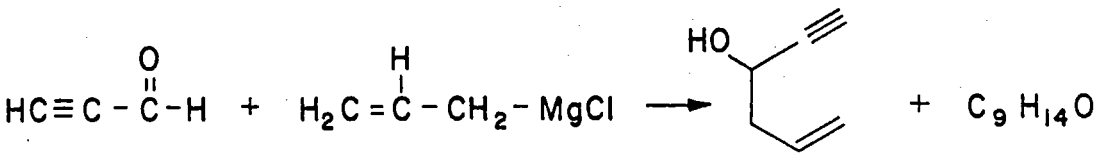
Investigation of Grignard additions to acetylenes

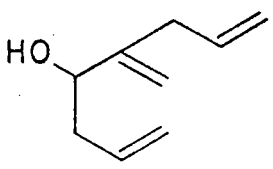
This investigation was undertaken only as a side project since it is not pertinent to the main objectives of this thesis.

During the synthesis of 5-hexen-1-yn-3-ol (63) by the reaction of propargylaldehyde with allylmagnesium chloride, a higher boiling constituent (97) was isolated in addition to the desired 63. For this reaction, an excess of Grignard reagent was used beyond that theoretically required to react with the aldehyde.



.2 mole .7 mole 63 97

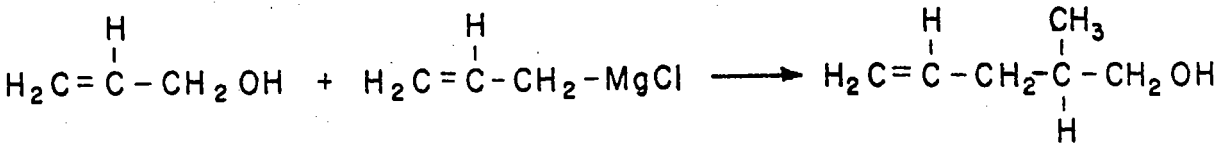
The physical constants and elementary analysis of the higher boiling compound were consistent with the formula $C_9H_{14}O$. The infrared spectrum indicated an olefinic alcohol with no acetylenic functionality. The n.m.r. spectrum consisted of olefinic multiplets corresponding to eight protons, a bis-allylic two proton doublet, an allylic two proton triplet and a carbinol proton triplet. The ultraviolet spectrum showed only end absorption thus precluding conjugation. On the basis of the analytical and spectral data the most likely structure for the higher boiling compound would appear to be 5-methylene-1,7-octadien-4-ol (97).



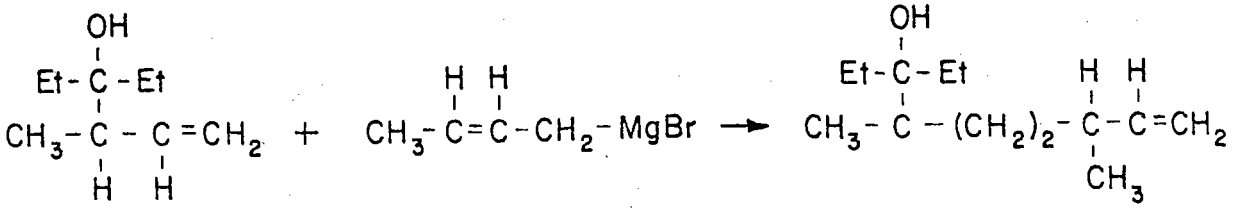
97

The proposed structure was confirmed by hydrogenation with Pd/C. The hydrogenation was nonquantitative and gave a saturated hydrocarbon a saturated ketone and a saturated alcohol. This mode of hydrogenation is characteristic of allylic alcohols[32]. The ketone and alcohol were isolated by preparative v.p.c. and identified as 5-methyl-4-octanone and 5-methyl-4-octanol respectively. The v.p.c. retention times, infrared spectra, indices of refraction and boiling points of the hydrogenation products were identical to those of authentic 5-methyl-4-octanone and 5-methyl-4-octanol.

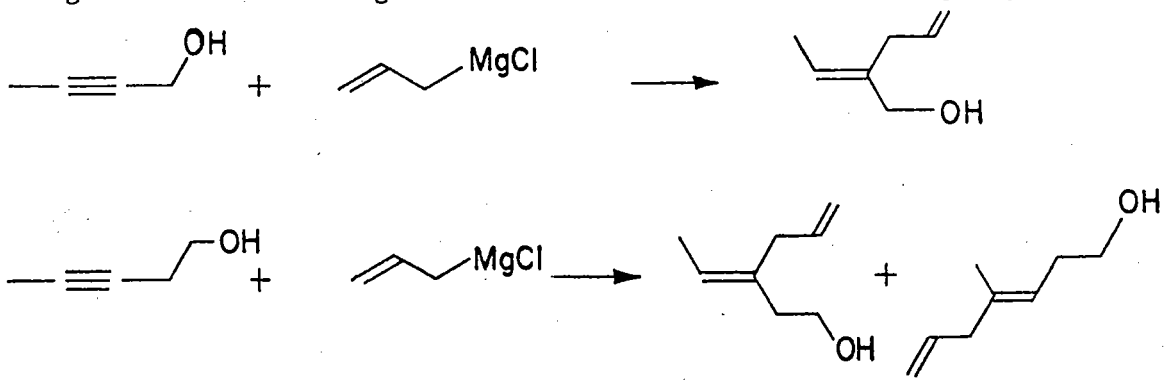
The above reaction appears to be an example of a Grignard reagent adding to an acetylenic group of a propargylic alcohol. The addition of Grignard reagents to allylic alcohols such as allyl alcohol has been reported. These reactions were reviewed in the Ph.D. thesis of Iorio[4]. As an example, Cherest[55] has reported the addition of allyl and benzyl Grignard reagents to the internal carbon atom of allyl alcohol to give branched compounds.



Benkeser and Broxterman[56] have recently reported addition of the crotyl Grignard reagent to an isolated double bond (a homoallylic alcohol).

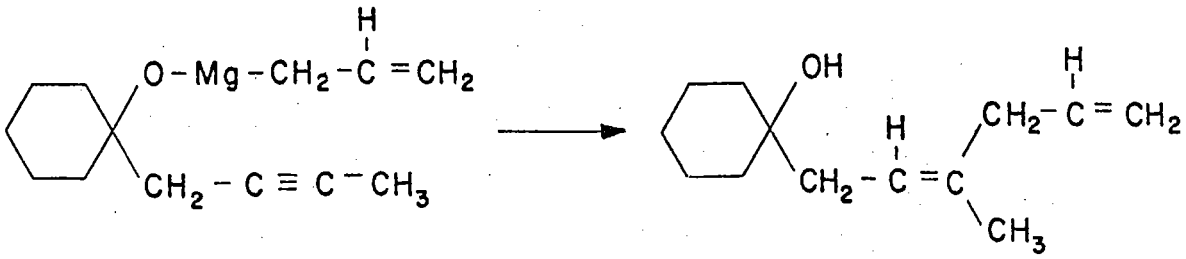


After completion of this investigation, two papers appeared giving examples of Grignard additions to triple bonds of propargylic alcohols. Richey and VonRein[58] have reported the allyl and vinyl Grignard reagents to add to the alkyne carbon nearer to the OH group in 2-butyn-1-ol. The allyl Grignard was found to give both modes of addition with 3-pentyn-1-ol.



These results for 2-butyn-1-ol were in general agreement with our findings. The authors believed <u>trans</u> addition of R and of magnesium to occur for the reactions where R becomes attached to the alkyne carbon nearer the hydroxyl group.

Eisch and Merkley[57] reported stereospecific addition of allylmagnesium bromide to 1-(2-butynyl) cyclohexanol (<u>110</u>). In this reaction the R group became attached to the alkyne carbon farthest removed from the hydroxyl group.



The authors consider this <u>cis</u> addition strongly indicative of an intramolecular mechanism for Grignard addition.

In order to investigate the generality of the addition of Grignard reagents to propargylic alcohols, the reaction of propargyl alcohol with several Grignard reagents was investigated. All reactions were carried out using a 3:1 molar ratio of appropriate halide to alcohol. The same reaction volumes and approximately the same reaction times were used. No attempts were made to maximize yields as it was desired only to ascertain relative reactivity. The results are given in Table XII.

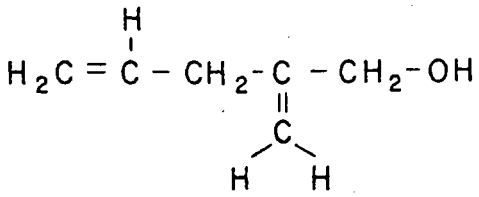
Table XII

Summary of Grignard Addition Data

Alcohol	R-Mg-X	React. Time	Adduct	Yield
5-Hexen-1-yn-3-ol(63)	Allyl-	3 Hr.	97	10%
Propargyl-	"	15	2-Methylene-4-penten-1-ol (98)	35
"	Methallyl-	18	2-Methylene-4-methyl-4-penten-1-ol(99)	28
"	Propargyl-	15	2-Methylene-4-pentyn-1-ol (100)	27
"	Benzyl-	18	2-Methylene-3-phenyl-1-propanol (101)	12
"	n-Propyl	15	2-Methylene-1-propanol (102)	5
3-Butyn-2-ol(103)	Allyl-	18	3-Methylene-5-penten-2-ol(104)	22
2-Methyl-3-butyn-2-ol(107)	"	15	-------	N.R.
3-Butyn-1-ol(108)	"	18	-------	N.R.
1-Hexyne (109)	"	35	-------	N.R.
Allyl-	"	15	2-Methyl-4-penten-1-ol(106)	13
"	n-Propyl-	"	-------	N.R.

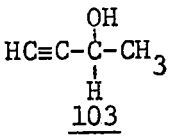
It is seen that allyl, methallyl, propargyl, benzyl and n-propyl Grignard reagents all added to the internal carbon of the triple bond in propargyl alcohol to give the corresponding allylic alcohols. All compounds gave physical constants, elementary analyses, infrared and n.m.r. spectra and hydrogenation data consistent with the proposed structures and inconsistent with the corresponding product in which the Grignard reagent added to the terminal carbon of the triple bond. All yields were low, with propargyl alcohol always being recovered. The data for these reactions is detailed in the experimental section.

In a typical structure elucidation, the Grignard adduct obtained from the reaction of propargyl alcohol with allylmagnesium chloride was isolated by preparative v.p.c. The physical constants and elementary analysis were consistent with the formula $C_6H_{10}O$. The infrared spectrum indicated an olefinic alcohol with no acetylenic functionality. The n.m.r. spectrum showed olefinic and allylic absorption in the integral ratio 5:4 and contained a two proton allylic singlet plus a two proton bis-allylic doublet. The ultraviolet spectrum showed only end absorption. Hydrogenation with Pd/C gave a saturated aldehyde as the major product and a saturated alcohol as a minor product. The v.p.c. retention time and infrared spectrum of the aldehyde were identical to those for authentic 2-methylpentanal. The 2,4-dinitrophenylhydrazone melted in agreement with the literature and showed no melting point depression on admixture with an authentic sample. The saturated alcohol gave a v.p.c. retention time and infrared spectrum identical to authentic 2-methylpentanol. On the basis of the above data the 2-methylene-4-penten-1-ol (98) structure is assigned to the Grignard adduct.



98

The compound 3-butyn-2-ol (103) was also found to add the allyl Grignard internally, however, 2-methyl-3-butyn-2-ol (107), 3-butyn-1-ol (108), and 1-hexyne (109) failed to give Grignard addition products under these conditions. Allyl alcohol (105) was found to add the allyl Grignard internally in agreement with the report of Cherest, however, the n-propyl Grignard reagent failed to add to allyl alcohol under these conditions.



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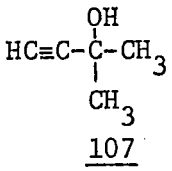

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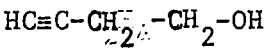

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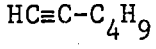
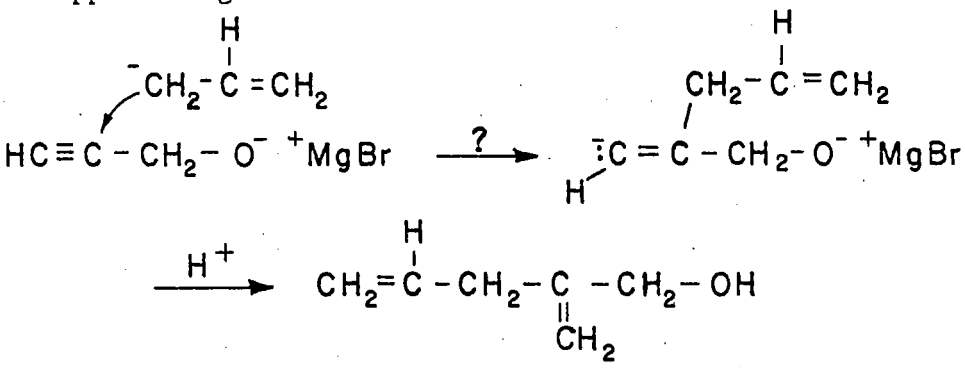


109

Although the amount of data for this new reaction is limited, the following constraints seem to be operative in the addition. The fact that 1-hexyne (109) fails to add the allyl Grignard reagent even after prolonged stirring indicates that the hydroxyl function is necessary for the addition to occur. The failure of the tertiary alcohol 2-methyl-3-butyn-2-ol (107) to react indicated a possible steric retardation of the addition. The failure of 3-butyn-1-ol (108) to add a Grignard reagent shows that the carbinol function must be alpha to an alkyne carbon

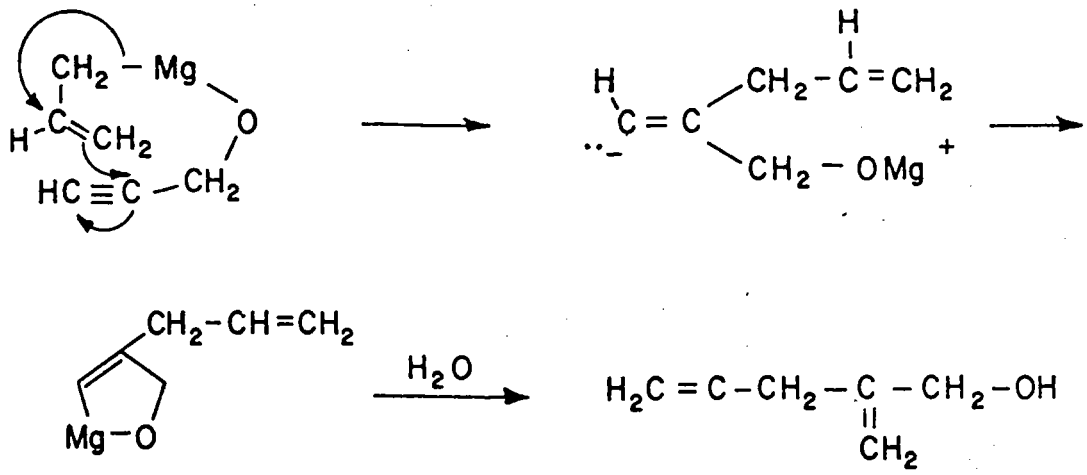
for an addition to occur. This result is in apparent disagreement with Richy[58] and Eisch[57] although their reactions were run for considerably longer periods. Also, it appears that saturated Grignard reagents (i.e. n-propylmagnesium chloride) react at slower rates than the unsaturated Grignard reagents.

Due to the limited data available and the complex nature of the Grignard reagent, any mechanistic interpretation seems tenuous at best. A direct nucleophilic attack at the internal acetylenic carbon would be a possibility. However, since the neighboring oxygen bears a negative charge in its complexation with the magnesium, it should electrostatically repel an approaching carbanion.

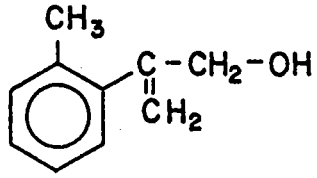


Since the presence of the oxygen is required for the reaction to proceed, this mechanism does not explain the data. 1-Hexyne would be expected to react faster than propargyl alcohol by this mechanism.

Another possible mechanism would involve a cyclic seven membered transition state in which the magnesium is complexed to one oxygen and an allylic carbanion. This mechanism is favored by Eisch and Merkley[57].

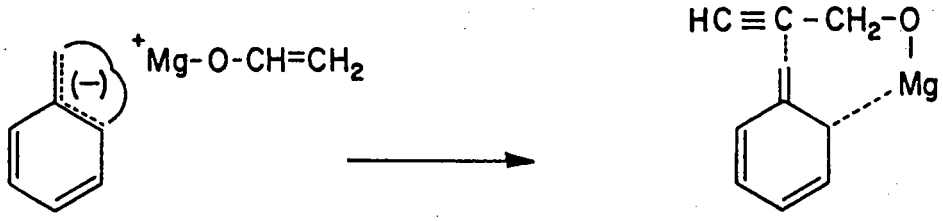


However this mechanism does not explain the addition of the n-propyl Grignard reagent to propargyl alcohol. The addition of the benzyl Grignard reagent to propargyl alcohol by this mechanism might be expected to yield 112.



112

However, the product of the reaction was rigorously shown to be 2-methylene-3-phenyl-1-propanol (101). It is conceivable that the benzyl Grignard reacts through its ortho resonance form via the above mechanism.



It is evident that further study of this reaction is necessary in order to establish its mechanistic pathway. The reaction has potential synthetic utility for the production of 2-methylene substituted alcohols.

Addition of allylmagnesium chloride to 5-hexen-1-yn-3-ol (63)

The compound 97 obtained as a high boiling byproduct in the synthesis of 5-hexen-1-yn-3-ol was purified by preparative v.p.c. (yield of about 10%), b.p. 188-9°(1 atm), n_D^{27} 1.4675.

Anal. Calcd. for $C_9H_{14}O$: C, 78.22 ; H, 10.21.

Found: C, 77.93 ; H, 10.25.

The infrared spectrum showed bands at 3400(m), 3050(m),2960(m), 2900(m),1830(w,overtone),1650(m),1440(m),1415(m),1310(w),1210(w), 1120(w),1055(m),1030(m),995(s),905(s),and 875(w) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a singlet at 2.05 (1H, hydroxyl, collapses upon addition of D_2O), a triplet at 2.35 (2H, allylic), a doublet at 2.8 (2H,allylic), a triplet at 4.10 (1H, methine), a complex centered at 5.1 (6H, terminal vinyl), and a complex centered at 5.78 (2H, internal vinyl).

The ultraviolet spectrum showed only end absorption above 220mμ.

Hydrogenation of 5-methylene-1,7-octadiene-4-ol.(97)

A 0.741 g (5.38 mmols) sample of the alcohol in pentane, over Pd/C, was found to absorb 360 ml of hydrogen at 298°K, which was 92% of the 394 ml theoretically required to saturate three double bonds. After filtration to remove the catalyst, the pentane was evaporated, to yield a colorless liquid. V.p.c. analysis indicated the liquid to contain three components which were separated by preparative v.p.c. The lowest boiling product (12% of the mixture)

was shown to be a saturated hydrocarbon by its infrared spectrum. This component, believed to be 4-methyl-octane, was isolated in only trace quantity and was not further identified. The major component (71% of the mixture) was shown to be a saturated ketone by its infrared spectrum. Its physical constants were b.p.179-81°, n_D^{25} 1.4145. The highest boiling component (17% of mixture) was shown by infrared to be a saturated alcohol. The latter two components were identified by comparison to synthetic samples, as described below, as 5-methyl-4-octanone and 5-methyl-4-octanol respectively.

Authentic 5-methyl-4-octanol was synthesized by the reaction of the Grignard reagent prepared from 2-bromopentane with butanal, followed by workup and purification by standard procedures.

The infrared spectrum and v.p.c. retention time of the synthetic material were found to be identical to those of the alcohol obtained from the hydrogenation of 5-methylene-1,7-octadien--4-ol.

Authentic 5-methyl-4-octanone was synthesized by oxidation of 5-methyl-4-octanol with potassium dichromate/sulfuric acid according to standard procedures.

The boiling point, index of refraction, infrared and n.m.r. spectra of the synthetic 5-methyl-4-octanone were identical to those of the ketone obtained from the hydrogenation of 5-methylene--1,7-octadien-4-ol.

Addition of allylmagnesium chloride to propargyl alcohol.

In a 5 liter three neck flask, equipped with mechanical stirrer, dropping funnel, and condenser were placed 72 g (3 mols) of magnesium turnings, 500 ml of dry ether and several crystals of iodine. Then 50 ml of a solution of 115 g (1.5 mols) redistilled allyl chloride in 500 ml of dry ether was added in one portion and the mixture stirred vigorously. After five minutes, the reaction commenced as evidenced by formation of a white solution and vigorous ether reflux. The remainder of the solution was then added dropwise over six hours. Midway through the addition 50 ml of dry tetrahydrofuran was added to redissolve precipitated Grignard complex. After completion of the chloride addition, the solution was stirred for one hour. Then a solution of 28 g (0.5 mol) redistilled propargyl alcohol in 200 ml ether was added, dropwise, over a period of three hours. A vigorous reaction occurred resulting in considerable ether evaporation. At the end of the addition, 300 ml additional ether was added and the solution was then stirred for fifteen hours. The mixture was decomposed with ice/ammonium chloride and the two layers were separated. The aqueous layer was extracted with two 200 ml ether portions. The combined ether layers were washed twice with 100 ml portions of water and dried with magnesium sulfate. The ether was removed, on a steambath, to yield a light yellow oil. Careful fractionation of the oil, under aspirator pressure, with the Tantalum wire column, yielded 22 g of crude material b.p. 75-90° (30 mm).

2-Methylene-4-penten-1-ol (98)

Preparative v.p.c. of the crude distillation mixture described above afforded 17 g (35% yield) of a pure compound, subsequently identified as 2-methylene-4-penten-1-ol, b.p.158-9°, n_D^{27} 1.4535, d_4^{29} 0.860. The compound had not previously been reported. A higher boiling product also was obtained. See page 175.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43 ; H, 10.27.

Found: C, 73.32 ; H, 10.32.

The infrared spectrum showed bands at 3400(s),3050(m),2970(w), 2900(m),1830(w,overtone),1650(m),1440(m),1420(m),1230(m),1100(w), 1060(m),1030(m),1000(m),920(s), and 905(m) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a singlet at 1.92 (1H, hydroxyl, collapses on addition of D_2O), a singlet at 4.10 (2H,aliphatics), a doublet at 2.82 (2H,allylic), a multiplet centered at 5.1 (4H, terminal vinyl), and a multiplet centered at 5.8 (1H, internal olefinic).

The ultraviolet spectrum showed only end absorption above 210 mμ.

Hydrogenation of 2-methylene-4-penten-1-ol

A 0.567 g (5.8 mmols) sample of the alcohol was dissolved in pentane, over 10% Pd/C and hydrogenated until gas absorption ceased. The sample absorbed 295 ml at 298°K, which was 104% of the 284 ml theoretically required to saturate two double bonds. After filtering off the catalyst and evaporation of the pentane, the residue was analyzed by v.p.c. Three hydrogenation products were detected. The

first product, 20% of the mixture, had a v.p.c. retention time in line with that expected for 2-methyl-pentane and was not characterized further. The remaining two products were purified by preparative v.p.c. The major product (70% of the mixture) had a v.p.c. retention time and infrared spectrum identical to those of authentic 2-methylpentanal. The 2,4-dinitrophenylhydrazone was prepared by the method of Shriner and Fuson[60] and recrystallized from ethanol/water, m.p. 101-102° (lit.[62]: m.p. 103°). The compound showed no melting point depression on admixture with an authentic sample. The remaining hydrogenation product, 10% of the mixture, had a v.p.c. retention time and infrared spectrum identical to those of authentic 2-methylpentanol.

The high boiling product (3.14 g) from the reaction of allylmagnesium chloride with propargyl alcohol, was isolated by preparative v.p.c. A Rast determination gave a molecular weight of 180±10. The physical constants were consistent for a twelve carbon alcohol. B.p. 188-9°, n_D^{27} 1.4767.

Anal.	Calcd. for $C_{12}H_{20}O_2$:	C, 73.43 ;	H, 10.27.
	Found:	C, 73.29 ;	H, 10.40.

The infrared spectrum showed bands at 3400(s),3030(w),2900(s), 2850(m),1650(w),1440(w),1360(w),1320(w),1300(w),1265(w),1220(w), 1150(w),1045(s),1015(m),985(m),950(w),935(w),905(w),and 825(w)cm^{-1}.

The n.m.r. spectrum (δ scale) showed a multiplet centered at 2.2 (12H,aliphatics), a broad singlet at 3.95 (2H,hydroxyl,collapses

with D_2O), a multiplet at 4.15 (2H, deshielded aliphatics), and a multiplet at 5.6 (2H, olefinics). No further structure determination was undertaken.

Addition of methallylmagnesium chloride to propargyl alcohol.

A 2-liter three neck flask was fitted with mechanical stirrer, dropping funnel and condenser. Then 54 g (2.25 mols) magnesium, several crystals of iodine, 500 ml dry ether and 20 ml of a solution containing 109 g (1.2 mols) redistilled methallyl chloride in 150 ml ether were added to the flask. After five minutes vigorous bubbling occurred and stirring was commenced. The remaining chloride solution was added dropwise over a period of six hours. A 10 ml portion of anhydrous THF was added during the addition to dissolve precipitated complex. A solution of 20 g (0.35 mol) redistilled propargyl alcohol in 75 ml of dry ether was then added dropwise over a period of two hours so as to maintain a moderate ether reflux. After complete addition, 400 ml additional ether was added and the mixture stirred for 18 hours. After decomposition and extraction in the usual manner, the ether layer was dried with magnesium sulfate and the ether was removed to yield a yellow oil. Fractionation under aspirator pressure gave pure 2-methylene-4-methyl-4-penten-2-ol (99), 11.08 g (28% yield). B.p. 60-61° (10 mm), n_D^{22} 1.4600, d_4^{25} 0.863.

Anal.			
	Calcd. for $C_7H_{12}O$:	C, 74.95 ;	H, 10.78.
	Found:	C, 74.76 ;	H, 11.00.

The infrared spectrum showed bands at 3350(s),3050(w),2950(m), 2900(m),1800(overtone),1650(m),1450(s),1380(m),1230 (m),1065(s), 1025(s),990(m),955(w),895(v.s.), and 825(w)cm^{-1}.

The n.m.r. spectrum (δ scale) showed a broad singlet at 3.4 (1H,hydroxyl), a singlet at 4.0 (2H,aliphatics), a singlet at 2.8 (2H,aliphatics), a triplet (J< 1 cps) at 1.7 (3H,methyl), multiplets at 4.9 and 5.1 (total 2H,methylene) and a multiplet at 4.75 (2H, terminal vinyl).

The following Grignard additions were successfully accomplished using ether volumes and reaction times proportional to those described for the addition of methallylmagnesium chloride to propargyl alcohol.

Addition of n-propylmagnesium chloride to propargyl alcohol.

79 g (1 mol) n-propyl chloride, 18.5 g (0.33 mol) propargyl alcohol and 60 g (2.5 mol) Mg were reacted by the previously described procedure. Preparative v.p.c. yielded 1.57 g of material, 102, (5% yield), b.p. 165-6°, n_D^{27} 1.4355.

Anal. Calcd. for $C_6H_{12}O$: C, 71.95 ; H, 12.08.
Found: C, 72.03 ; H, 12.01.

The infrared spectrum showed bands at 3400(s),3050(m),2930(s), 2860(s),1650(m),1460(m),1380(m),1220(w),1050(s),1030(s),995(m), 980(w),900(s),880(w), and 745(w) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a distorted triplet at 0.90

(3H,methyl), a multiplet at 1.5 (2H,aliphatics), a distorted triplet at 2.0 (2H,aliphatics), a doublet with fine splitting into triplets at 4.95 (2H,methylene), a singlet at 4.05 (2H,aliphatics),and a broad singlet at 3.35 (1H,hydroxyl, collapses on addition of D_2O).

Hydrogenation of 2-methylene-1-pentanol (102)

A 0.535 g (5.35 mmols) sample of the alcohol in pentane, over Pd/C, was found to absorb 140 ml of hydrogen at 298°K which corresponded to 107% of the 131 ml theoretically required to saturate one double bond. The catalyst was removed by filtration and the pentane evaporated yielding a colorless liquid. Extensive hydrogenolysis evidently occured since less than half of the hydrogenated alcohol was recovered. V.p.c.analysis showed the material to consist of three products. The lowest boiling constituent, 13% of the product, had a v.p.c. retention time in line with that expected for 2-methylpentane and was not further characterized. The highest boiling product, 8% of the mixture, had a retention time identical to that of authentic 2-methylpentanol. The major component, 79%, had a v.p.c. retention time and infrared spectrum identical to those of authentic 2-methylpentanal. The 2,4-dinitrophenylhydrazone was prepared by the Shriner and Fuson[60] procedure. Recrystallization from ethanol yielded yellow crystals, m.p. 100-102° (lit.[62] m.p. 103°) which showed no melting point depression on admixture with an authentic sample. A 50/50 mixture with hexanal DNPH, m.p. 103°, was depressed and melted at 85 -90°.

Addition of propargylmagnesium bromide to propargyl alcohol.

48 g (2 mols) magnesium, 0.1 g $HgCl_2$, 400 ml dry ether and a solution of 99 g propargyl bromide (0.84 mol) + 300 ml ether were reacted at -25° by the procedure given in the syntheses of 1-phenyl -3-butyn-1-ol (see page 152). A solution of 15 g (0.27 mol) of propargyl alcohol in 100 ml dry ether was added to the cold Grignard prepared above, over a period of two hours, while allowin the flask to warm from the heat of the reaction. After stirring for fifteen hours the mixture was worked up in the usual manner. Preparative v.p.c. gave 6.80 g (26.4%) of product, b.p. 89-90° (30 mm), n_D^{28} 1.4705. 100 gave the following analysis and spectra.

Anal. Calcd. for C_6H_8O : C, 74.97 ; H, 8.39.

Found: C, 74.53 ; H, 8.62.

The infrared spectrum showed bands at 3400(s),3300(spike), 3080(w),2870(m),2120(w),1650(m),1420(m),1200(w),1290(w),1280(w), 1060(s),1020(s),990(s),905(s), and 620(s) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a triplet at 2.2 (1H, acetylenic), a multiplet centered at 3.0 (2H,aliphatics), a broad singlet at 4.30 (1H,hydroxyl,collapses on addition of D_2O), a singlet at 4.1 (2H,aliphatics), and a multiplet centered at 5.2 (2H,methylene).

Hydrogenation of 2-methylene-4-pentyn-1-ol (100).

A 0.410 g (4.28 mmols) sample of the alcohol, in pentane, over Pd/C, was found to absorb 450 ml of hydrogen at 293° K which corres-

ponded to 145% of the 310 ml theoretically required to saturate three double bonds. The catalyst was filtered off and the pentane evaporated. Extensive hydrogenolysis appeared to have occurred as less than 25% of the initial alcohol volume was recovered. V.p.c. analysis showed the material to contain four products. Two low boiling constituents (17% of the mixture) were probably residual pentane and 2-methylpentane. The major product (62%) had a v.p.c. retention time equal to that of authentic 2-methylpentanal. The longest eluting product (21%) gave a v.p.c. retention time equal to that of authentic 2-methylpentanol. The hydrogenated product was dissolved in ethanol and was then treated with 2,4-dinitrophenylhydrazine reagent. The resulting precipitate was recrystallized twice from ethanol to yield yellow crystals, m.p. 98-100° (lit.[62] m.p. 103°). The crystals showed no melting point depression on admixture with an authentic sample of 2-methylpentanal-2,4-dinitrophenylhydrazone.

Addition of allylmagnesium chloride to allyl alcohol.

The Grignard reagent prepared from 60 g (2.5 mols) magnesium and 77 g (1 mol) allyl chloride was treated with 19 g (0.33 mol) of allyl alcohol. The yield was 4.10 g (13%), b.p. 56° (12 mm), n_D^{21} 1.4347.

Anal.			
	Calcd. for $C_6H_{12}O$:	C, 71.95 ;	H, 12.08.
	Found:	C, 71.81 ;	H, 11.80.

Compound 106 had the following spectral properties.

The infrared spectrum showed bands at 3400(s),3080(m),2960 (s), 2900(s),2870(s),1640(m),1450(m),1430(m),1410(m),1380(m),1210(w), 1090(w),1040(s),990(s),950(w),910(s), and 870(w) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a distorted doublet at 0.95 (3H,methyl), a multiplet at 1.90 (3H,allylic + methine), a singlet overlapping a doublet centered at 3.4 (3H,hydroxyl + aliphatics), which collapsed to a clean doublet (2H) at 3.4 on addition of D_2O, a multiplet at 5.0 (2H,terminal vinyl) and a multiplet centered at 5.8 (1H,internal vinyl).

Hydrogenation of 2-methyl-4-penten-1-ol (106)

A 0.879 g (8.79 mmols) sample of the alcohol in pentane over 10% Pd/C was found to absorb 235 ml of hydrogen at 295°K which corresponds to 109% of the 215 ml theoretically required to saturate one double bond. The catalyst was removed by filtration and the pentane evaporated yielding a colorless liquid. V.p.c. of the hydrogenated product showed a low boiling constituent (10% of the mixture), believed to be residual pentane. A higher boiling product (10%) had a v.p.c. retention time identical to that of authentic 2-methylpentanal. The major hydrogenation product, isolated by preparative v.p.c., had v.p.c. retention time and infrared spectrum identical to those of authentic 2-methylpentanol but different from those of authentic 1-hexanol.

The aldehydic component was isolated as its 2,4-dinitrophenylhydrazone. Recrystallization from ethanol/water gave yellow crys-

tals, m.p. 104-105.5°(lit.[62] m.p. 103°) which showed no melting point depression on admixture with the authentic derivative of 2-methylpentanal.

Addition of benzylmagnesium chloride to propargyl alcohol.

The Grignard reagent prepared from 60 g (2.5 mols) Mg and 154 g (1.25 mols) benzyl chloride was treated with 19.5 g propargyl alcohol (0.35 mol). The yield was 5.70 g (12%) b.p. 96-97° (2 mm), n_D^{25} 1.5427. Compound 101 gave the following spectra.

The infrared spectrum showed bands at 3400(s),3050(m),3040(m), 3010(m),2920(m),2870(m),1640(m),1600(m),1490(s),1450(s),1435(m), 1400(m),1075(m),1055(s),1030(s),990(m),900(s),840(w),825(w),740(s) and 700(s) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a broad singlet at 3.0 (1H,hydroxyl), a singlet at 3.20 (2H,methylene), a singlet at 3.90 (2H,benzylic), broad singlets with fine splitting at 4.85 and 5.10 (2H,olefinics) and a singlet at 7.20 (5H,phenyl).

Hydrogenation of 3-phenyl-2-methylene-1-propanol (101)

A 1.90 g (1.28 mmols) sample of the alcohol, in pentane, over 10% Pd/C, absorbed 225 ml of hydrogen at 300°K which corresponded to 72% of the 316 ml theoretically required to saturate one double bond. Analysis by v.p.c. showed three products. The low boiling constituent (29%) had a retention time in line with isobutyltoluene. The major product (62%) had a v.p.c. retention time in line with

that expected for 2-methyl-3-phenylpropanal. The remaining high boiling product had a v.p.c. retention time in line with that expected for 2-methyl-3-phenyl-1-propanol. Two derivatives of the major hydrogenation product were prepared. Recrystallization of the 2,4-dinitrophenylhydrazone from 1:1 ethanol/ethyl acetate yielded yellow crystals m.p. 120-122° (lit.[62]: m.p. 119° for DNPH derivative of 2-methyl-3-phenylpropanal). The semicarbazone, after recrystallization from ethanol/water, gave m.p. 118-121° (lit.[62]: m.p. 123-4°).

Addition of allylmagnesium chloride to 3-butyn-2-ol.

The Grignard reagent prepared from 30 g (1.25 mols) Mg, 250 ml ether and 54 g (0.7 mol) allyl chloride was treated with 13 g (0.185 mol) 3-butyn-2-ol in 50 ml ether. After stirring for 18 hours, the solution was decomposed and worked up in the usual manner. Preparative v.p.c. gave 4.63 g (22% yield) of pure compound. B.p. 64-5° (22 mm).

The infrared spectrum showed bands at 3400(s), 3030(m), 2960(s), 2900(m), 1640(m), 1425(m), 1410(m), 1370(m), 1280(m), 1100(m), 1070(m), 995(m), 960(m), and 905(s) cm^{-1}.

The n.m.r. spectrum (δ scale) showed a doublet at 1.25 (3H, methyl), a doublet at 2.75 (2H, aliphatic methylenes), a broad singlet at 3.0 (1H, hydroxyl, collapses with D_2O addition), a quartet at 4.1 (1H, methine), a multiplet at 4.8 (4H, terminal olefinic), and a multiplet at 5.6 (1H, internal olefinic). The 3-methylene-5-penten-2-ol (104) structure assignment is based solely on the above data.

The following attempted reactions did not afford Grignard addition products under the same conditions as those previously described and only afforded recovered starting materials.

With allylmagnesium chloride

a) 1-hexyne (109)

b) 2-methyl-3-butyn-2-ol (107)

c) 3-butyn-1-ol (92)

With n-propylmagnesium chloride

a) 1-hexyne

b) 2-methyl-3-butyn-2-ol

c) 3-butyn-1-ol

d) allyl alcohol (105)

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