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## Note on the Preparation of Some Acetylenic Glycols\*

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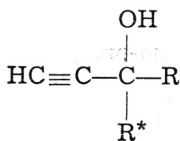
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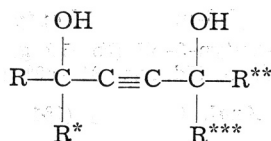
In connection with our investigation of the relationships between chemical structures and odors<sup>1,2</sup> we needed some branched acetylenic glycols of type II.

The Grignard derivative of the acetylenic alcohol Ia was condensed in benzene solution<sup>3</sup> with di-*iso*-propyl ketone, pinacolone and *t*-butyl-*iso*-propyl ketone respectively, and the glycols IIa, IIb and IIc were obtained. Similarly di-*iso*-propyl ketone and 1-butyn-3-ol (Ib) gave glycol IIc. Glycol IIc we prepared also from Ic and acetaldehyde. Ic can be obtained in a good yield by applying the method of Görlich and Hildebrand<sup>4</sup> (sodium amide in dimethyl formamide).

Glycol IIb has been prepared earlier by means of sodium amide but in a lower yield<sup>5</sup>.



I



II

- a) R = R\* = H  
b) R = H, R\* = Me  
c) R = R\* = *iso*-Pr

- a) R = R\* = H, R\*\* = R\*\*\* = *iso*-Pr  
b) R = R\* = H, R\*\* = *t*-Bu, R\*\*\* = Me  
c) R = R\* = H, R\*\* = *t*-Bu, R\*\*\* = *iso*-Pr  
d) R = H, R\* = Me, R\*\* = R\*\*\* = *iso*-Pr

### EXPERIMENTAL

All melting points are uncorrected.

#### General procedure for the preparation of acetylenic glycols

Dry benzene (100 ml.) was added to a solution of ethyl magnesium bromide (from 7.3 g. of magnesium and 34.3 g. of ethyl bromide in 120 ml. of ether), and about 100 ml. of ether were removed by distillation. To the resulting benzene solution of the Grignard reagent, the acetylenic alcohol (0.15 mole) in benzene (25 ml.) was added with stirring and cooling. The mixture was then heated on a water bath for 30 minutes.

The appropriate ketone (0.15 mole) was dissolved in 20 ml. of dry benzene and added into the warm solution of the Grignard reagent. The mixture was refluxed for 30 to 60 minutes until a clear solution resulted. After standing overnight diluted

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(10%) acetic acid was added. The water layer was extracted with ether and the combined organic layers washed with sodium hydrogen carbonate and water and dried over magnesium sulfate. The solvent was evaporated and the residue recrystallized or distilled. Analytical samples were recrystallized from petroleum-ether and dried 4—5 hrs. at room temperature *in vacuo*.

#### 4-iso-Propyl-5-methyl-2-hexyne-1,4-diol (IIa)

Propargylic alcohol (Ia, 8.7 g., b.p. 113—114.5°, freshly distilled) and 17.2 g. of di-iso-propyl ketone (b.p. 123.5—124.5°) gave 18 g. (70%) of IIa, m.p. 80—81° (from petroleum-ether). Hydrogenation over Pd/C catalyst in ethanol consumed the theoretical amount of hydrogen.

Anal.  $C_{10}H_{18}O_2$  (170.24) calc'd.: C 70.54; H 10.66%  
found: C 70.33; H 10.80%

#### 4,5,5-Trimethyl-2-hexyne-1,4-diol (IIb)

Propargylic alcohol (8.7 g.) and 15 g. of pinacolone gave 12.5 g. (53.5%) of IIb, recryst. from petroleum-ether m.p. 94.5—95.5° (lit. m.p. 91°).

Anal.  $C_9H_{16}O_2$  (156.22) calc'd.: C 69.19; H 10.32%  
found: C 69.09; H 10.43%

#### 5,5-Dimethyl-4-iso-propyl-2-hexyne-1,4-diol (IIc)

Propargylic alcohol (4.3 g.) and *t*-butyl-iso-propyl ketone<sup>6</sup> (9.6 g.) gave 3.7 g. of IIc (27%), recryst. from petroleum-ether m.p. 75—76°.

Anal.  $C_{11}H_{20}O_2$  (184.27) calc'd.: C 71.69; H 10.94%  
found: C 71.57; H 10.78%

#### 5-iso-Propyl-6-methyl-3-heptyne-2,5-diol (IIId)

a) 1-Butyn-3-ol<sup>7</sup> (Ib, 5.3 g., 0.075 mole) and 9 g. of di-iso-propyl ketone gave 3.1 g. (23%) of IIId, m.p. 81—82° (from petroleum-ether).

Anal.  $C_{11}H_{20}O_2$  (184.27) calc'd.: C 71.69; H 10.94%  
found.: C 71.94; H 10.88%

b) The same glycol IIId was prepared by the usual technique (without benzene) from 1.8 g. (0.076 gat) of magnesium turnings, 8.3 g. (0.076 mole) of ethyl bromide and 40 ml. of dry ether with 5.3 g. (0.038 mole) of 3-iso-propyl-4-methyl-1-pentyn-3-ol (Ic, dissolved in 30 ml. of dry ether); into this mixture (after boiling during 30 minutes) 2 g. of acetaldehyde (0.045 mole) was added under cooling. After the usual treatment an oil resulted (b.p. 78—82°/0.1 mm), which gave crystals by scratching, m.p. 80—81° (without depression when mixed with the product described above).

#### 3-iso-Propyl-4-methyl-1-pentyn-3-ol (Ic)

Powdered sodium amide (25.5 g., 0.65 mole) was suspended in 300 ml. of dimethyl formamide and the mixture saturated with a rapid stream of purified and dried acetylene at  $-10^\circ$  (about 26 g.). Into the mixture a solution of 57 g. (0.5 mole) of di-iso-propyl ketone in 70 ml. of dimethyl formamide was added during 3 hrs. keeping the temperature between  $-10^\circ$  and  $-5^\circ$ . Stirring was continued for additional 2 hrs. and the mixture left overnight at room temperature.

The mixture was hydrolyzed with 19 g. of sulfuric acid and 60 g. of ice, 400 ml. of water was added and extracted with ether. After drying and evaporating the solvent, the product was distilled, b.p. 55—58° at 10 mm, using a Widmer-type column. The remaining oil crystallized on cooling, m.p. 108—110° as 2,7-dimethyl-3,6-di-iso-propyl-4-octyn-3,6-diol<sup>8</sup>. To obtain a better yield of alcohol Ic, 0.5 g. of potassium carbonate was added<sup>9</sup> to the crystalline substance and distilled again slowly. Both distillates were redistilled through a Widmer-column, b.p. 55.5—56.5°/10 mm, 28 g. (59%); 18 g. of di-iso-propyl ketone was regenerated. Hydrogenation over Pd/C catalyst in ethanol consumed the theoretical amount of hydrogen.

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## IZVOD

## Bilješka o sintezi nekih acetilenskih glikola

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Sintetizirana su četiri acetilenska glikola tipa II, opće poznatom metodom pomoću Grignardovih reagensa iz odgovarajućih ketona i acetilenskih alkohola (I)

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