

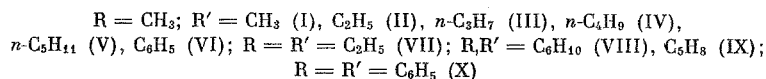
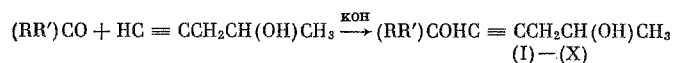
SYNTHESIS OF SECONDARY—TERTIARY ACETYLENIC δ -GLYCOLS

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In previous communications we reported the synthesis of primary-tertiary δ -glycols by the Favorskii reaction [1-3].

The present investigation established that the condensation of ketones of different structure with 1-pentyn-4-ol leads to the formation of secondary—tertiary acetylenic δ -glycols.



The reaction was carried out in a medium of absolute ether at room temperature. The yield of secondary-tertiary δ -glycols of the aliphatic series is 68–95%. Glycols of the aliphatic-aromatic series (VI), (X) in ether are obtained in a yield of not more than 39.5%. The replacement of ether by tetrahydrofuran (THF) increases the yield. Thus, in the case of the condensation of 1-pentyn-4-ol with acetophenone, the yield of glycol (VI) is increased by 11%.

A secondary-tertiary δ -glycol with a five-membered ring (IX) was synthesized by the condensation of cyclopentanone with the Iotsich reagent from 1-pentyn-4-ol, as under the conditions of the Favorskii reaction a self-condensation of cyclopentanone into 2-cyclopentylidenecyclopentanone and 2,5-bicyclopentylidenecyclopentanone [3] occurs.

The structures of the glycols obtained were confirmed spectroscopically. IR spectra are characterized by the presence of the broad absorption band of the hydroxyl group in the 3300–3400 cm⁻¹ region, and also by the weak band at a frequency of 2240 cm⁻¹ corresponding to the triple bond.

Physicochemical constants of the δ -glycols are presented in Table 1.

EXPERIMENTAL

1-Pentyn-4-ol was synthesized by the condensation of propylene oxide and sodium acetylide in liquid ammonia, bp 123–124°; n_D^{20} 1.4390. Literature values [4]: bp 74.6° (100 mm); n_D^{16} 1.4406.



2-Methyl-3-heptyne-2,6-diol (I, R = R' = CH₃). To a solution of 42 g of 1-pentyn-4-ol in 300 ml of abs. ether was added with stirring 140 g of powdered KOH. Over 3 h was added an ether solution of 32 g of acetone. The temperature of the reaction mixture was kept at ~20°. The next day the reaction complex was decomposed with ice water. The ether extracts combined with the main ether layer were washed with a 5% solution of acetic acid and dried over K₂CO₃. After distillation of the ether and distillation of the residue in a vacuum of 2 mm was obtained 58.6 g of glycol (I).

Glycols (II)–(VIII) and (X) were synthesized under analogous conditions.

1-(1-Hydroxycyclopentyl)-1-pentyn-4-ol (IX). To a Grignard reagent prepared from 26 g of magnesium and 110 g of ethyl bromide in 200 ml of ether was added 42 g of 1-pentyn-4-ol. The reaction mixture was heated for 3 h to the boiling temperature of ether and left overnight. The ether was distilled, 200 ml of benzene was added, and 42 g of cyclopentanone was added dropwise. The mixture was heated an additional 3 h to the boiling temperature of benzene and left overnight. The next day the mixture was decomposed with a saturated solution of ammonium chloride, and the benzene layer was separated, and dried over K₂CO₃. After distillation of the benzene and distillation of the residue in vacuum, 67.3 g of glycol (IX) was obtained.

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TABLE 1

| No. | Compound | Yield, % | Mol. wt. | bp, °C (p. mm Hg) | d_4^{20} | n_D^{20} | MR | | Found, % | | Empirical formula | Calculated, % | |
|------|--|------------------------|----------|----------------------|------------|------------|-------|------------|----------|-------|-------------------|---------------|-------|
| | | | | | | | found | calculated | C | H | | C | H |
| I | $(CH_3)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 82.4 | 142 | 99—100 (2) | 0.9764 | 1.4650 | 40.19 | 40.19 | 67.35 | 9.89 | $C_8H_{14}O_2$ | 67.60 | 9.85 |
| II | $(CH_3C_2H_5)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 83 | 156 | 112 (2) | 0.9712 | 1.4730 | 45.05 | 44.80 | 69.18 | 10.14 | $C_9H_{16}O_2$ | 69.20 | 10.33 |
| III | $(CH_3C_3H_7)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 75 | 170 | 108—110 (2) | 0.9541 | 1.4708 | 49.78 | 49.43 | 70.89 | 10.43 | $C_{10}H_{18}O_2$ | 70.58 | 10.58 |
| IV | $(CH_3-n-C_4H_9)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 68 | 184 | 130 (4) | 0.9438 | 1.4682 | 53.84 | 54.04 | 71.85 | 10.73 | $C_{11}H_{20}O_2$ | 71.74 | 10.87 |
| V | $(CH_3-n-C_6H_{11})_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 77 | 198 | 139 (4) | 0.9335 | 1.4690 | 59.07 | 58.66 | 72.29 | 11.42 | $C_{13}H_{24}O_2$ | 72.66 | 11.18 |
| VI | $(CH_3C_6H_5)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 32 (ether) 43 (THF) | 204 | 171—172 (2.5) | 1.0713 | 1.5435 | 60.05 | 59.70 | 76.53 | 7.58 | $C_{13}H_{16}O_2$ | 76.47 | 7.84 |
| VII | $(C_2H_5)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 73 | 170 | 111.5 (2.5) | 0.9685 | 1.4750 | 49.40 | 49.42 | 70.64 | 10.83 | $C_{10}H_{16}O_2$ | 70.58 | 10.58 |
| VIII |  $-(OH)C \equiv CCH_2CH(OH)CH_3$ | 95 | 182 | 98 (mp) | — | — | — | — | 72.52 | 9.74 | $C_{11}H_{18}O_2$ | 72.52 | 9.89 |
| IX |  $-(OH)C \equiv CCH_2CH(OH)CH_3$ | 80.1 | 168 | 48—49 (mp) | — | — | — | — | 71.43 | 9.37 | $C_{10}H_{16}O_2$ | 71.42 | 9.52 |
| X | $(C_6H_5)_2C(OH)C \equiv CCH_2CH(OH)CH_3$ | 39.5 | 266 | 102—103 (mp) | — | — | — | — | 81.38 | 6.99 | $C_{18}H_{18}O_2$ | 81.20 | 6.76 |

2-Phenyl-3-heptyn-2,6-diol (VI). To a mixture of 21 g of 1-pentyn-4-ol and 140 g of KOH in 300 ml of THF was added 30 g of acetophenone. After the corresponding workup of the reaction products, 22 g of the glycol (VI) was obtained.

CONCLUSIONS

1. The condensation of 1-pentyn-4-ol with different ketones gives secondary-tertiary δ -glycols according to the Favorskii reaction. 1-(1-Hydroxycyclopentyl)-1-pentyn-4-ol was synthesized by the reaction of cyclopentanone and the Iotsich reagent from 1-pentyn-4-ol.
2. The substitution of tetrahydrofuran for ether makes possible the increase of yields of glycols.

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