Preparation of acetylenic alcohols by addition of propargyl Grignard reagents activated at low temperatures with mercury ion to α,β-unsaturated aldehydes and ketones.

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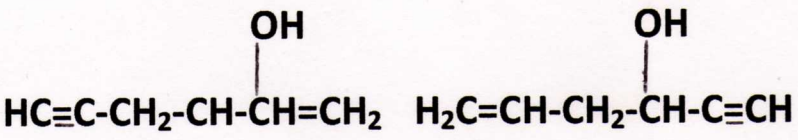
Abstract:

Addition of propargyl Grignard reagents to α,β-unsaturated aldehydes and ketones, with Grignards synthesized at low (-30 to -10 ^{o} C) temperatures and activated at theses temperatures by trace amounts of mercuric chloride, gave acetylenic alcohols in good yields. No trace of products resulting from rearrangement of propargyl Grignards to internal acetylenic or allenic species could be detected. In contrast, room temperature reactions gave alcohol product mixtures resulting from the rearrangement of propargyl Grignards to internal alkynyl or allenyl Grignards. This synthetic modification is of great utility in preparation of alcohol precursors for annulene synthesis [1] or acetylenic oxy Cope rearrangements [2].

Discussion:

Six carbon acetylenic alcohols functionalized at the 3-position, such as 1-hexen-5-yne-3ol, (1), 5-hexen-1-yne-3-ol, (2), and 1,5-hexadiyne-3-ol (3), find utility as precursors for annulene synthesis[1] in the case of 3, and as precursors for acetylenic oxy- Cope rearrangements[2], in the case of 1, 2 and 3.



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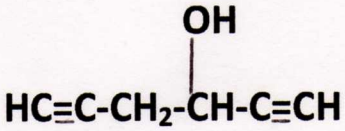

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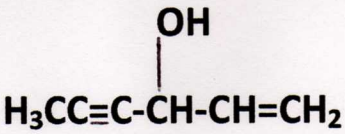
Standard Grignard procedures involve activation of the Grignard reagent with iodine and heating, followed by addition of the halide to complete the reaction. However, for synthesis of structures 1-3 or other acetylenic alcohols, this procedure risks rearrangement of the propargyl Grignard to an internal alkyne or allenic Grignard. For example, a room temperature standard Grignard synthesis of 1-hexen-5-yne-3ol (1) gives an approximate 50/50 mixture of 1 with the rearranged internal alkyne product 1-hexen-4-yn-3ol (4).



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In contrast, low temperature reaction, with the Grignard activated with traces of mercuric chloride, gives 1 in high yield with no trace of rearranged product. Likewise, 2, 3 and many other acetylenic alcohols were prepared in fair to excellent yield by this procedure, with no traces of rearranged internal alkyne or allenic products. Their synthesis and characterization are detailed in the experimental

section, alcohols 5-11. The mercuric chloride is postulated to form an active amalgamated surface on the magnesium during the Grignard synthesis, allowing the Grignards to form readily at low temperatures. At these temperatures rearrangements to internal alkyne or allenic Grignards do not occur.

Experimental Section

The technique of "flash distillation" was often used to remove non volatile materials from crude reaction mixtures. The procedure consisted of slowly dropping the material into a 3-neck flask heated to a temperature well above the expected distilling temperature, while maintaining the system under appropriate reduced pressure. The volatile constituent was trapped with a water condenser and collected. Non volatile materials accumulated in the still pot.

Preparation of 1-hexen-5-yn-3ol, (1), Attempted normal Grignard procedure, isolation of 1-hexen-4-yn-3ol (4).

A one liter three neck flask was equipped with a mechanical stirrer, heating mantle, dropping funnel, nitrogen inlet, Friedrich condenser and calcium chloride drying tube. It was charged with 0.1g mercuric chloride, 20g (0.83 mol) magnesium turnings, 4g redistilled propargyl bromide and 200 ml diethyl ether dried over sodium wire. The mixture was warmed, with stirring, until reaction commenced as evidenced by reflux of the ether. A solution of 56g redistilled propargyl bromide (total 0.5 mol) in 150ml dry ether was then added drop wise, with stirring, over three hours. The reaction was stirred for

one hour, after which a solution of 21g (0.38 mol) of redistilled acrolein in 150ml dry ether was added drop wise over two hours. After standing for one half hour, the mixture was decomposed over ice/ammonium chloride. The ether and aqueous layers were separated and the aqueous layer shaken with two 50ml ether portions. The combined ether layers were shaken with 50 ml water to remove salts and then dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam both in a fume hood yielded a dark brown oil. The oil was flash distilled under water aspirator pressure, yielding only 3.5g of volatile material. Vapor phase chromatography showed two products in approximately a 1:1 ratio. One product was shown by IR and NMR to be the desired 1-hexen-5-yn-3ol, (1) , while the other proved to be the isomeric 1-hexen-4-yn-3ol, (4). Several modifications of the above procedure, involving reaction times or changing amounts of one or more reactants, failed to increase the amount of volatile product. The undesired internal acetylenic isomer 4 was also always present. Therefore this procedure was abandoned.

Characterization of 1-hexen-4-yne-3ol, (4).

This compound, produced during the standard Grignard synthesis of 1, was isolated by preparative v.p.c. b.p. 147-9 ^{o}C, n_D^{29} 1.4695.

IR (neat film), 3400(s), 3080 (m), 2950 (m), 2970 (w), 2900(w), 2200 (m), 1650 (m), 1400 (s), 1265 (s), 1150(s), 1010 (m), 985 (s), and 920 (s), and 800 (s) cm^{-1}.

^{1}H NMR (60 MHz,$CDCl_3$) δ 1.85 (d,3H, J=2Hz, methyl), 2.95 (s, broad, 1H, hydroxyl), 4.8 (m, 1H. methine), 5.3 (m, 2H, terminal vinyl), 5.9 (m, 1H, internal vinyl).

<u>Low temperature mercuric chloride catalyzed synthesis of 1-hexen-5-yne-3-ol, (1).</u>

In order to avoid the internal rearrangement of the propargyl Grignard reagent, a modification of the procedure reported by Sondheimer [1], was utilized.

A one liter three neck flask was equipped with a mechanical stirrer, heating mantle, dropping funnel, nitrogen inlet, Friedrich water condenser and calcium chloride drying tube. It was charged with 0.1g mercuric chloride, 24 g (1 mol) magnesium turnings and 4 g redistilled propargyl bromide. The mixture was stirred, then gently warmed until reaction commenced, as evidenced by vigorous ether reflux. The flask was then immersed in a dry ice/acetone bath maintained at approximately -30^o C. A solution of 67 g redistilled propargyl bromide (total 0.60 mol) and 25 g freshly distilled acrolein (0.45 mol) in 200 ml dry ether was then added drop wise, with vigorous stirring, over three hours. The bath was maintained at ~-25^o C. The mixture was stirred for an additional half hour, let come to room temperature, and decomposed over ice/ammonium chloride. The ether layer was separated and the aqueous layer shaken with two 50ml ether portions. The combined ether layers were shaken with several small portions of de ionized water and dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam both in a fume hood yielded a dark brown oil. Flash distillation of the oil, under water aspirator pressure, afforded 29.2 g of crude distillate, b.p, 53-4^o

C (20mm), containing about 5% low boiling impurities. Careful re distillation yielded 24 g of product (56% based on the amount of acrolein used), which gave only a single v.p.c. peak, and which contained no isomeric internal acetylenic alcohol 4.

b.p. 53-44 ^{o} C (20mm), n_D^{25} 1.4670 (lit. [3]: b.p. 49^{o}C (20mm),

Anal. Calc. For C_6H_8O : C, 74.97; H, 8.39.

Found: C, 75.10; H, 8.61

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s) 3120(w), 3070 (w), 2950 (m), 2140 (w), 1650 (m), 1440 (s), 1130 (s), 1040 (s), 990 (s), 930 (s) cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 2.05 (1H, acetylenic), 2.45 (d of d, 2H, aliphatic), 2.75 (s, broad, 1H, OH), 4.25 (q, 1H, methine), 5.25 (2H, terminal vinyl), 5.90 (1H, internal vinyl).

Low temperature mercuric chloride catalyzed synthesis of 3-Methyl-1-hexen-5-yne-3ol, (5).

This compound was prepared in a totally analogous fashion to 1 above, by the low temperature reaction of propargyl magnesium bromide with methyl vinyl ketone.

24 g (1 mol) magnesium was reacted with 59 g (0.7 mol) redistilled propargyl bromide and 27 g (0.39 mol) of redistilled methyl vinyl ketone. Workup as in compound 1 gave 26.5 g (62%) of v.p.c pure material, b.p. 54-5^{o}/25mm, n_D^{22} 1.4576, d_4^{25} 0.8930.

IR (neat film), 3400(s), 3300 (spike, s) 3120(w), 3040 (m), 2950 (m), 2930 (m), 2910 (m), 2120 (w), 1640 (m), 1450 (s), 1410(s),1370 (s),

1270(m), 1240(m), 1170 (s), 1110 (s), 995 (s), 920(s), 870 (m), 760 (m), 750(m) and 650 (m) cm^{-1}.

^1H NMR (60 Mhz,$CDCl_3$) δ 1.40 (s, 3H, methyl), 2.45 (d , 2H, aliphatics), 3.35 (s, broad, 1H, OH),), 5.20 (d of d, 2H), terminal vinyl), 6.10 (m, 1H, internal vinyl).

<u>Preparation of 5-hexen-1-yne-3-ol, (2)</u>

This Compound was prepared by the addition of freshly prepared propargyl aldehyde[3] to a cooled solution of allyl magnesium chloride in ether.

A one liter three neck flask was equipped with a mechanical stirrer, heating mantle, dropping funnel, nitrogen inlet, Friedrich water condenser and calcium chloride drying tube. It was charged with 300 ml dry diethyl ether and 34 g (1.4 mol) of magnesium turnings. A crystal of iodine was added, followed by a solution of 54 g (0.7 mol) of redistilled allyl chloride in 100 ml dry ether, which was added drop wise with stirring over two hours. During the course of the addition a thick white Grignard complex precipitated, which was re dissolved by addition of 1 ml dry tetrahydrofuran. After the addition was complete, the flask ws immersed in a dry ice /acetone bath maintained at -25 to -30 ^{o} C. Then 11 g (0.2 mol) of freshly distilled propargyl bromide in 100 ml dry ether was added dropwise over one hour, with bath temperature maintained as above. The reaction was allowed to reach room temperature and decomposed over ice/ammonium chloride. The ether layer was separated and the aqueous layer shaken with two 50ml ether portions. The combined ether layers were shaken with 2o ml of deionized water and dried over anhydrous magnesium sulfate. Evaporation of the ether on a

steam both in a fume hood yielded a light yellow oil. The oil was first flash distilled under water aspirator pressure then carefully re distilled. The fraction boiling at 67-9 ^{o} C (35 mm) was collected and appeared to be homogeneous on v.p.c. The yield of 2 was 11g, (57%), based upon the amount of propargyl aldehyde used.

b.p. 67-9 ^{o} C (35mm), n_D^{21} 1.4580, d_4^{25} 0.8953.

<u>Anal.</u> Calc. For C_6H_8O : C, 74.97; H, 8.39.

Found: C, 74.93; H, 8.42

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s), 3080 (m), 2900 (m), 2130 (w), 1650 (m), 1435 (m), 1300 (m), 1260 (w), 1220 (w), 1120 (m), 1030 (s), 990 (s),955 (m), and 920 (s), 880 (w), 865 (w), 800 (w), 640 (s), cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 2.50 (4H,m, allylic, acetylenic and hydroxyl, collapsed with D_2O to 3H multiplet), 4.43 (m, 1H, methine), 5.20 (2H, terminal vinyl), 5.90 (1H, internal vinyl).

<u>Low temperature mercuric chloride catalyzed synthesis of 1,5-hexadiyne-3ol, (3).</u>

In order to avoid the internal rearrangement of the propargyl Grignard reagent, a modification of the procedure reported by Sondheimer [1], was utilized.

A one liter three neck flask was equipped with a mechanical stirrer, heating mantle, dropping funnel, nitrogen inlet, Friedrich water condenser and calcium chloride drying tube. It was charged with 0.1g mercuric chloride, 24 g (1 mol) magnesium turnings and 3 g

redistilled propargyl bromide. The mixture was stirred, then gently warmed until reaction commenced, as evidenced by vigorous ether reflux. The flask was then immersed in a dry ice/acetone bath maintained at approximately -35° C. A solution of 57 g redistilled propargyl bromide (total 0.50 mol) and 14 g freshly prepared and distilled propargyl aldehyde (0.26 mol) in 150 ml dry ether was then added drop wise, with vigorous stirring, over 3.5 hours. The bath was maintained at -30° C-40° C . The mixture was let come to room temperature, and decomposed over ice/ammonium chloride. The ether layer was separated and the aqueous layer shaken with two 50 ml ether portions. The combined ether layers were shaken with several 10 ml portions of de ionized water and dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam both in a fume hood yielded a dark brown oil. Flash distillation of the oil, under water aspirator pressure, followed by careful fractionation under water aspirator pressure, yielded 11.7 g of product (48% based on the amount of propargyl aldehyde used), which gave only a single v.p.c. peak, and which contained no isomeric allenic alcohol.

b.p. 79-80° C (25mm), n_D^{25} 1.4728 (lit.[1]: b.p. 73-5°C (20mm),

n_D^{25} 1.4728

IR (neat film), 3400(s), 3300 (spike, s),2900 (w), 2130 (w), 1420 (m), 1395 (m), 1300 (m), 1220 (m), 1190 (w), 1050 (s), 980 (w), 955(m), 935 (w), 880 (w), 850 (m), 810 (w), 790 (w), 705 (m), and 650 (s) cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 2.20 (t, 1H, acetylenic), 3.4 (s, broad, 1H, OH), 2.73 and 2.63 (overlapping doublets, 3H, aliphatics and acetylenic), 4.6 (triplet split into doublets, 1H, methine).

The following methyl substituted 1.5-hexadiyne-3-ols were synthesized using low temperature mercuric chloride catalyzed procedures entirely analogous to 1,5-hexadiyne-3ol, (3).

<u>3-Methyl-1,5-hexadiyne-3ol, (6).</u>

24 g (1 mol) Magnesium, 0.1 g mercuric chloride and 56 g (0.5 mol) redistilled propargyl bromide were treated with 23 g (0.34 mol) of redistilled methyl ethynyl ketone (Farchan Laboratories). The yield was 36.8 g (66%).

b.p. 50 ^{o} C (10 mm), n_D^{25} 1.4628

<u>Anal.</u> Calc. For C_7H_8O : C, 77.75; H, 7.46.

Found: C, 77.59; H, 7.30.

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s), 2980 (m), 2900 (w), 2120 (w), 1450 (m), 1420 (m), 1380 (s), 1360 (s), 1290 (m), 1260 (m), 1160 (m), 1130 (m), 1090 (s), 980 (w), 950(m), 940 (m), 910 (w), 875 (m), and 650 (s) cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 1.65 (s, 3H, methyl), 2.25 (t, 1H, acetylenic), 2.65 (1H, acetylenic), 2.65 (d, 2H, aliphatics). 3.30 (s. broad, 1H. hydroxyl).

4,4-Dimethyl-1,5-hexadiyne-3ol, (7).

24 g (1 mol) Magnesium, 0.1 g mercuric chloride and 42 g (0.31 mol) redistilled 3-brom-3-methyl-1-butyne were reacted with 15 g (0.28 mol) of freshly prepared propargyl aldehyde. The bromide was prepared by the reaction of phosphorous tri bromide with 2-methyl-3-butyn-2-ol (Airco Chemical Company). The yield of 7 was 7.55 g (22%).

b.p. 57-8 ^{o} C (10 mm), n_D^{28} 1.4613

Anal. Calc. For $C_8H_{10}O$: C, 78.65; H, 8.25.

Found: C, 78.80; H, 8.24.

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s), 2980 (m), 2940 (w), 2900 (w), 2120 (w), 1470 (m), 1390 (m), 1370 (m), 1310 (w), 1260 (m), 1210 (w), 1140 (w), 1060 (s), 1020 (m), 970 (w), 940(w), 860 (w), 650 (s) cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 1.35 (s, 6H, methyl), 2.25 (s, 1H, acetylenic), 2.55 (d, J=2Hz, 1H, acetylenic), 2.85 (d, 1H, J = 7Hz, 1H, hydroxyl, collapses with D_2O)). 4.23 (d of d, J_1 = 7 Hz, J_2 = 2 Hz, 1H. methine, which collapses to a doublet, J = 2Hz, on shaking with D_2O).

4-Methyl-1,5-hexadiyne-3ol, (8).

24 g (1 mol) Magnesium, 0.1 g mercuric chloride and 27 g (0.2 mol) redistilled 3-bromo-1-butyne were reacted with 10 g (0.18 mol) of redistilled propargyl aldehyde. The bromide was synthesized by the reaction of phosphorous tri bromide with redistilled 3-butyn-2-ol (Farchan Chemical Company). The yield of 8 was 4.70 g (24%).

b.p. 86-7 ^{o} C (40 mm), n_D^{24} 1.4653

Anal. Calc. For C_7H_8O : C, 77.75; H, 7.46.

Found: C, 78.26; H, 7.70.

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s), 2980 (m), 2940 (m), 2880 (m), 2120 (w), 1460 (m), 1380 (m), 1290 (m), 1260 (m), 1120 (m), 1080 (m), 1065 (m), 1030 (s), 975 (m), 880 (w), 835 (w), 795 (w), 755 (w), and 650 (s) cm^{-1}.

^1H NMR (60 Mhz,$CDCl_3$) δ 1.30 (two doublets, J = 7Hz, , 3H, diastereometric methyls), 2.25 (d, J =3 Hz, 1H, acetylenic), 2.60 (d, J = 2Hz, 1H, acetylenic), 2.80 (m, 1H, methine). 3.50 (s. broad, 1H. hydroxyl, collapses with D_2O), 4.50 (m, 1H, carbinol proton, which collapses to two overlapping sets of doublets of doublets upon shaking with D_2O).

Three additional acetylenic alcohols were prepared in analogous manner to the procedure described above for 1-hexen-5-yne-3-ol,(1).

1-Phenyl-3-butyne-1-ol (9) ,

5-Hexyne-3-ol (10)

2-Methyl-4-pentyne-2-ol (11).

The low temperature mercuric chloride catalyzed formation of propargyl magnesium bromide was utilized, followed by the low temperature reaction with the appropriate aldehyde or ketone at low temperatures. As for the propargyl Grignard reactions employed

above, no trace of internal acetylenic or allenic alcohols from Grignard rearrangements was detected.

<u>Low temperature mercuric chloride catalyzed synthesis of 1-Phenyl-3-butyne-1-ol, (9).</u>

In order to avoid the internal rearrangement of the propargyl Grignard reagent, a modification of the procedure reported by Sondheimer [1], was again utilized.

A one liter three neck flask was equipped with a mechanical stirrer, heating mantle, dropping funnel, nitrogen inlet, Friedrich water condenser and calcium chloride drying tube. It was charged with 0.1g mercuric chloride, 24 g (1 mol) magnesium turnings, 200 ml dry diethyl ether and 1 g redistilled propargyl bromide. The mixture was stirred, then gently warmed until reaction commenced, as evidenced by vigorous ether reflux. The flask was then immersed in a dry ice/acetone bath maintained at approximately -20°C. A solution of 46 g redistilled propargyl bromide (total 0.40 mol) in 150 ml dry ether was then added drop wise, with vigorous stirring, over three hours. The bath was maintained at ~-20°C. After the addition was complete, a solution of 26 g freshly re distilled benzaldehyde (0.25 mol) in 150 ml dry diethyl ether was added drop wise over two hours, while maintaining bath temperatures of ~-10°C to 0 °C. The mixture was allowed to come to room temperature and decomposed with stirring over excess ice/ammonium chloride, until two clear layers were present, and all excess magnesium chips and salts had dissolved. The upper ether layer was separated and the aqueous layer extracted twice with 50ml ether portions. The combined ether layers were

shaken twice with 25 ml de ionized water portions and dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam both in a fume hood yielded a light yellow oil.. Careful fractionation of the oil under pump vacuum pressure yielded 28 g of product (77% based on the amount of benzaldehyde used), which gave only a single v.p.c. peak, and which contained no isomeric internal acetylenic or allenic alcohols.

b.p. 80 ^{o} C (0.5 mm), n_D^{26} 1.5457, d_4^{29} 1.0265, (lit.[4]: b.p. 89^{o}C (1 mm), n_D^{20} 1.5470.

<u>Anal.</u> Calc. For $C_{10}H_{10}O$: C, 82.16; H, 6.90.

Found: C, 82.10; H, 6.92

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s) 3030(m), 2900 (m), 2120 (w), 1600 (w), 1490 (s), 1450 (s), 1420 (m),1390 (m), 1320 (m), 1205 (m), 1085 (m), 1050 (s), 1015 (s), 945 (m), 915 (m), 865 (m), 830 (w), 775 (m), 755 (s) and 700 (s) cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 1.95 (t, 1H, acetylenic), 2.50 (d of d, 2H, aliphatics), 3.50 (s, broad, 1H, OH), 4.70 (t, 1H, methine), 7.25 (5H, aromatics).

Low temperature mercuric chloride catalyzed synthesis of 5-hexyne-3-ol, (10). *

This compound was prepared by the low temperature procedure employed for 1-hexen-5-yn-3ol, (1). The major modification was the extension of the aldehyde/bromide solution to nine hours.

A one liter three neck flask was equipped with a mechanical stirrer, heating mantle, dropping funnel, nitrogen inlet, Friedrich water condenser and calcium chloride drying tube. It was charged with 0.1g mercuric chloride, 24 g (1 mol) magnesium turnings, 200 ml dry diethyl ether and 4 g redistilled propargyl bromide. The mixture was stirred, then gently warmed until reaction commenced, as evidenced by vigorous ether reflux. The flask was then immersed in a dry ice/acetone bath maintained at approximately -25° C. A solution of 67 g redistilled propargyl bromide (total 0.60 mol) and 8.4 g freshly distilled propionaldehyde (0.145 mol) in 200 ml dry ether was then added drop wise, with vigorous stirring, over nine hours. The bath was maintained at ~-25° C. Workup as previously described gave a brownish liquid which was flash distilled to remove non volatile material. Careful re distillation gave 6.5g of product (45% based on the amount of propionaldehyde used), which gave only a single v.p.c. peak, and which contained no isomeric internal acetylenic or allenic alcohols.

b.p. 44° C (10mm), n_D^{23} 1.4435, d_4^{25} 0.8555 (lit.[5]: b.p. 58-9°C (25mm), n_D^{20} 1.4437, d_{20} 0.8918.

Anal. **Calc. For $C_6H_{10}O$: C, 73.43; H, 10.27.**

Found: C, 73.48; H, 10.25

Satisfactory

IR (neat film), 3400(s), 3300 (spike, s), 2900 (s), 2850 (m) 2120 (w), 1460 (s), 1420 (m), 1335 (m), 1240 (m), 1100 (s), 1060 (m), 1030 (s), 990 (s), 950 (m), 930 (w), 900 (w), 875 (w), 845 (w) and 770 (w) cm^{-1}.

^1H NMR (60 Mhz,$CDCl_3$) δ 0.9 (t, 3H, methyl, 1.55 (q of d, 2H, aliphatic), 2.05, (t, iH, acetylenic,) 2.40, (m, 4H, methylene and hydroxyl, which collapsed to a d of d , 2H, on D_2O exchange), 3.67 (pentuplet, 1H, methane).

***We wish to thank Dr. Robert Proverb for synthesizing this compound.**

Low temperature mercuric chloride catalyzed synthesis of 4-pentyne-2-ol, (11).

This compound was prepared in a totally analogous fashion to 10 above, by the low temperature reaction of propargyl magnesium bromide with acetone.

24 g (1 mol) magnesium was reacted with 71 g (0.6 mol) redistilled propargyl bromide, 0.1 g mercuric chloride and 26 g (0.44 mol) of reagent acetone. Workup as in compound 10 above gave 23.0 g (52%) of v.p.c pure material, b.p. 124°, n_D^{24} 1.4375, d_4^{25} 0.8729. (lit. [6]: b.p. 124-7°C (756 mm), n_D^{20} 1.4381.

IR (neat film), 3400(s), 3300 (spike, s), 2950 (s), 2920 (m) 2120 (m), 1470 (m), 1420 (m), 1380 (s), 1370 (s), 1300 w), 1240 (m), 1210 (m), 1140 (s), 1060 (m), 1010 (w), 985 (s), 950 (m), 900 (s), 870 (w), and 760 (m) cm^{-1}.

^{1}H NMR (60 Mhz,$CDCl_3$) δ 1.25 (s, 6H, methyl), 2.05, (t, 1H, J = 2.5Hz, acetylenic), 2.25 (d, 2H, J = 2.5Hz aliphatic), 3.35 (s, broad, !H, hydroxyl).

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