HYDRATION OF SECONDARY-TERTIARY

$\delta\text{-}GLYCOLS$ of the acetylene series

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In continuation of a study of acetylenic δ -glycols [1-3], we have investigated the hydration reaction of a series of acyclic, cyclic and aliphatic-aromatic secondary-tertiary δ -glycols in the presence of mercury sulfate. In this way it was established that an α -ketoglycol was formed in 60-80% yield in consequence of the principal course of the reaction. In the case of 1-(1-hydroxycyclopentyl) pent-1-yn-4-ol the corresponding ketoglycol failed to separate since it readily dimerizes under the reaction conditions and also on distillation into a tricyclic dioxane (IIIf).

Chromatography of the reaction product on aluminum oxide showed that the ketoglycols are contaminated by two substances one of which corresponds to the crystalline dioxane. The second contaminant was assumed by us to be tri-substituted δ -pyrone (V). The formation of δ -pyrones was observed previously during hydration of primary-tertiary δ -glycols [2] but in larger amount.

2, 6, 6-Trimethyltetrahydro- δ -pyrone (V) was separated with the aid of column chromatography on Al₂O₃ from 2-methylhept-3-yne-2, 6-diol. An absorption band of frequency 1724 cm⁻¹ was present in its IR spectrum; multiple bands and OH groups were absent. The conversions arising may be expressed by the scheme



$$\begin{split} R &= CH_3; \ R' = C_2H_5 \ (a), \ C_3H_7 \ (b), \ C_5H_{11} \ (c), \ C_6H_5 \ (d); \\ R &= R' = C_6H_5 \ (e); \ RR' = C_5H_8 \ (f) \end{split}$$

EXPERIMENTAL

<u>Hydration of 3-Methyloct-4-yne-3, 7-diol (Ia)</u>. Ether (200 ml) was added to a solution of $HgSO_4$, prepared from 2.04 g HgO, 1.8 ml conc. H_2SO_4 , and 10 ml water, and 25 g glycol added over 2 h. The reaction mixture was neutralized with Na_2CO_3 , the precipitate filtered off, and the filtrate dried with K_2CO_3 . After removal of the ether, the residue was distilled in vacuum. Two fractions were isolated: 1) $87-92^{\circ}$ (3 mm), 1.95 g; n_D^{20} 1.4548; 2) $97-100^{\circ}$ (3 mm), 22.30 g; n_D^{20} 1.4586. On a second distillation of fraction 2. 3-methyloctan-4-one-3, 7-diol (IIa) (21 g; 80.3%) was obtained with b.p. 97° (2 mm); n_D^{20} 1.4616; d_4^{20} 1.0218. Found: C 62.01; H 10.39% MR 46.7. $C_9H_{18}O_3$. Calculated: C 62.06; H 10.34%; MR 46.8. 2, 6, 6-Trimethyltetrahydro- δ -pyrone (Va) (0.4 g) was isolated, by column chromatography on Al_2O_3 using the system benzene-ether (3:2), from the products of several experiments on the hydration of 2-methylhept-3-yn-2, 6-diol.

<u>4-Methylnon-5-yne-4,8-diol (Ib)</u>. The glycol (15 g) was hydrated in ether in the presence of a solution of $HgSO_4$ prepared from 1.7 g HgO, 1.5 ml conc. H_2SO_4 and 2 ml H_2O . Two fractions were isolated from the reaction products on distillation in vacuum at 1.5 mm: 1) 96-101°, 0.9 g; n_D^{20} 1.4504. 2) 102-103°, 11.4 g; n_D^{20} 1.4606. After a second distillation of fraction 2 10 g (74.5%) 4-methylnonan-5-on-

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4,8-diol (IIb) was isolated of b.p. 105-105.5° (1.5 mm); n_D^{20} 1.4581; d_4^{20} 1.0026. Found: C 63.51; H 10.68%; MR 51.00. $C_{10}H_{20}O_{3}$. Calculated: C 63.78; H 10.71%; MR 51.4.

<u>6-Methylundec-7-yne-6, 10-diol (Ic)</u>. The glycol (30 g) was hydrated under analogous conditions. Two fractions were isolated on distillation of the hydration products in vacuum at 3 mm: 1) 111-120°, 2.1 g; n_D^{20} 1.4551; 2) 142-145°, 22.16 g; n_D^{20} 1.4582. 6-Methylundecan-7-one-6, 10-diol (IIc) (21.5 g; 74.3%) was obtained from a repeat distillation of fraction 2 having b.p. 128-130° (2 mm); n_D^{20} 1.4575; d_4^{20} 0.9780. Found: C 66.20; H 11.17%; MR 60.20 $C_{12}H_{24}O_3$. Calculated: C 66.66; H 11.11%; MR 60.10.

 $\frac{2-\text{Phenylhept-}2-\text{yne-}1, 6-\text{diol} (\text{Id}). \text{ The glycol} (30 \text{ g}) \text{ was hydrated under the same conditions. Two fractions were isolated on distillation in vacuum at 3 mm; 1) 151-158°, 0.91 g; n_D²⁰ 1.531; 2) 158.5-160°, 24.87 g; n_D²⁰ 1.5340. On repeat distillation of fraction 2), 23 g (76%) ketoglycol of b.p. 152-153° (2.5 mm); n_D²⁰ 1.5337 was obtained. Some (5 g) of fraction 2 was chromatographed on a column of Al₂O₃ and eluted with benzene and ether (3:2). A single <math>\alpha$ -ketoglycol (IId) (3 g) was isolated; n_D²⁰ 1.5309; d₄²⁰ 1.1132. Found: C 70.30; H 8.24%: MR 61.68. C₁₃H₁₃O₃. Calculated: C 70.27; H 8.10%; MR 61.69.

 $\begin{array}{c} 1,1-\text{Phenylhex-2-yne-1,5-diol} \quad (\text{Ie}). \\ \text{The glycol} (18 \text{ g}) \text{ was hydrated under analogous} \\ \text{conditions. Two fractions were obtained on vacuum distillation at 9 mm: 1) 177-184°, 4.72 g; n_D^{20} 1.5814; \\ \text{2) 184-185°, 7.35 g; n_D^{20} 1.5830. \\ \text{Fraction 2 (5 g) was chromatographed on a column of alumina. Ketoglycol (IIe) (3.5 g) was isolated; n_D^{20} 1.5718; d_4^{20} 1.1420. \\ \text{Found: C 76.13; H 7.18%; MR 81.81. } C_{18}\text{H}_{20}\text{O}_3. \\ \text{Calculated: C 76.0; H 7.00\%; MR 81.18.} \end{array}$

 $\frac{1 - (1 - Hydroxycyclopentyl)pent - 1 - yn - 4 - ol (If).}{100 - 108^{\circ}, 1.37 \text{ g; n}_{D}^{20} 1.4747; 2) 110 - 114^{\circ}, 15.5 \text{ g; n}_{D}^{20} 1.4839.}$ The glycol (21 g) was hydrated under the same conditions. Two fractions were isolated on distillation of the reaction product in vacuum at 6 mm:

Both fractions were mixed with crystals and on keeping for a day crystallized as 2, 5-dicyclopentyl-3, 6-di-(2-methyl-tetrahydro- α -furfuryl) dioxane (IIIf); m.p. 64-65° (n-pentane). IR spectrum (frequency in cm⁻¹): 2995 strong, 2880 medium, 1450 medium, 1385 medium, 1360 medium, 1315 medium, 1280 medium, 1200 medium, 1150 very strong, 1085 very strong, 1050 strong, 1003 very strong, 960 strong, 890 medium, 855 medium, 820 weak, 776 very weak.

CONCLUSIONS

The hydration of five secondary-tertiary δ -glycols of acyclic, alicyclic and aliphatic-aromatic structure has been studied. The corresponding α -ketoglycol is formed from the main course of the reaction. In the case of 1-(1-hydroxy-cyclopentyl)pent-1-yn-4-ol, the ultimate product of hydration is the corresponding tricyclic dioxane.

LITERATURE CITED

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