

then ether and dried; yield, 4.3 g., m. p. 328–330° with decomposition.

The other members of the series were prepared in a similar manner. *p*-Acetamidobenzenesulfonic acid, 0.12 mole was dissolved in about 200 ml. of aqueous (50–75%) ethanol and exactly neutralized with sodium hydroxide; 0.05 mole of the alkyl dihalide was added and the mixture refluxed for from eight to twelve hours. If the acetamidophenyl sulfone had precipitated, it was removed by filtration, otherwise it was precipitated by pouring the mixture into 700 ml. of water. The crude material was purified by recrystallization from ethanol.

The hydrolysis to the aminophenyl sulfone dihydrochloride and to the free amine was carried out as described above.

We wish to thank Parke, Davis and Company for generously supplying the *p*-acetamidobenzene-sulfonyl chloride and the pentamethylene bromide used in this work.

Summary

A series of polymethylene-bis-(*p*-acetamidophenyl sulfones) has been prepared. These have been hydrolyzed to the corresponding amino compounds and their properties recorded.

DETROIT, MICHIGAN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

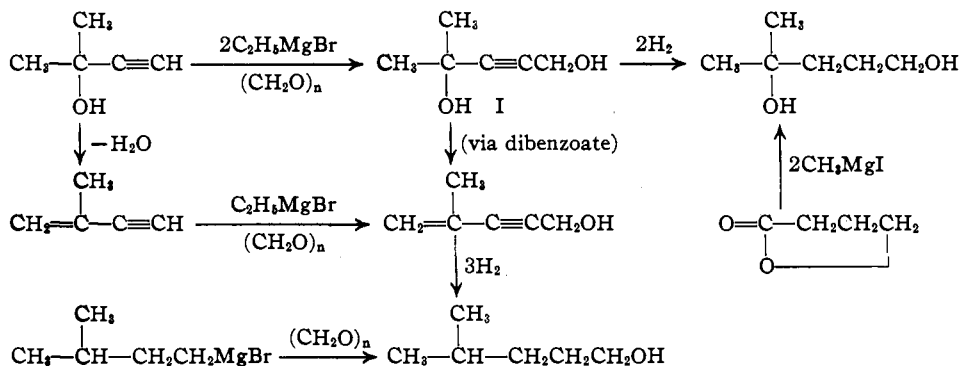
The Reaction of Bromomagnesium Derivatives of Acetylenic Alcohols with Formaldehyde

BY MELVIN S. NEWMAN, WILLIAM S. FONES¹ AND WILLIAM T. BOOTH, JR.

The organomagnesium compounds of acetylenic alcohols have been shown to react with a variety of carbonyl functions² including aldehydes (but not formaldehyde), ketones and carbon dioxide. In this paper we show that the dibromomagnesium compound of dimethylethynylcarbinol reacts smoothly with formaldehyde to yield 4-methyl-2-pentyne-1,4-diol,³ I. This compound was characterized by means of its di-*p*-nitrobenzoate and a monotrityl derivative. On treatment with acetyl chloride and pyridine under conditions similar to those involved in the preparation of the di-*p*-nitrobenzoate, a monoacetate was formed. On catalytic reduction of I two moles of hydrogen were absorbed to yield 4-methyl-1,4-pentanediol

authentic glycol made by treating butyrolactone with methylmagnesium iodide.⁴

The selective dehydration of the tertiary hydroxyl was accomplished by pyrolysis of the liquid dibenzoate of I. The structure of the resulting 4-methyl-4-penten-2-yn-1-ol obtained on hydrolysis was established by comparison with an authentic sample using the crystalline 3,5-dinitrobenzoate. The structure of the authentic 4-methyl-4-penten-2-yn-1-ol, prepared by treating 3-methyl-3-buten-1-ynylmagnesium bromide with formaldehyde, was supported by its method of synthesis and the absorption of 3 moles of hydrogen on catalytic reduction to form 4-methylpentanol-1. These reactions are summarized in the chart.



the structure of which was established by comparison of the di-*p*-nitrobenzoate with that of the

(1) Part of the material herein presented was taken from the thesis presented by William S. Fones to the Ohio State University, 1942, for the M. A. degree.

(2) Ouvert, *Compt. rend.*, **146**, 294 (1908); Zalkind and Ivanov, *J. Gen. Chem., U. S. S. R.*, **11**, 803 (1941); Marvel and co-workers, *THIS JOURNAL*, **58**, 972 (1936); **61**, 2006 (1939); **62**, 1880 (1940); *J. Org. Chem.*, **7**, 93 (1942); Heilbron and co-workers, *J. Chem. Soc.*, **140**, 141 (1944).

(3) A compound, b. p. 102–104° at 2 mm. made by condensing dimethylethynylcarbinol with aqueous formaldehyde has been reported, U. S. Patent 2,238,471 (1941), but no proof of structure was given.

In addition to I, we have also prepared 3-(1-hydroxycyclohexyl)-2-propyn-1-ol by condensing the bromomagnesium derivative of 1-ethynylcyclohexanol with paraformaldehyde.

Experimental⁵

Dimethylethynylcarbinol.—In a 5-liter three-necked flask containing 2.5 liters of liquid ammonia and equipped with a sealed stirrer and an all-metal reflux condenser

(4) Henry, *Compt. rend.*, **143**, 1221 (1907).

(5) All melting points corrected. Analyses marked ^a by J. E. Varner, ^b by The Arlington Laboratories, Fairfax, Virginia. ^c by Sterling Olsen.

cooled with Dry Ice and acetone, was placed 3.6 g. of hydrated ferric nitrate as catalyst.⁶ Twelve gram moles of clean sodium cubes were gradually added during forty minutes. A rapid stream of acetylene, purified by bubbling through sulfuric acid and passing through a tower of soda lime and calcium chloride, was passed in until the milky white color initially produced was entirely displaced by gray-black. While a slow stream of acetylene was kept flowing through the apparatus, 12.9 moles of dry acetone was added dropwise during one and one-half hours. Stirring was continued for another half hour and the reaction mixture was then neutralized by adding 14 moles of ammonium chloride during ninety minutes. The ammonia was allowed to evaporate and the product was extracted with ether. On fractionation through a 10-12 plate packed column, there was obtained 677 g. (67%) of pure dimethylethynylcarbinol, b. p. 103° at 750 mm.

4-Methyl-2-pentyne-1,4-diol, I.—One hundred sixty-eight grams (2 moles) of dimethylethynylcarbinol was added dropwise during about one hour with good stirring, to 2 liters of 2 *M* ethylmagnesium bromide. Then 170 g. (5.7 moles) of dry trioxymethylene was added. Unless a powerful stirrer is used at this point, the complex which separates will form a hard cake which cannot be stirred and which is extremely difficult to hydrolyze. After being stirred for twelve hours at room temperature and refluxed for one hour, the mixture was decomposed with ammonium chloride solution. The aqueous portion was continuously extracted with ether for five days. The ether layers were then combined and on fractionation there was obtained 139 g. (61%) of I, b. p. 102-103° at 2 mm., n_D^{20} 1.4702.

Anal.^b Calcd. for $C_8H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.0, 63.0; H, 8.8, 8.8.

Derivatives of I.—The derivatives were prepared by treating I in ethereal pyridine solution with the following chlorides: acetyl, benzoyl, *p*-nitrobenzoyl and trityl. In the first three cases the reaction was rapid but in the last case the mixture was allowed to stand overnight to go to completion.

1-Acetoxy-4-hydroxy-4-methyl-2-pentyne, a colorless liquid, b. p. 77° at 1 mm., n_D^{20} 1.4522, was obtained in 73% yield.

Anal.^b Calcd. for $C_8H_{12}O_3$: C, 61.5; H, 7.8. Found: C, 61.7, 61.4; H, 8.0, 7.8.

The di-*p*-nitrobenzoate of I formed slightly yellow crystals, m. p. 137-138°, in 30% yield.

Anal.^a Calcd. for $C_{20}H_{10}O_8N_2$: C, 58.3; H, 3.9; N, 6.8. Found: C, 58.5, 58.3; H, 3.9, 3.9; N, 6.7, 6.8.

1-Triphenylmethoxy-4-hydroxy-4-methyl-2-pentyne formed colorless crystals, m. p. 99-100°, in 55% yield when crude, but large losses were sustained on purification.

Anal.^a Calcd. for $C_{25}H_{24}O_2$: C, 84.3, H, 6.7. Found: C, 84.6, 84.5; H, 6.7, 6.8.

Hydrogenation of I.—The acetylenic glycol, I, absorbed two moles of hydrogen over Adams platinum catalyst to yield 83% of 4-methyl-pentane-1,4-diol,⁴ b. p. 107° at 5.5 mm. The crystalline di-*p*-nitrobenzoate melted at 157-158° and the melting point was not depressed when mixed with the di-*p*-nitrobenzoate of Henry's glycol.⁴

Anal.^a Calcd. for $C_{20}H_{20}N_2O_8$: C, 57.7; H, 4.8; N, 6.8. Found: C, 57.7, 57.7; H, 5.0, 4.9; N, 6.8, 6.7.

(6) Vaughn, Vogt and Nieuwland, *THIS JOURNAL*, **66**, 2120 (1934).

Preparation of 4-Methyl-4-penten-2-yn-1-ol.—(a) From I: Twenty-one grams of I was benzoylated by the Schotten-Baumann reaction. The benzoate was taken into ether and washed with carbonate. On evaporation of the ether and pyrolysis of the crude benzoate at 150° for four hours, much benzoic acid was obtained. The residue was saponified and the product distilled under reduced pressure. A small but undetermined amount of 4-methyl-4-penten-2-yn-1-ol, b. p. 74° at 11 mm., was obtained. This was converted into its crystalline 3,5-dinitrobenzoate, m. p. 52-53°. A mixed melting point with the same dinitrobenzoate, prepared as described below, was not depressed.

(b) From 2-methyl-1-buten-3-yne: A mixture of 168 g. of dimethylethynylcarbinol and an equal volume of 30% sulfuric acid was refluxed a short time. The 2-methyl-1-buten-3-yne, b. p. 32°, formed amounted to 72 g. (54.5%). This was slowly distilled into an equivalent of titrated ethylmagnesium bromide. After the addition of 60 g. of dry paraformaldehyde the mixture was stirred at room temperature for sixty hours and refluxed for twelve hours. After hydrolysis with ammonium chloride solution 4-methyl-4-penten-2-yn-1-ol was obtained as a colorless liquid, b. p. 64° at 5 mm., 76° at 13 mm., in 55% yield.

The 3,5-dinitrobenzoate, m. p. 52-53°, and the trityl derivative, m. p. 87-88°, were prepared in about 50% yields by treating the alcohol in pyridine with the appropriate chloride.

Anal.^a Calcd. for $C_{25}H_{22}O$: C, 88.7; H, 6.6. Found: C, 88.7, 88.8; H, 6.6, 6.5. Calcd. for $C_{13}H_{10}O_6N_2$: C, 53.8; H, 3.5; N, 9.7. Found: C, 54.2; H, 3.8; N, 9.6, 9.5.

On hydrogenation the enynol readily absorbed 3 moles of hydrogen over Adams platinum catalyst to yield 4-methylpentanol-1, b. p. 150-151°. We prepared a sample of this alcohol by the reaction of iso-amyilmagnesium bromide with paraformaldehyde⁷ and established its identity with the above reduction product by the method of mixed melting points, using the crystalline 3,5-dinitrobenzoate, m. p. 70-71°.⁸

1-(Hydroxymethylethynyl)cyclohexanol (experiments by Miss Helen Ginsberg).—In a reaction quite similar to the preparation of I, except that it was found advantageous to add benzene to the reaction mixture, the acetylenic diol, b. p. 112-114° at 1 mm., m. p. 50.4-50.8°, was prepared in 66% yield.⁹ The crystalline di-*p*-nitrobenzoate melted at 144.8-145.4°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 70.1; H, 9.1. Found:^b C, 70.3, 70.3; H, 9.2, 9.0. Calcd. for $C_{23}H_{20}N_2O_8$: C, 61.1; H, 4.4; N, 6.2. Found:^c C, 61.0, 61.3; H, 4.9, 4.8; N, 5.9, 5.8.

Summary

It is shown that the bromomagnesium complex of dimethylethynylcarbinol condenses with formaldehyde to give 4-methyl-2-pentyne-1,4-diol in good yield. The structure of this diol was established.

COLUMBUS, OHIO

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(7) Grignard and Tissier, *Compt. rend.*, **134**, 108 (1902).

(8) Malone and Reid, *THIS JOURNAL*, **51**, 3424 (1929).

(9) Compare Zeile and Meyer, *Ber.*, **75**, 356 (1942).