SYNTHESIS OF UNSYMMETRICAL DIACETYLENE GLYCOLS

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Our previous communications described the synthesis [1-3] and conversion [4-7] of primary- and secondary-tertiary acetylene α-glycols. It seemed of interest to obtain diacetylene analogs of these glycols and study them, primarily in dehydration and hydration reactions.

The diacetylene glycols were obtained by the Cadiot–Chodkiewicz method [8] by condensing tert-acetylene alcohols (I) and the bromoderivatives of pent-1-yn-4-ol (II) and but-1-yn-4-ol (IV):

$$\underset{(I)}{RR'COHC} \equiv CH + BrC \equiv CCH_2CH\underset{(II)}{(CH_3)}OH \xrightarrow{Cu+} RR'COH\underset{(III)}{C \equiv C} - C \equiv CCH_2CH(CH_3)OH$$

$$R = CH_3;\ R' = CH_3\ (a),\ C_2H_5\ (b),\ n\text{-}C_3H_7\ (c);$$

$$R,R' = \text{cyclo-}C_6H_{10}\ (d)$$

$$(I) + BrC \equiv \underset{(IV)}{CCH_2}CH_2OH \rightarrow RR'COHC \equiv C - \underset{(V)}{C} \equiv CCH_2CH_2OH$$

$$R = CH_3;\ R' = CH_3\ (a),\ C_2H_5\ (b)$$

The base was usually ethylamine; in the case of n-butylamine the yield of glycol (Va) was 20% less. Diacetylene glycols (IIIa-IIId) and (Va, Vb) were obtained with yields of 60-81%. These glycols were very viscous, sometimes vitreous liquids. Crystallization after one day is observed in the case of (IIIa, IIId) and (Va). As in the case of acetylene σ-glycols, their diacetylene analogs are stable on keeping. Their infrared spectra (IIIa-IIId, Va, and Vb) have bands characteristic of the ternary bond at about 2250 cm^{-1} and broad bands at 3400 cm^{-1} due to the hydroxyl group. Note that in the infrared spectra of the previously described [2, 3, 6] σ-glycols $RR'COHC \equiv CCH_2CH_2OH$ and $RR'COHC \equiv CCH_2CH(CH_3)OH$ weak bands with frequencies of 2240-2250 cm^{-1} corresponded to the ternary bond. The presence of conjugation in the diacetylene glycols obtained does not have a marked effect on the vibrational frequency of the ternary bond, but the intensity of the absorption band of the $-C\equiv C-C\equiv C$ group is approximately twice as great as in acetylene σ-glycols.

The physicochemical constants of the glycols are given in Table 1.

EXPERIMENTAL

Synthesis of 1-Bromopent-1-yn-4-ol (II). We mixed 100 g of crushed ice with 50 ml of 10 N NaOH and then added 11 ml of bromine, 16.8 g of pent-1-yn-4-ol in 10 ml of tetrahydrofuran (THF). The mixture was stirred for 5 h, treated with a saturated solution of NH_4Cl, extracted with ether, and the extract dried with $MgSO_4$. After the solvent had been removed at the pump, we obtained 27 g of (II) (80% of the theoretical); the n_D^{20} was 1.5040.

2-Methylnonane-3,5-diyn-2,8-diol (IIIa). To a solution of 9.8 g dimethylacetylenyl carbinol (Ia) in 10 ml of methanol was added 1 g of hydroxylamine hydrochloride and a solution of 0.1 g of CuCl in 28 ml of 33% aqueous ethylamine. We then added a solution of 16.3 g of (II) in methanol for 1 h. The mixture was stirred for another half hour at 25-27°C. Hydroxylamine hydrochloride was added as it was consumed. A total of 4 g of $NH_2OH \cdot HCl$ was consumed. The reaction mixture was treated with 10% H_2SO_4, extracted with ether, and the extract dried with K_2CO_3. Distillation in vacuum gave 12.8 g of glycol (IIIa). According to Prevost et al. [9], the mp is 72° and the IR spectrum (cm^{-1}) as follows: 3340 v.s (v.b), 2982 v.s, 2935 s, 2920 s, 2250 m, 1455 s, 1415 s, 1315 s, 1255 s, 1215 s, 1160 v.s, 1115 v.s, 1085 v.s, 1010 s, 1040 m, 961 v.s, 939 v.s, 900 s, 825 m, 795 m. The spectra were recorded in a UR-10.

3-Methyldeca-4,6-diyn-3,9-diol (IIIb). From 16.3 g (II) and 9.8 g of 3-methylpent-yn-1-3ol under the same conditions we obtained 11.7 g of glycol (IIIb). The IR spectrum (cm^{-1}) was as follows: 3348 v.s (v.b), 2941 (v.s), 2930 s, 2880 s, 2256 m, 1456 s, 1415 s, 1376 s, 1326 s, 1280 s, 1236 s, 1155 v.s, 1116 v.s, 1086 v.s, 1050 s, 1030 s, 995 s, 940 v.s, 916 v.s, 883 w, 827 m, 801 m.

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TABLE 1

Compound	Yield, %	Boiling point, °C (p, mm Hg) mp, °C	n_D^{20}	Found, %		Empirical formula	Calculated, %		Characteristic frequencies, cm^{-1}
				C	H		C	H	
2-Methylnona-3,5-diyn-2,8-diol (IIIa)	80	142-144(2) 61-62 (benzene)	1.5255	72.12 72.25	8.32 8.44	$C_{10}H_{14}O_2$	72.26	8.49	3340s(OH) 2250m(C≡C)
3-Methyldeca-4,6-diyn-3,9-diol (IIIb)	65	138-139(2)	1.5238	73.26 73.12	8.93 8.97	$C_{11}H_{16}O_2$	73.31	8.95	3348s(OH) 2256m(C≡C)
4-Methyldeca-5,7-diyn-4,10-diol (IIIc)	60.8	136-137(2)	1.5210	74.01 74.28	9.23 9.31	$C_{12}H_{18}O_2$	74.17	9.34	3355s(OH) 2253m(C≡C)
1-(1-Hydroxycyclohexyl)-hepta-1,3-diyn-6-ol (IIId)	75	162-163(4) 91-93 (benzene)		75.85 75.66	8.98 8.77	$C_{13}H_{18}O_2$	75.68	8.80	3430s(OH) 2252m(C≡C)
2-Methylocta-3,5-diyn-2,8-diol (Va)	71* 50†	138-139 (2.5) 54-55 (benzene)		71.20 71.36	7.96 8.01	$C_9H_{12}O_2$	71.00	7.90	3350s(OH) 2250m(C≡C)
3-Methylnona-3,5-diyn-3,9-diol (Vb)	80.7	158-160(4)	1.5320	72.34 72.50	8.38 8.50	$C_{10}H_{14}O_2$	72.29	8.43	3359s(OH) 2252m(C≡C)

*By the first method. † By the second method.

4-Methylenedeca-5,7-diyn-4,10-diol (IIIc). From 8.3 g of (II) and 5.6 g of 3-methylhex-1-yn-3-ol we obtained 6.1 g of glycol (IIIc). The IR spectrum (cm^{-1}) was as follows: 3355 v.s (v.b), 2960 v.s, 2935 v.s, 2873 s, 2253 m, 1455, s, 1420 s, 1375 s, 1360 s, 1285 s, 1220 m, 1160 s, 1120 v.s, 1082 v.s, 1060 m, 1020 m, 940 s, 860 w, 825 m.

1-(1-Hydroxycyclohexyl)hepta-1,3-diyn-6-ol (IIId). From 16.3 g of (II) and 12.4 g of acetylenylcyclohexanol we obtained 115.5 g of (IIId). The IR spectrum (cm^{-1}) was as follows: 3430 v.s (v.b), 2960 v.s, 2913 v.s, 2888 v.s, 2850 v.s, 2252 m, 1454 s, 1366 m, 1288 s, 1250 v.s, 1126 v.s, 1089 v.s, 1046 s, 966 m, 936 m, 887 v.s, 874 v.s, 831 w. The spectrum was recorded in dioxane.

2-Methylocta-3,5-diyn-2,8-diol (Va). Condensation of 8.4 g of (Ia) with 14.5 g of (II) gave 10.8 g of (Va). The IR spectrum (cm^{-1}) was as follows: 3350 s (v.b), 2985 s, 2935 s, 2900 m, 2250 m, 1455 s, 1415 s, 1380 v.s, 1340 m, 1259 s, 1212 s, 1164 v.s, 1047 v.s, 960 s, 385 m, 842 m.

From 8.4 g of (Ia) and 14.9 g of (II) in n-butylamine at 30-25° we obtained 7.7 g (50%) of glycol (Va). According to Gusev and Kucherov [10], the bp is 118-120° (0.45 mm) and the n_D^{20} 1.5276.

3-Methylnona-3,5-diyn-3,9-diol (Vb). By reacting 9.8 g of (Ib) with 14.9 g of (II) we obtained 13.4 of glycol (Vb). The IR spectrum (cm^{-1}) was as follows: 3360 s, 2975 s, 2949 s, 2880 m, 2252 m, 1459 s, 1410 s, 1372 s, 1390 s, 1290 s, 1232 s, 1160 v.s, 1130 v.s, 1044 v.s, 994 s, 9150 s, 745 m, 785 w.

CONCLUSIONS

We obtained and characterized six diacetylene primary and secondary-tertiary glycols.

LITERATURE CITED

1. M. F. Shostakovskii, V. M. Vlasov, A. S. Lozhenitsyna, and A. A. Gavrilovskay, Izv. AN SSSR, Ser. Khim., 1965, 709.
2. T. A. Favorskaya, M. F. Shostakovskii, V. M. Vlasov, and A. S. Lozhenitsyna, ZhOKh, 35, 402 (1965).
3. T. A. Favorskaya, A. S. Medvedeva, V. M. Vlasov, and G. G. Chichkareva, Izv. AN SSSR, Ser. Khim., 1967, 219.
4. V. M. Vlasov, T. A. Favorskaya, A. S. Medvedeva, and G. G. Chichkareva, ZhOKh, 37, 1967 (1967).
5. V. M. Vlasov, T. A. Favorskaya, A. E. Lozhenitsyna, and T. S. Kuznetsova, Izv. AN SSSR, Ser. Khim., 1966, 764.
6. T. A. Favorskaya, V. M. Vlasov, A. S. Lozhenitsyna, and G. G. Chichkareva, ZhOKh, 36, 1892 (1966).

7. T. A. Favorskaya, V. M. Vlasov, A. S. Lozhenitsyna, and G. A. Kalabin, ZhOKh, 36, 1886 (1966).
8. W. Chodkiewicz, J. A. Alhuwalia, P. Cadiot, and A. Willemart, Compt. rend., 245, 321 (1955); W. Chodkiewicz and P. Cadiot, Compt. rend., 241, 1055 (1955).
9. S. Prevost, J. Meier, W. Chodkiewicz, P. Cadiot, and A. Willemart, Bull. Soc. chim. France, 1961, 2171.
10. B. P. Gusev and V. F. Kucherov, Izv. AN SSSR, Ser. Khim., 1962, 1067.