Formation of 1-cyclopenten-1-ylcarbinols from the reaction of excess allylmagnesium chloride with acetylenic alcohols

John H. MacMillan and Alfred Viola
Department of Chemistry, Northeastern University, Boston,
Mass 02115

Abstract

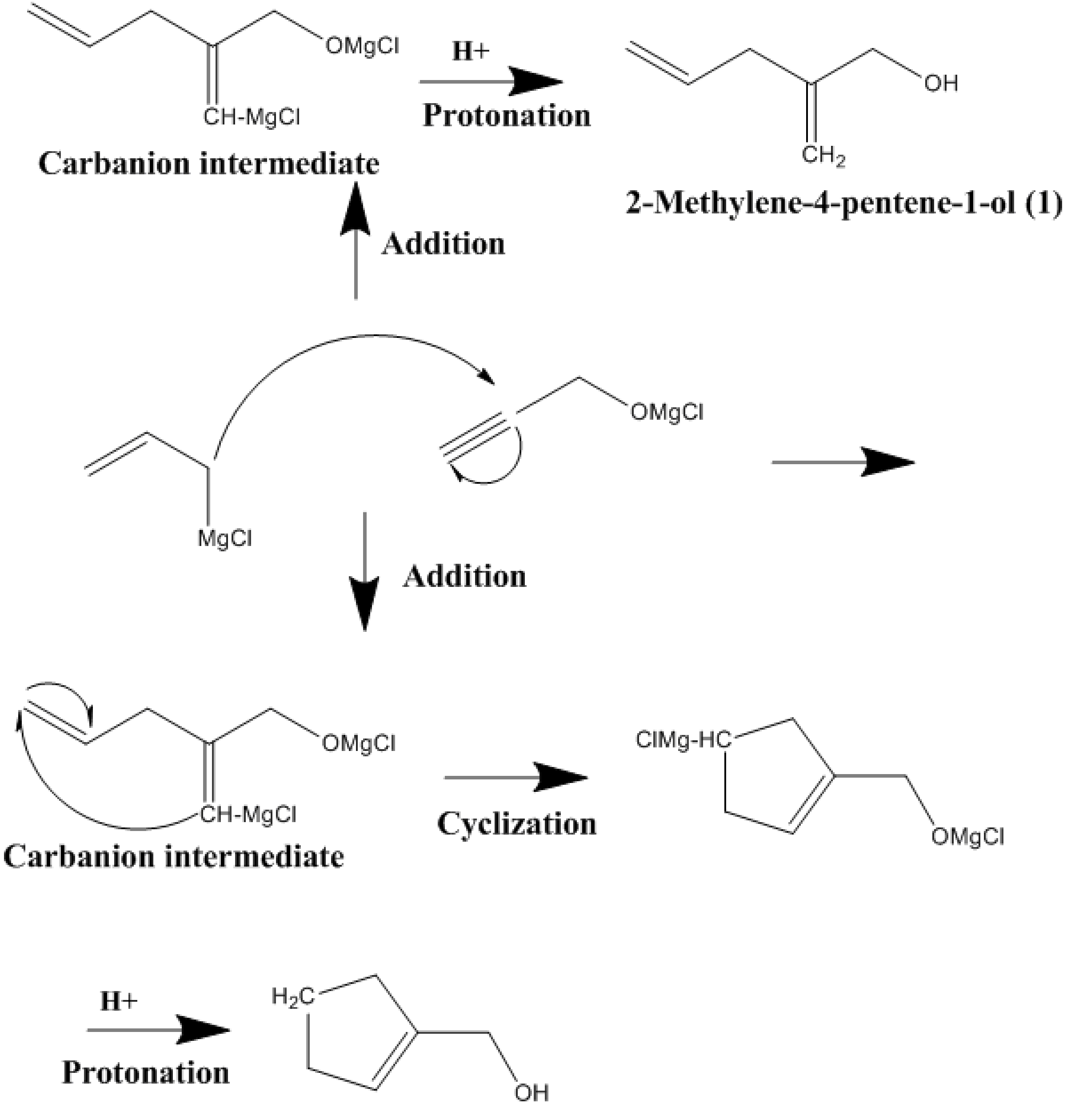
1-Cycopent-1-yl carbinols are shown to be unexpected byproducts from the reaction of excess allyl Grignard with acetylenic alcohols. A mechanistic scheme is proposed.

Discussion

1-Cyclopenten-1-yl carbinols were shown to be unexpected byproducts of the reaction of excess allyl magnesium chloride with the internal alkyn carbon of propargyl alcohol or 3-butyn-2-ol, which yield methylene substituted unsaturated alcohols [1]. Propargyl alcohol with allyl magnesium chloride yields, in addition to the expected addition product, 2-methylene-4-pentene-1-ol (1), the cyclic product 1-cyclopenten-1-ylmethanol (2) in 5-10% yields. Likewise, the reaction of excess allyl magnesium chloride with 3-butyn-2-ol yields, in addition to the expected addition product, 3-methlyne-5-hexene-2-ol, (3), the cyclic product 1-cyclopenten-1-ylethanol (4) in 5-10% yields. See plates 1 and 2.

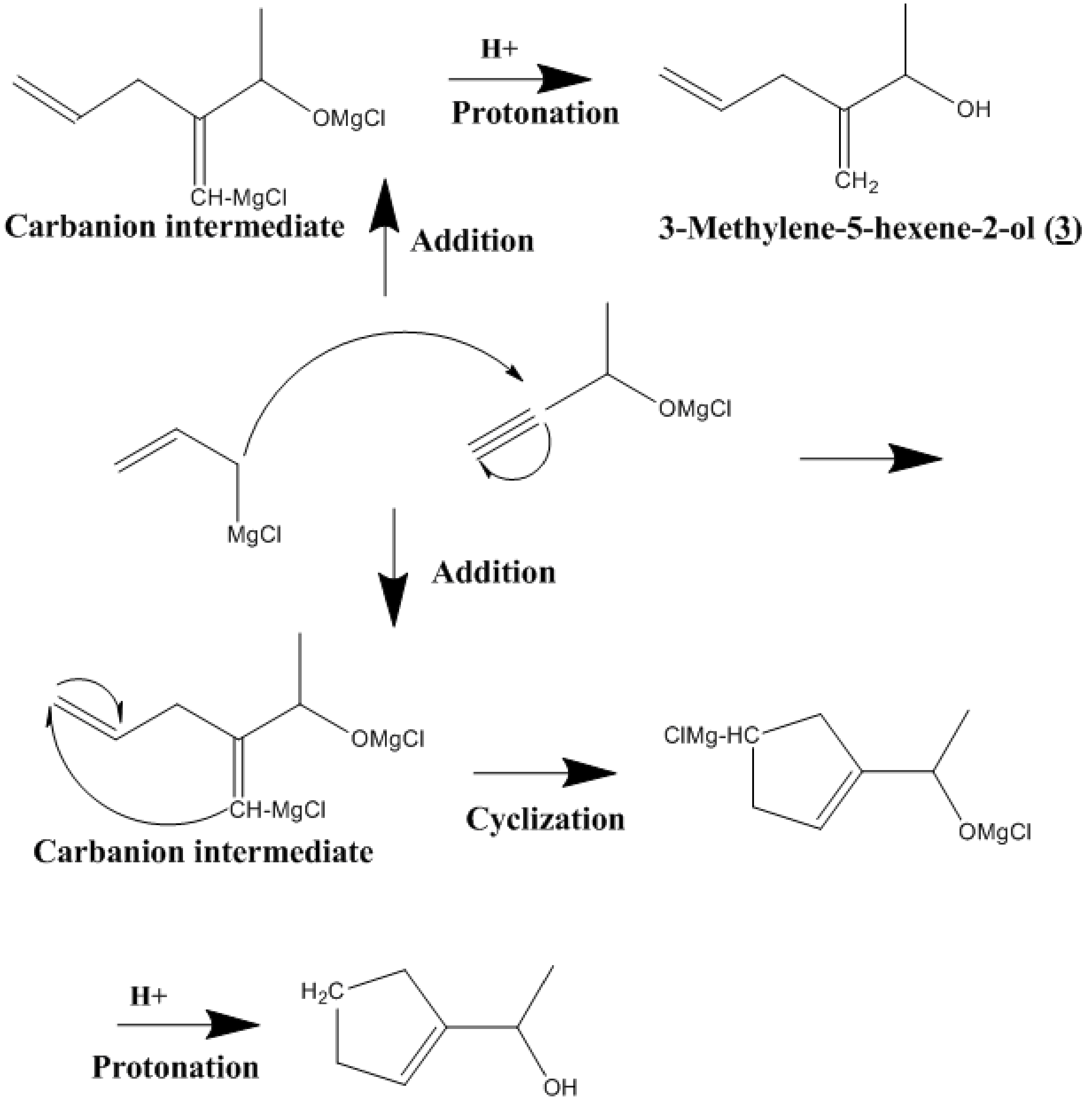
These compounds are postulated to arise from intra molecular cyclo addition of an intermediate vinyl carbanion to the terminal vinyl group of the intermediate, followed by hydrolysis. The vinyl carbanion is probably complexed to magnesium ion, which should facilitate additions to the terminal double bond via a cyclic transition state. These reactions are of limited synthetic utility for preparing the cyclopentyenyl carbinols. Longer reaction times and larger Grignard/alcohol molar ratios may give more cyclopentenyl products.

Plate 1, Reaction of allylmagnesium chloride with propargyl alcohol



1-Cyclopent-1-ylmethanol (2)

Plate 2, Reaction of allylmagnesium chloride with 3-butyn-2-ol



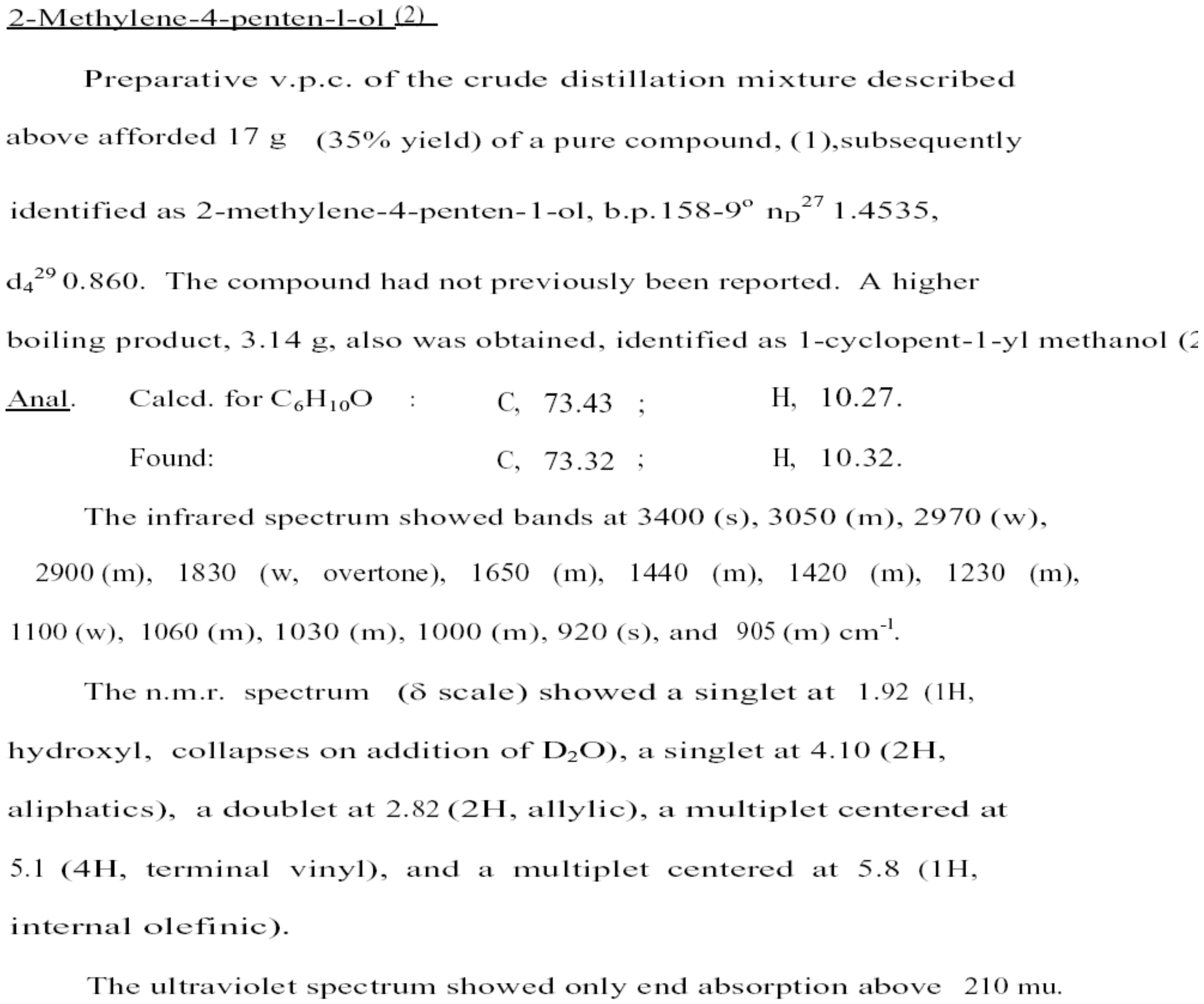
3-Methylene-5-hexene-2-ol (<u>3</u>)

1-Cyclopent-1-ylethanol (<u>4</u>)

Experimental:

Addition of allyl magnesium 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) of 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 drop wise over six hours. Midway through the addition 50 ml of dry tetrahydrofuran was added to re dissolve 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, drop wise, 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 steam bath, 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-l-ol (2)

Preparative v.p.c. of the crude distillation mixture described above afforded 17 g (35% yield) of a pure compound, (1),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, 3.14 g, also was obtained, identified as 1-cyclopent-1-yl methanol (

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

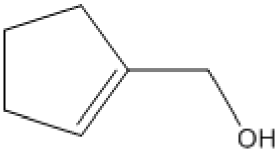
Found: C, 73.32 ; H, 10.32.

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 mu.

3.14 g of the cyclic product above were obtained by preparative v.p.c. Spectroscopic analysis showed the product to be 1-cyclopenten-1-ylmethanol (2)



1-cyclopenten-1-ylmethanol (2)

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

Found: C, 73.29 ; H, 10.44.

b.p.188-90º , n_D^{27} 1.4767

The infrared spectrum (neat) showed bands at 3400 (s), 3030 (w), 2900 (s), 2850 (s), 1650 (w), 1440 (m), 1420 (m), 1360 (w), 1320(w), 1300 (w), 1265 (w),1220(w),1100 (w), 1150(w),1045 (s), 1050 (m), 985(m), 950(w), 935(w), 905 (w), and 825(w), cm^{-1}.

The pmr spectrum (60MHz), $CDCl_3$, showed a multiplet at δ2.20 (6H, aliphatics), a broad singlet at 3.95 (1H, hydroxyl, collapses on addition of D_2O), a multiplet centered at 4.15 (2H, deshielded aliphatics), and a multiplet centered at 5.60 (1H,internal olefinic).

The ultraviolet spectrum showed only end absorption above 210 mu.

Catalytic hydrogenation of the compound gave a 139% hydrogen absorption of that theoretical for saturating one double bond and yielded a saturated aldehyde as the major product, due to the now well documented [2] hydrogen transfer reaction of allylic alcohols on palladium catalysts. Treatment of the compound with 2,4-dinitrophenylhydrazine reagent by the procedure of Shriner and Fuson [3] gave yellow powder. Recrystallization from ethanol/water gave yellow crystals, m.p. 159-161º, lit: [4], m.p. 159.5-160º.

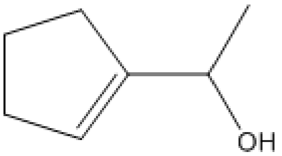
Addition of allyl magnesium chloride to 3-butyn-2-ol .

The Grignard reagent prepared from 30 g (1.25 mole) 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. (3) 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 D2O 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-hexen-2-ol (3) structure was assigned solely on the above data.

Preparative g.c. of the above mixture also gave 4,32 g of 1-cyclopenten-1-ylethanol(4).



1-cyclopenten-1-ylethanol (4)

b.p. 76° (22mm)

The infrared spectrum (neat) showed bands at 3400 (s), 3030 (w), 2960 (s) 2900 (s), 2850 (s), 1640 (w), 1440 (m), 1400 (m), 1370 (m), 1310(m), 1290 (m), 1250 (m),1205 (w),1100 (w), 1155(m),1070 (s), 1040 (m), 1025 (m), 1005 (m) 990(m), 945(m), 910(w), 890 (w), 850 (w) and 820(m), cm^{-1}.

The pmr spectrum (60MHz), $CDCl_3$, showed a doublet at δ 1.25 (3H, J= 6Hz, methyl), a multiplet at 2.10 (6H, aliphatics), a broad singlet at 3.45 (1H, hydroxyl), a quartet centered at 4.25 (1H, J= 6Hz, methine), and a multiplet centered at 5.40 (1H,internal olefinic).

References:

1. John H. MacMillan and Alfred Viola,"Addition of unsaturated propargyl, allyl and benzyl Grignard Reagents to acetylenic or allylic alcohols.", internet archive, 2012.

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2. J. Wiemann and G. Laude, C. R. Acad. Sci. Paris, 226, 345, (1948).

3. P. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th ed., John Wiley and Sons, Inc., New York, N. Y., 1964.

4. http://chemyq.com/En/xz/xz3/28128hhogo.htm