarbinol (**32**), treated with carbon dioxide to form the lactone **33**, or, finally, oxidized with *tert*-butyl perbenzoate[10] to yield the (3-allyl-2-*tert*-butoxycyclohexyl)-diphenylcarbinol (**34**) (Scheme II).

The stereochemical assignments for the structures **32**, **33**, and **34** rest upon careful NMR spectral analysis of the lactone **33** and the *tert*-butoxy ether **34**. In the NMR spectrum of the lactone the CH group attached to the $(C_6H_5)_2COH$ side chain was split into a doublet of triplets [one large coupling (J = 11.5 Hz) and two protons with a smaller coupling (J = 6 Hz)]. Since the $(C_6H_5)_2COH$ group must be equatorial, the adjacent CH must be axial and must be split by adjacent axial C–H (J = 11.5 Hz) and the two adjacent equatorial C–H (J = 6 Hz) groups. Thus, the lactone ring in **33** must be cis fused (**33a**). The spatial relationship of the allyl group to the lactone ring could be shown to be cis by examining the partially obscured splitting of the C_3-H of the ring. Since it was split by one proton with a large coupling ($J \sim 10$ Hz) and by one proton with a smaller coupling (J = 6 Hz), it must be axial and the allyl group equatorial. (The coupling of C_2-H (equatorial) and C_3-H (axial) is <2 Hz.) Thus, the allyl group at C_3 and the carboxyl function at C_2 appear to be cis to the $(C_6H_5)_2COH$ side chain.

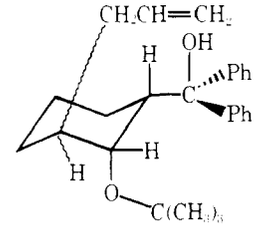
Scheme II



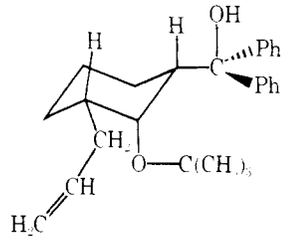


33a

In a similar manner, the butoxy ether **34** displayed its CH–OC_4H_9 at δ 4.05 as a broad doublet (J < 7 Hz) and its CH–$(C_6H_5)_2COH$ at δ 2.4–2.84 as a broad doublet (J = 11 Hz). Since the $(C_6H_5)_2COH$ must again be equatorial, the CH at C_2 must be equatorial and the butoxy group axial (**34a**). Because the C_2-H signal was broadened, this could have arisen from either an axial or an equatorial C_3-H coupling (point of attachment for the allyl group). Either a J_{ae} or J_{ee} would be a small enough coupling to be responsible for the broadened C_2-H signal. Thus, the stereochemistry of the allyl group could not be deduced from these data alone. However, by the cautious dehydration of **34** with thionyl chloride and pyridine, 3-allyl-2-*tert*-butoxy-1-(diphenylmethylene)cyclohexane (**35**) was obtained (eq 10), whose C_2-H was split by coupling of J < 6 Hz. Since it is reasonable that the *tert*-butoxy group will now occupy an equatorial position, the axial C_2-H must now be coupled with an equatorial C_3-H (J < 8 Hz). Accordingly, the allyl at C_3 must be axial and hence cis to the butoxy group. This finding, taken together with an NMR analysis of **34** itself, means that the allyl, butoxy, and hydroxydiphenylmethyl groups are all cis to each other in **34**. (This conclusion implies that the configuration at C_2 in **33** and **34** is the same as that in **31**; i.e., carbonation and alkoxylation of **10** occurred with retention of configuration. Cf. infra for a discussion of this assumption.) By extrapolation from **33** and **34** then, **31** must possess a cis stereochemistry and **10** must have undergone a syn carbomagnesiation cis with respect to the hydroxymethyl side chain. The possibility that a kinetic anti carbomagnesiation occurred followed by an equilibration to the syn



34a



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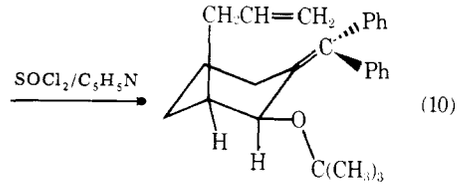

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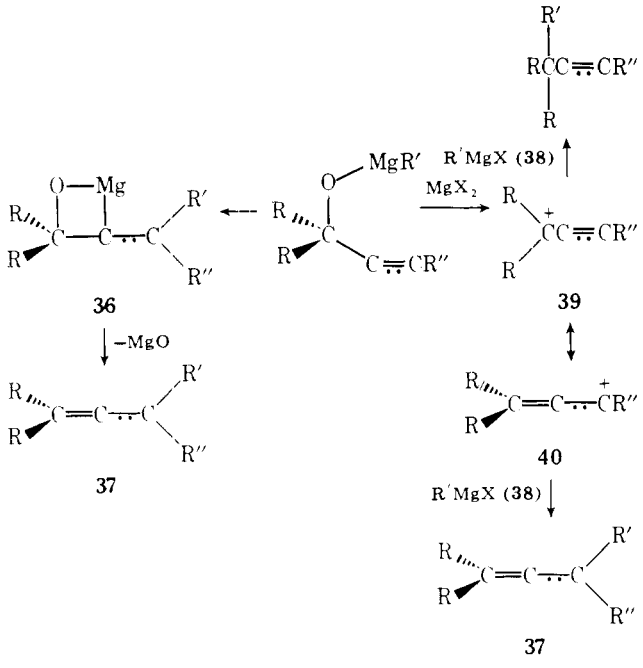
Scheme III

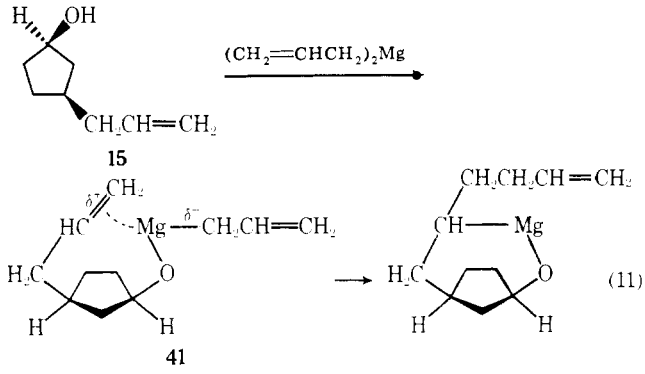


configuration of **31** is much less likely. If equilibration were to have occurred, one would have expected that the substituents at C_1 and C_2 would have taken up equatorial positions and that accordingly some of a 1,2-trans isomer of **31** (and **33** and **34**) would have resulted.

Discussion

Although all of the unsaturated alcohols examined did undergo allylation by organomagnesium reagents with varying ease, only with 3-cyclopentenol, 1-(2-butynyl)cyclohexanol, and (2-cyclohexenyl)diphenylcarbinol did such reaction clearly involve carbomagnesiation. In these latter cases the alcohols obtained upon hydrolysis were found to have added the elements of C_3H_6. With 2-cyclopentenol and 1-propynylcyclohexanol, however, the products were formed by the substitution of the original hydroxy by an allyl group (**13** and **14** in eq 6 and **25** in eq 8). The formation of these products could be viewed as arising either via a carbomagnesiated intermediate (**36**) and an elimination step (**37**) or by a Lewis acid promoted heterolysis of the C–O bond and coupling of the anionic allyl group (**38**) at the carbonium ion centers (**39** and **40**, Scheme III). The only actual point of difference in these views is that the carbonium ion pathway predicts that a mixture of allylic isomers or of allenic–alkynic hydrocarbons should be formed. Indeed, in coupling studies of propargylic halides with organometallic reagents such mixtures of allenes and isomeric alkynes are generally found.[11] In these studies, however, wherever isomers would have been readily detectable (e.g., not 2-cyclopentenol, but with 1,1-diphenyl-2-propen-1-ol[1] and 1-propynylcyclohexanol), the allyl group was introduced exclusively at the carbon γ to the hydroxyl group. For this reason the carbomagnesium–elimination sequence is favored for the formation of **37**. The general ease with which β eliminations of metal salts occur[12] should make **36** a most labile intermediate.

As to the stereochemistry of carbomagnesiation, where the structure of the allylated compound could be properly analyzed (**15**, **27**, and **34a**), the reaction was found to involve cis addition with respect to the neighboring hydroxylate group. In the one case where such cis carbomagnesiation was the principal, but not the exclusive, course, namely, with 3-cyclopentenol (**5**) and allylmagnesium bromide (eq 7), it is conceivable that the initial product **15** slowly underwent epimerization to **16**. Such isomerization may arise either by an



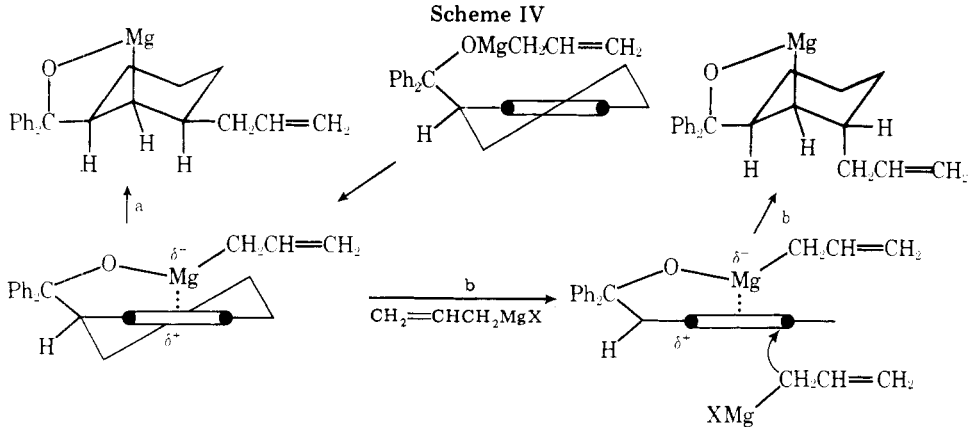
elimination of magnesium hydride from **15** and readdition to yield **16**[13] or by a transition metal catalyzed epimerization, similar to that observed to occur with *cis*-1,2-dialkylcyclopentanes.[14] Diallylmagnesium, on the other hand, added to **5** in an exclusively cis fashion and gave fewer polymeric products. Possibly the precipitation of magnesium bromide involved in preparing the latter reagent also served to precipitate transition metal impurities responsible for the epimerization of **15** and its polymerization.

That **15** underwent further allylation furnishes further proof for the cis relationship of the hydroxyl and allyl groups. In a previous study it was shown that 4-penten-1-ols were very slow in undergoing carbomagnesiation and that 6-hepten-1-ols were unreactive.[1] The greater reactivity of 3-allylcyclopentanol (equivalent to a 5-hexen-1-ol) must lie in the greater proximity of the *cis*-allyl and allylmagnesiumoxy functions (**41**, eq 11). Thus, although the stereochemistry of 3-(5-hexenyl)cyclopentanol (**18**) could not be proved directly, it is most probably the cis isomer.

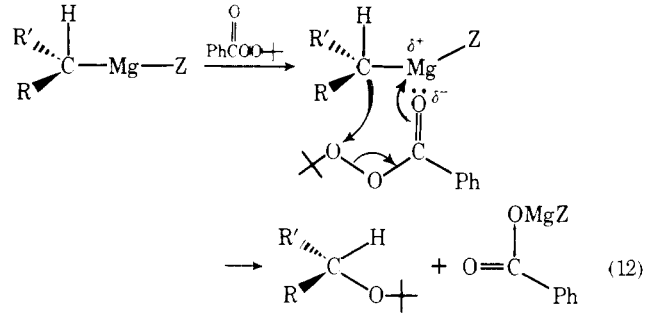
Finally, the syn carbomagnesiation observed for the C=C and C≡C bonds in **10** and **7** is in best accord with an electrophilic attack of an allylmagnesium reagent on the carbon–carbon π bond.[1] Previous studies have shown that a hydroxyl or alkoxyl group proximate to such carbon–carbon unsaturation exerts a fostering and a regiochemical influence on such carbomagnesiations (eq 1). From the course of the syn addition with **10** (and by implication with **5** and **15**), namely, cis with respect to the hydroxyldiphenylmethyl group, it is now clear that the allylmagnesium complexed at oxygen is the one that adds to the C=C bond intramolecularly (Scheme IV, path a). If such a complexed group were simply to provide electrophilic assistance to a second allylmagnesium reagent (path b), a trans or anti addition would have been expected. Thus, these stereochemical results with an unstrained olefinic alcohol agree with those reported for acetylenic[3] and norbornenyl[4] alcohols. [For related kinetic and stereochemical work on the allylation of allylic alcohols by allylmagnesium bromide, cf. ref 4b and 4c. This allylation clearly involves a different mechanism than the one proposed here for homoallylic alcohols; such allylic alcohols undergo additions with an anti stereochemistry and with a regiochemistry the reverse of that shown here (i.e., the allyl group is attached next to the hydroxylate site and the magnesium at the further carbon). Furthermore, the kinetic results of ref 4b are consistent with the magnesium bromide catalyzed attack of allylmagnesium bromide on the magnesium alkoxide of cinnamyl alcohol, an intermolecular process].

One conclusion emerges as a bonus from the structural studies on the carbomagnesiation of **10**, namely, that the carbonation and *tert*-butoxylation of **31** must have occurred in the same stereospecific manner. Since Grignard reagents that are structurally constrained, such as the 2,2-dimethylcyclopropyl system, can be carbonated with retention of configuration,[15] it is reasonable to conclude that **10** was carbonated with complete retention, rather than inversion, of

Scheme IV



configuration. Therefore, the butoxylation must also have occurred with retention. Such stereospecificity supports the occurrence of an electrophilic front-side attack of the oxidant on the carbon–magnesium bond (eq 12). Furthermore, it is evident that the intramolecular alkoxymagnesium bond in **31**



(12)

(or its dimer) must help maintain the configuration of the carbon–magnesium bond at C_2. Without such special structural constaints (cf. ref 16) Grignard reagents undergo rapid epimerizations of their carbon–magnesium bonds at room temperature. Witness the failure to convert optically active alkyl halides into optically active Grignard reagents.[17] Therefore, it can be concluded that a proximate alkoxide site not only accelerates the carbomagnesiation of alkenols but also stabilizes the configuration of the resulting organomagnesium compound.

Experimental Section

General Procedures. Techniques for the preparation, analysis, and manipulations of organomagnesium reagents have already been described in a preceding publication.[1] The chromatographic purification and spectroscopic analytical procedures were also performed in the manner and with the instrumentation detailed in the same reference. All organomagnesium reactions were conducted under an atmosphere of dry, oxygen-free nitrogen.

Chemical shifts of the proton magnetic resonances are reported on the δ scale in parts per million downfield from internal tetramethylsilane.

Starting Materials. 2-Cyclopentenol (4). In a modification of a published procedure,[18] a stream of dry hydrogen chloride gas was passed into 375 mL of cyclopentadiene (prepared from dicyclopentadiene) which was cooled to −10 °C by an alcohol–ice bath, until the volume had increased by ca. 50 mL (2 h). The product was separated by distillation under reduced pressure; after a forerun of ca. 200 mL of cyclopentadiene, 179 g of the 3-chlorocyclopentene was collected: bp 42–43 °C (50 mm); n^{23}_D 1.4370. The chloride darkens quickly in air.

The distilled chloride was immediately added dropwise at 0 °C to a stirred solution of 90 g of sodium bicarbonate dissolved in 500 mL of water. After the addition was completed, the mixture was vigorously stirred for 60 min and then saturated with solid sodium chloride. After extraction with ether, the resulting ether extract was dried over anhydrous calcium sulfate and then freed of ether. Distillation of the residue gave 79 g (54%) of 2-cyclopentenol: bp 64–66 °C (50 mm); n^{23}_D 1.4712 (lit.[18] bp 52 °C, n^{20}_D 1.4717).

3-Cyclopentenol (5). Diborane, prepared separately by the addition of 107 g (0.75 mol) of distilled boron trifluoride etherate to 108 g (2.25 mol) of sodium borohydride dissolved in 500 mL of purified diethylene glycol dimethyl ether (diglyme), was led into a solution of 320 g (4.95 mol) of cyclopentadiene dissolved in 500 mL of anhydrous diethyl ether by means of a connecting glass tubing extending below the surface of the ethereal solution. After the addition the excess cyclopentadiene and the solvent were removed under reduced pressure (under a nitrogen atmosphere). The residual borane was then treated with 1 L of 5 M aqueous sodium hydroxide solution and oxidized by the dropwise addition of 100 mL of 30% hydrogen peroxide. Ether was added, the ether extract was dried over anhydrous $CaSO_4$, and the ether was then removed. Distillation of the residue yielded 105 g (25%) of 3-cyclopentenol: bp 79–80 °C (70 mm); n^{25}_D 1.4670 (lit.[19] n^{25}_D 1.4673).

1-(2-Butynyl)cyclohexanol (7). To 50.0 g (0.71 mol) of 2-butyn-1-ol (Farchan Chemical) dissolved in a mixture of 100 mL of anhydrous diethyl ether and 2 mL of dry pyridine was slowly added 25 mL (0.26 mol) of phosphorus tribromide. The resulting solution was then heated at reflux for 2 h, cooled, washed first with 25 mL of a saturated, aqueous potassium carbonate solution and then with water, and finally dried over anhydrous calcium sulfate. After removal of the ether, the residue was distilled to provide 55.1 g (45%) of 4-bromo-2-butyne: bp 89–90 °C (150 mm); n^{25}_D 1.5040 [lit.[20] bp 82 °C (36 mm)].

This bromide could not be made to react with magnesium metal in a diethyl ether medium, even by attempted initiation with iodine or 1,2-dibromoethane. But a slurry of 6.0 g (0.25 g-atom) of magnesium turnings in 150 mL of dry tetrahydrofuran reacted readily with 13.2 g (0.10 mol) of 4-bromo-2-butyne dissolved in 100 mL of the same solvent when the latter solution was introduced dropwise over 2 h (85% yield of 2-butynylmagnesium bromide by titration).

The above organomagnesium reagent was added dropwise to a solution of 9.8 g (0.1 mol) of cyclohexanone in 50 mL of THF. After being heated at reflux for 2 h, the reaction mixture was cooled and hydrolyzed with an aqueous ammonium chloride solution. The organic layer was stripped of solvent, and the residue was chromatographed on a column of Florisil (600 g) by use of hexane as eluent. An overall 70% yield of two isomeric alcohols was obtained. (1) The first hexane fractions contained 6.0 g (40%) of 1-(1,2-butadien-3-yl)cyclohexanol (**8**): bp 103–105 °C (18 mm); NMR (multiplicity, J, assignment) δ 4.61 (q, 3 Hz, CH_2=C=C(CH_3)–), 3.44 (br s, OH), 1.7 (t, 3 Hz, –(CH_3)-C=C=CH_2), and 1.55 (br s, 10); IR (neat) 3450 (O–H), 1955 (C=C=C), 1450 and 1365 (CH_3), 1060 (C–O), and 960 (C=C=CH_2) cm^{-1}. (2) Later hexane fractions contained 4.5 g (30%) of 1-(2-butynyl)cyclohexanol (**7**): bp 104–105 °C (12 mm); NMR δ 2.87 (br s, OH), 2.2 (q, 2.5 Hz, –CH_2C≡C), 1.94 (t, 2.5 Hz, CH_3C≡C), and 1.49 (br s, 10); IR (neat) 3400 (O–H), 1450 and 1365 (CH_3) cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.85; H, 11.11.

(2-Cyclohexenyl)diphenylcarbinol (10). This compound had already been isolated and characterized as a product from the photoreaction of benzophenone with cyclohexene.[21] Isolated in 27% yield, it was accompanied by 47% of 1,1,2,2-tetraphenylethylene glycol and 13% of the 2 + 2 cycloaddition product, the oxetane. A more convenient method of preparing **10** was the following. To a stirred suspension of 43.5 g (0.388 mol) of alcohol-free potassium *tert*-butoxide in 390 mL of degassed and redistilled cyclohexene, which was cooled in an ice bath, was added 245 mL of a 1.58 M solution of *n*-butyllithium (0.387 mol) in hexane over a period of 15 min. After being stirred for 17 h at 25–30 °C, the reaction mixture was rechilled in an ice bath and treated with 70.6 g (0.388 mol) of solid benzophenone in portions

over a 30-min period. After another 10 min at 0 °C and 30 min at 25 °C, the mixture was cautiously hydrolyzed and the resulting organic layer separated and dried over anhydrous magnesium sulfate. The solvent was removed and the residue fractionally distilled to yield 35 g (35%) of pure **10**: bp 120–125 °C (0.1 mm); NMR ($CDCl_3$–CCl_4) δ 7.7–6.9 (m, 10), 6.10–5.28 (m, 2), 3.37 (br m, 1), 2.18 (s, 1, OH), and 2.1–0.8 (m, 7).

Products. 3-Allylcyclopentanol (17). Diborane, prepared by the addition of 190 mL of redistilled boron trifluoride etherate in diglyme to a slurry of 190 g (4.7 mol) of sodium borohydride in diglyme, was led over a period of 4 h into a solution of 180 mL (2.75 mol) of cyclopentadiene dissolved in a mixture of 450 mL of anhydrous ether and 700 mL of dry pentane. The boron adduct precipitated from the solution as a white slurry. After most of the solvent was removed under reduced pressure, the residual slurry was cooled in an ice bath, treated with a solution of 76 g of sodium hydroxide dissolved in 2.3 L of ethanol, and then oxidized by the dropwise addition of 700 mL of 30% hydrogen peroxide. Much of the solvent was removed under reduced pressure, and the remaining solution was continuously extracted with ether for 100 h. Distillation of the ether extract yielded 50 g (20%) of a cis,trans mixture of 1,3-cyclopentanediol (**20**): bp 90–91 °C (0.8 mm); n^{28}_D 1.4841 (lit.[22] n^{25}_D 1.4832); NMR (70% v/v in D_2O) δ 4.95 (s, 2), 4.50 (m, 2), and 2.0 (m, 6); IR (neat) 3400 (OH), 3000, 1430, 1340, 1175, 1060, 1010, 918, and 834 cm^{-1}.

Heating a sample with phenyl isocyanate and the usual workup gave two isomeric phenylurethanes: (1) fractional recrystallization from petroleum ether gave (*cis*-1,3-cyclopentanediol)bis(phenylurethane), mp 172.5–173.5 °C (lit.[23] mp 172 °C); and (2) fractional recrystallization from CCl_4 gave the trans isomer, mp 162–164 °C (lit.[23] mp 163 °C).

1,3-Dibromocyclopentane (21). To a sample of 1,3-cyclopentanediol (5.0 g, 0.05 mol) cooled to −10 °C was added 5 mL (0.053 mol) of phosphorus tribromide over a period of 30 min. The reaction was allowed to warm to room temperature overnight (heating did not improve the yield). With external cooling the reaction mixture was treated first with ether and then with 20 mL of concentrated H_2SO_4. The solution was then slowly poured onto 25 g of K_2CO_3 and allowed to stand until the odor of hydrogen bromide had disappeared. The ethereal layer was freed of ether and distilled to give 5.3 g (45%) of 1,3-dibromocyclopentane, bp 77–79 °C (8 mm). Gas chromatographic analysis showed the presence of a 1:1 mixture of the cis and trans isomers (**21**): NMR δ 4.62 (br m, 2), 2.68 (t, 2), and 2.32 (m, 4); IR 2990, 1425, 1310, 1220, 900, and 745 cm^{-1}.

Anal. Calcd for $C_6H_8Br_2$: C, 26.35; H, 3.54. Found: C, 26.34; H, 3.56.

1-Allyl-3-bromocyclopentane (22). To 10.2 g (44 mmol) of 1,3-dibromocyclopentane in benzene was added 44 mmol of allylmagnesium bromide in ether. The ether was replaced with benzene by distillation, and the reaction mixture was heated at reflux for 96 h. Usual hydrolytic workup and distillation gave 2.0 g (25%) of 1-allyl-3-bromocyclopentane (**22**): bp 90–91 °C (7 mm); NMR δ 5.99 (m, C**H**=CH_2, J_t = 18 Hz, J_c = 10 Hz, J_{CH_2} = 6 Hz), 5.08 (q, CH=C**H**$_2$), 4.65 (m, CHBr), 2.70 (t, -C**H**$_2$CH=CH_2), and 1.95–2.60 (m, 7); IR 3050, 1660 (C=C), 1440, 1320, 1225, 995 and 912 (-CH=CH_2), and 750 cm^{-1}.

3-Allylcyclopentyl Acetate. To 25 g (0.15 mol) of silver acetate dissolved in 150 mL of glacial acetic acid was added 20 g (0.11 mol) of 1-allyl-3-bromocyclopentane in 50 mL of the same solvent. The reaction mixture was heated at reflux for 12 h and then poured slowly with stirring into a 20% aqueous sodium carbonate solution. The aqueous layer was extracted with ether, and the organic extract was dried and freed of solvent. Distillation of the residue gave a fraction, bp 75–80 °C (0.55 mm), consisting largely of the 3-allylcyclopentyl acetates and 3-allylcyclopentanols (>80%). An NMR spectrum of this crude product exhibited a quartet at δ 5.85 (1), a quartet at δ 5.00 (2), a multiplet between δ 0.95 and 2.35, and a methyl singlet at δ 1.95.

3-Allylcyclopentanol (17). The foregoing crude mixture of acetates and alcohols was stirred at 25 °C for 48 h with 100 mL of a 1:1 ethanol–water pair in which was dissolved 15 g of K_2CO_3. This biphasic mixture was extracted with ether, and the ether extract was dried and freed of solvent. Although some traces of the acetates were still evident by infrared spectroscopic analysis, this product was principally a mixture of *cis*- and *trans*-3-allylcyclopentanols: IR 3400 (OH), 1650 (C=C), and 990 and 910 (CH=CH_2) cm^{-1}; NMR δ 5.85 (m, -C**H**=CH_2), 5.10 (m, -CH=C**H**$_2$), 4.20 and 3.50 (both m, cis and trans >CHOH), and 1.85–2.20 (m, 9).

Grignard Reactions of the Unsaturated Alcohols. 2-Cyclopentenol. Admixture of 19.7 g (0.234 mol) of 2-cyclopentenol and 0.56 mol of allylmagnesium bromide in diethyl ether yielded a suspension from which the ether was largely replaced by toluene through distillation. The final toluene mixture was heated at reflux for 7 days and then hydrolyzed with an aqueous NH_4Cl solution. Drying of the organic layer with anhydrous magnesium sulfate and concentration of the solution gave a residue whose infrared spectrum showed no hydroxyl group absorption. Attempted separation of components by fractional distillation under reduced pressure only caused tar formation. Column chromatography of the organic product on silica gel gave a product (ca. 60%) that seemed to be an allylcyclopentene: bp 59–62 °C (11 mm); NMR δ 5.80 (m, -C**H**=CH_2, m, -CH=CH-) and 5.10; IR 3025, 2900, 1620 (C=C), 995 and 910 (CH=CH_2), and 730 cm^{-1}. However, in all attempts to purify by distillation much polymerization occurred.

Attempted reactions in ether at 25–30 °C or in refluxing benzene over periods of 1 week gave no allylated product. In both cases, ca. 85% of 2-cyclopentenol was recovered and the remaining portion formed a tar.

3-Cyclopentenol. (a) Allylmagnesium Bromide. To 8.4 g (0.1 mol) of 3-cyclopentenol in 100 mL of benzene was added 0.54 mol. of allylmagnesium bromide in ether. The ether was removed by distillation and replaced by benzene (final volume of the reaction mixture was 500 mL). After heating at reflux for 48 h, the reaction mixture was hydrolyzed and worked up as in the foregoing procedure. Fractional distillation at 4 mm gave three principal fractions: (1) bp 77–78 °C, n^{25}_D 1.4669, 1.9 g (15%), 95:5 mixture of two components (by GLC); (2) bp 84–85 °C, 0.5 g (4%); (3) bp 75–100 °C, presumably a mixture of oligomers containing only a small amount of an alcoholic component (by IR).

The preponderant component in the first fraction was *cis*-3-allylcyclopentanol (**15**): NMR δ 5.80 (m, J_t = 17.5 Hz, J_c = 9.5 Hz, -C**H**=CH_2), 4.95 (q, CH=C**H**$_2$), 4.69 (s, OH), 4.20 (m, C**H**OH), 2.14 (br, 2), 2.03 (br, 1), 1.64 (br, 4), and 1.00 (br, 2); IR 3333 (OH), 3110, 2900, 1640 (C=C), 1060 (C-O), and 990 and 910 (CH=CH_2) cm^{-1}.

The second fraction consisted of principally *trans*-3-allylcyclopentanol (**16**): NMR δ 5.86 (m, J_t = 17.4 Hz, J_c = 9.0 Hz, -C**H**=CH_2), 4.98 (q, -CH=C**H**$_2$), 3.95 (s, OH), 3.50 (m, C**H**OH), 2.14 (br, 2), 2.07 (br, 1), 1.64 (br, 4), and 0.90 (br, 2); IR 3400 (OH), 3050, 2950, 1640 (C=C), 1060 (C-O), and 990 and 910 cm^{-1}.

When the foregoing reaction was attempted in ether at 25–30 °C, no reaction was observed after 48 h and 95% of the alcohol could be recovered. Conducting the reaction in refluxing toluene gave ca. 50% allylation, but much dehydration and oligomer formation ensued.

(b) Diallylmagnesium. To 25 g (0.30 mol) of 3-cyclopentenol in benzene was added 0.72 mol of diallylmagnesium in benzene. The ether was removed, benzene was added, and the reaction mixture was stirred under reflux for 14 days. Usual hydrolytic workup and distillation yielded, besides recovered starting material, 5.5 g (15%) of *cis*-3-allylcyclopentanol (**15**), bp 108–110 °C (40 mm), as verified by NMR and infrared spectral data. A later fraction, bp 95–100 °C (15 mm), appeared to consist chiefly of 3-(5-hexenyl)cyclopentanol (**18**) and its dehydrated isomers (**19**): NMR δ 5.59 (m, C**H**=CH_2), 4.91 (m, CH=C**H**$_2$), 3.20 (br s, CHOH), and 0.75–2.39 (ca. 17); IR 3400 (OH), 1650 (C=C), and 990 and 910 (CH=CH_2) cm^{-1}.

1-(1-Propynyl)cyclohexanol (6). A mixture of 9.7 g (70 mmol) of 1-(1-propynyl)cyclohexanol and 0.19 mol of allylmagnesium bromide was heated to remove the ether, and then 200 mL of toluene was added. After a reflux period of 4 days, the usual hydrolytic workup and solvent removal gave a residual liquid that was chromatographed on 400 g of Florisil. Elution with hexane and distillation of combined fractions yielded 9.1 g (80%) of (2-allyl-2-methylvinylidene)cyclohexane (**25**): bp 90–91 °C (10 mm); n^{23}_D 1.4935; NMR δ 5.81 (q of t, J_t = 17.5 Hz, J_c = 9.5 Hz, J_{CH_2-H} = 6 Hz, C**H**=CH_2), 4.99 m, CH=C**H**$_2$), 2.65 (d, 6 Hz, C**H**$_2$CH=CH_2), 1.62 (s, CH_3), and 1.55–2.10 (br m, 10); IR 2950, 2880, 1960 (C=C=C), 1440, 1360 (CH_3), and 990 and 910 (CH=CH_2) cm^{-1}.

No reaction had occurred between the magnesium salt of the carbinol and the Grignard reagent after 96 h in refluxing ether; in refluxing benzene after 96 h ca. 20% of the carbinol had been allylated. However, from a reaction of 0.1 mol of the carbinol and 0.25 mol of the Grignard reagent, to which 3.1 mmol of nickel acetylacetonate had been added, a 96-h reflux period in ether gave a 70% yield of (2-allyl-2-methylvinylidene)cyclohexane and 22% of recovered starting material.

Anal. Calcd for $C_{12}H_{18}$: C, 88.89; H, 11.11. Found: C, 88.82; H, 11.05.

1-(2-Butynyl)cyclohexanol (7). To 4.1 g (27 mmol) of the carbinol was added 68 mmol of allylmagnesium bromide in ether (formation of a dark green precipitate). Since no reaction had occurred after 96 h at 25–30 °C, the mixture was heated at reflux for another 96 h. Usual hydrolytic workup and collection of the product by preparative gas chromatography gave a 60% yield of 1-[(*E*)-3-methyl-2,5-hexadienyl]cyclohexanol (**27**): bp 60–61 °C (0.4 mm); NMR δ 5.89 (q of t, J_t = 17.5 Hz, J_c = 9 Hz, J_{CH_2-H} = 6.5 Hz, C**H**=CH_2), 5.31 (t, 7.5 Hz,

CH=C(CH_2)CH_2–), 5.00 (q, J_t = 17.5 Hz, J_c = 9 Hz, CH=CH_2), 2.72 (d, 6.5 Hz, CH_2CH=CH_2), 2.10 (d, 7.5 Hz, CH_2), 1.58 (d, 0.8–1.0 Hz, CH_3), and 1.0–2.0 (br m, 11); IR 3410 (OH), 2910, 2860, 1440, 1375 (CH_3), 990 and 910 (CH=CH_2), and 835 cm^{-1}.

Anal. Calcd for $C_{13}H_{22}O$: C, 77.15; H, 10.9. Found: C, 77.31; H, 10.56.

(2-Cyclohexenyl)diphenylcarbinol (10). (a) Hydrolysis. To a stirred solution of 2.152 g (8.15 mmol) of allylic alcohol **10** in 45 mL of anhydrous ether was added, over a 5-min period, 35.5 mL of a 0.574 M solution of allylmagnesium bromide (20.4 mmol) in ether. The solution was heated at reflux for 7.5 days, cooled, and hydrolyzed with an aqueous NH_4Cl solution. After drying the organic layer over anhydrous $MgSO_4$ and removing most of the solvent, the residue was chromatographed on a silica gel column and the components were eluted, first with hexane and then with hexane–ether mixtures. With 2% ether 875 mg of **10** was obtained, followed by 227 mg of a 1:1 mixture of **10** and the product. Elution with 3–4% ether gave 781 mg of pure product (66%, with consideration of recovered **10**). Based upon the NMR spectral data, this product is (3-allylcyclohexyl)diphenylcarbinol (**32**): NMR ($CDCl_3$) δ 7.60–6.95 (m, 10), 6.10–5.23 (m, 1, CH=CH_2), 5.25–4.75 (m, 2, CH=CH_2), 2.5–1.95 (m, 4, CH_2CH=CH_2, COH, CHCPh_2OH), 1.90–0.70 (m, 9). For further evidence on the position of the allyl group and on the stereochemistry of the substituents on the cyclohexane ring, cf. infra.

(b) Carbonation. The reaction of 3.96 g (15 mmol) of **10** in 75 mL of ether with 78.4 mL of a 0.574 M ethereal solution of allylmagnesium bromide (45 mmol) was carried out as described above. The reaction solution was cooled to 0 °C, and an excess of solid CO_2 was added as rapidly as possible. After warming to 25 °C, the mixture was hydrolyzed with 1 M aqueous H_2SO_4. The organic layer was extracted with 10–15 mL portions of 5% aqueous NaOH. These combined aqueous extracts were then acidified with 1 M aqueous H_2SO_4 and extracted several times with ether. The ether extracts were washed with a saturated, aqueous NaCl solution, dried over anhydrous Na_2SO_4, and then evaporated to give 2.19 g of crude product. This material was dissolved in 100 mL of benzene, and the solution was heated at reflux in a Dean-Stark apparatus. The benzene was then evaporated and the residue chromatographed on silica gel. Using a hexane–ether eluting gradient gave 1.67 g of lactone **33** (33%) (obtained by a 6% ether–hexane mixture), which recrystallized from hexane as fluffy needles: mp 112–113 °C; NMR ($CDCl_3$) δ 7.66–7.09 (m, 10), 6.10–5.33 (m, CH=CH_2), 5.20–4.78 (m, CH=CH_2), 3.50–3.00 (overlapping d of t, 11.5 and 6 Hz, CH(axial)–CPh_2O), 2.63 (d, 6 Hz, CH(equat)–C=O), 2.20 (d, 5.5 Hz, CH_2CH=CH_2), 2.12–1.75 (C_3-H, 6 and 10 Hz), 1.69–1.0 (m, 6); IR (neat) 1765 (five-membered lactone) and 1640 (C=C) cm^{-1}.

Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.13; H, 7.22. Found: C, 83.08; H, 7.24.

(c) Oxidation. The reaction of 3.77 g (14.3 mmol) of **10** in 110 mL of ether with 30 mL of a 1.21 M ethereal solution of allylmagnesium bromide (36 mmol) was carried out as described above. Then a solution of 4.85 g (25 mmol) of *tert*-butyl perbenzoate in 15 mL of ether was added over a 15-min period to the ice-cooled reaction mixture. After a further 20 min at 25–30 °C, the mixture was hydrolyzed with an aqueous NH_4Cl solution. The separated organic layer was washed successively with 100 mL of water, 200 mL of 5% aqueous NaOH solution, and 100 mL of a saturated aqueous NH_4Cl solution. The separated organic layer was washed successively with 100 mL of water, 200 mL of 5% aqueous NaOH solution, 100 mL of a saturated aqueous solution of $FeSO_4$, and finally water. After drying over anhydrous $MgSO_4$ and solvent removal, the organic residue was chromatographed twice on silica gel columns using hexane–ether eluting gradients. The pure *tert*-butyl ether **34** (2.02 g, 37%) was eluted by 2.5% ether–hexane: NMR (CCl_4) δ 7.79–6.90 (m, 10), 6.10–5.40 (m, CH=CH_2), 5.40–4.83 (m, OH and CH=CH_2), 4.05 (br, 10 Hz, CHOC_4H_9), 2.84–2.4 (br d, 11 Hz, CH(axial)–CPh_2O), 2.3–2.0 (br d, 6 Hz, CH_2CH=CH_2), 2.0–1.0 (m, 7), and 0.95 (s, 9).

Dehydration of (3-Allyl-2-*tert*-butoxycyclohexyl)diphenylcarbinol (34). Attempted dehydration of **34** by heating in refluxing benzene with a catalytic amount of *p*-toluenesulfonic acid led to loss of both the hydroxyl and *tert*-butoxy groups. Milder conditions proved successful. Thus, a solution of 233 mg (0.62 mmol) of **34** in 10 mL of dry pyridine was cooled in ice and treated with 1 mL of thionyl chloride. The mixture was allowed to come to 25 °C over 1 h and then poured into 100 mL of ether. The organic layer was washed with water, with 5–25 mL portions of 1 N aqueous HCl, and with 25 mL of 5% aqueous $NaHCO_3$ solution. After drying over anhydrous $MgSO_4$, the organic extract was evaporated and the residue was chromatographed on basic alumina. The major product, (*cis*-3-allyl-2-*tert*-butoxycyclohexylidene)diphenylmethane (**35**) (107 mg, 47%), was eluted with a 5% ether–hexane mixture: NMR (CCl_4) δ 7.09 (s, 10) 5.90–5.35 (m, CH=CH_2), 5.2–4.8 (m, CH=CH_2), 4.07 (br s, 6 Hz wide), 2.7–2.1 (m, 4, CH_2CH=CH_2, CH_2C=CPh_2), 2.0–1.2 (m, 5), 1.0 (s, 9).

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Registry No.—**4**, 3212-60-0; **5**, 14320-38-8; **7**, 26929-49-7; **8**, 68479-41-4; **10**, 5723-84-2; **15**, 68479-42-5; **16**, 68479-43-6; **18**, 68479-44-7; **19** (isomer 1), 68479-45-8; **19** (isomer 2), 68479-46-9; *cis*-**20**, 16326-97-9; *trans*-**20**, 16326-98-0; *cis*-**21**, 68479-47-0; *trans*-**21**, 68479-48-1; *cis*-**22**, 68479-49-2; *trans*-**22**, 68479-50-5; **24**, 697-37-0; **25**, 68479-51-6; **27**, 68479-52-7; **32**, 68479-53-8; **33**, 68479-54-9; **34**, 68479-55-0; **35**, 68479-56-1; 3-chlorocyclopentene, 96-40-2; 4-bromo-2-butyne, 3355-28-0; *cis*-3-allylcyclopentyl acetate, 68479-57-2; *trans*-3-allylcyclopentyl acetate, 68479-58-3; cyclopentadiene, 542-92-7; cyclohexanone, 108-94-1; cyclohexene, 110-83-8; benzophenone, 119-61-9; allyl bromide, 106-95-6; 3-allylcyclopentene, 14564-97-7; 4-allylcyclopentene, 765-99-1.

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