SYNTHESIS OF SECONDARY—TERTIARY ACETYLENIC δ-GLYCOLS

T. A. Favorskaya, A. S. Medvedeva,
V. M. Vlasov, and G. G. Chichkareva

UDC 542.91 + 547.424.2

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.

$$(RR')CO + HC \equiv CCH_2CH(OH)CH_3 \xrightarrow{KOH} (RR')COHC \equiv \underset{(I)-(X)}{CCH_2CH(OH)CH_3}$$

$$R = CH_3;\ R' = CH_3\ (I),\ C_2H_5\ (II),\ n\text{-}C_3H_7\ (III),\ n\text{-}C_4H_9\ (IV),$$
$$n\text{-}C_5H_{11}\ (V),\ C_6H_5\ (VI);\ R = R' = C_2H_5\ (VII);\ R,R' = C_6H_{10}\ (VIII),\ C_5H_8\ (IX);$$
$$R = R' = C_6H_5\ (X)$$

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' = CH_3). 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 K_2CO_3. 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 K_2CO_3. After distillation of the benzene and distillation of the residue in vacuum, 67.3 g of glycol (IX) was obtained.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2107-2109, September, 1967. Original article submitted March 14, 1967.

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 67.13	9.89 9.76	$C_8H_{14}O_2$	67.60	9.85
II	$(CH_3C_2H_5)C(OH)C{\equiv}CCH_2CH(OH)CH_3$	83	156	112(2)	0.9712	1.4730	45.05	44.80	69.18 69.18	10.14 10.27	$C_9H_{16}O_2$	69.20	10.33
III	$(CH_3C_3H_7)C(OH)C{\equiv}CCH_2CH(OH)CH_3$	75	170	108—110 (2)	0.9541	1.4708	49.78	49.43	70.89 70.97	10.43 10.72	$C_{10}H_{18}O_2$	70.58	10.58
IV	$(CH_3\text{-}n\text{-}C_4H_9)C(OH)C{\equiv}CCH_2CH(OH)CH_3$	68	184	130 (4)	0.9438	1.4682	53.84	54.04	71.85 71.43	10.73 10.51	$C_{11}H_{20}O_2$	71.74	10.87
V	$(CH_3\text{-}n\text{-}C_5H_{11})C(OH)C{\equiv}CCH_2CH(OH)CH_3$	77	198	139 (4)	0.9333	1.4690	59.07	58.66	72.29 72.17	11.42 11.11	$C_{12}H_{21}O_2$	72.66	11.18
VI	$(CH_3C_6H_5)C(OH)C{\equiv}CCH_2CH(OH)CH_3$	32 (ether) 43 (THF)	204	171—172 (2,5)	1.0713	1.5435	60.05	59.70	76.53 76.14	7.58 7.79	$C_{13}H_{16}O_2$	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 70.90	10.83 10.50	$C_{10}H_{18}O_2$	70.58	10.58
VIII	 —(OH)C≡CCH₂CH(OH)CH₃	95	182	98 (mp)	—	—	—	—	72.52 72.19	9.74 9.51	$C_{11}H_{18}O_2$	72.52	9.89
IX	 —(OH)C≡CCH₂CH(OH)CH₃	80.1	168	48—49 (mp)	—	—	—	—	71.43 71.66	9.37 9.33	$C_{10}H_{16}O_2$	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 81.21	6.99 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.

LITERATURE CITED

1. T. A. Favorskaya, M. F. Shostakovskii, V. M. Vlasov, and A. S. Lozhenitsyna, Zh. obshch. khim., 35, 402 (1965).
2. M. F. Shostakovskii, V. M. Vlasov, A. S. Lozhenitsyna, and A. A. Gravrilovskaya, Izv. AN SSSR, Ser. khim., 1965, 109.
3. T. A. Favorskaya, V. M. Vlasov, A. S. Lozhenitsyna, and G. G. Chichkareva, Zh. obshch. khim., 36, 1892 (1966).
4. L. J. Haynes and E. R. H. Jones, J. Chem. Soc., 1946, 956.