SYNTHESIS OF ACETYLENIC DERIVATIVES OF 1,4-DIOXANE

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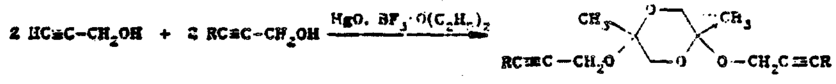
Cyclic ketals – 2,5-dimethyl-2,5-bis(4-penten-2-ynyloxy)-1,4-dioxane and 2,5-dimethyl-2,5-bis(3-phenyl-2-propynyloxy)-1,4-dioxane – were isolated in the reaction of propargyl alcohol with vinyl- and phenylethynylcarbinols in the presence of $HgO–BF_3.O(C_2H_5)_2$ catalytic system.

It has already been shown that, depending on the temperature and solvent, the exothermic reaction of propargyl alcohol by the action of the $HgO–BF_3.O(C_2H_5)_2$ catalytic system leads preferentially to a tetramer – 2,5-dimethyl-2,5-bis(2-propynyloxy)-1,4-dioxane – or a polymer with a system of conjugated bonds [1]. Under similar conditions, the nonterminal α-acetylenic alcohols – vinylethynylcarbinol and phenylethynylcarbinol – form exclusively polyconjugated polymers, while in the presence of propargyl alcohol, they can form 1,4-dioxane derivatives – 2,5-dimethyl-2,5-bis-(4-penten-2-ynyloxy)-1,4-dioxane (I) and 2,5-dimethyl-2,5-bis(3-phenyl-2-propynyloxy)-1,4-dioxane (II), respectively:



I, II

I $R=CH_2=CH–$; II $R=C_6H_5$

In the PMR spectra of the compounds obtained, there are signals of axial and equatorial protons (H_a, H_e) of the CH_2 group of the 1,4-dioxane ring (the AB spin system), and in the IR spectra, the absorption bands of the $–C≡CH$ group in the 300 and 2120 cm^{-1} region are absent, while absorption bands of the disubstituted acetylenic group in the 2240 cm^{-1} region are present. The above spectral data indicate the participation of only terminal acetylenic bonds in the mercury-catalyzed reaction of the electrophilic addition of the alcohol, leading to the formation of cyclic ketals I and II by the mechanism previously described in [1]. By special experiments, the possibility was also shown of transetherification of the cyclic ketals by the acetylenic alcohol, whereby hydroxyacetone is formed, a product of hydrolysis of the cyclic ketals. A hydroxyacetone was also observed in the transformation products of the reaction studied. Compound I polymerizes at 80-90°C in the presence of benzoyl peroxide, forming cross-linked polymers containing conjugation blocks in the main chain and dioxane rings as cross-links. Compound II does not polymerize thermally.

EXPERIMENTAL

A freshly distilled propargyl alcohol with n_D^{20} 1.4320 was used. Vinylethynylcarbinol [2], phenylethynylcarbinol [3], and 2,5-dimethyl-2,5-bis(2-propynyloxy)-1,4-dioxane [1] were obtained by known methods. The IR spectra of the samples were run on a UR-20 spectrophotometer in KBr tablets, while the PMR spectra were recorded on a "Varian 60A" spectrometer (60 MHz) in $CDCl_3$ with HMDS as an internal standard. The GLC analysis was carried out on a LKhM-8MD apparatus using a heat conductivity detector, a 2000 × 0.4 mm column, 5% Apiezon on W-AW chromosorb, carrier gas helium, 60-80 ml/min, column temperature 160°C, and evaporator temperature 215°C. The TLC analysis was carried out on Silufol UV-254 plates, using an 8:3 hexane–ether mixture as the mobile phase and iodine vapor as a developer.

2,5-Dimethyl-2,5-bis(4-penten-2-ynyloxy)1,4-dioxane (I). A mixture of 5.6 g (100 mmoles) of propargyl alcohol, 8.2 g (100 mmoles) of vinylethynylcarbinol, and 0.2 g (0.9 mmole) of HgO and 14 ml of benzene was cooled to –5°C. A 0.1 ml portion (0.8 mmole) $BF_3.O(C_2H_5)_2$ was

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added and the mixture was stirred for 8 h at 20°C. It was then neutralized by dry K_2CO_3, and, after distilling benzene, cooled at 0-5°C for 24 h. The crystals that separated were filtered. Yield, 4.8 g (35%), mp 87°C (from ethanol), R_f 0.52. IR spectrum: 1020, 1045, 1080, 1140, 1190 (the 1,4-dioxane ring and the C–O–C–O–C group), 910, 950, 1610, 3065 ($-CH=CH_2$ conjug.), 2240 cm^{-1} ($-C\equiv C-$). PMR spectrum: 1.23 (6H, s, CH_3); 3.68 and 3.47 ppm ($2H_a$, m, $2H_e$, J = 11.8 Hz, ring CH_2). Found: C 69.6; H 7.6%. $C_{16}H_{20}O_4$. Calculated: C 69.5; H 7.3%.

2,5-Dimethyl-2,5-bis(3-phenyl-2-propynyloxy)-1,4-dioxane (II). A mixture of 5.6 g (100 mmoles) of propargyl alcohol, 13.2 g (100 mmoles) of phenylethynylcarbinol, 0.5 g (2.3 mmoles) of HgO, and 0.2 ml (1.6 mmoles) of $BF_3.O(C_2H_5)_2$ was stirred at 45-50°C for 12 h, and then cooled for 0-5°C for 24 h. The crystals that separated were filtered. Yield, 7.5 g (40%), mp 158-159°C (from 3:1 ethanol–benzene mixture), R_f 0.64. IR spectrum: 1040, 1080, 1135, 1190 (the 1,4-dioxane ring and the C–O–C–O–C group), 700, 770, 1450, 1595, 3035 ($-C_6H_5$), 2220, 2260 cm^{-1} ($-C\equiv C-$). PMR spectrum: 1.25 (6H, s, CH_3), 3.40 and 3.70 ($2H_a$, m, $2H_e$, J = 10.0 Hz, ring CH_2), 4.20 (4H, s, OCH_2), 7.0-7.2 (10H, m, C_6H_5). Found: C 76.6; H 6.5%. Calculated: C 76.6; H 6.4%.

Transetherification. A mixture of 2.05 g (9 mmoles) of 2,5-dimethyl-2,5-bis(2-propynyloxy)-1,4-dioxane, 4.0 g (3 mmoles) of phenylethynylcarbinol in 10 ml of dioxane was heated at 50°C for 5 h in the presence of 0.01 ml (0.81 mmole) of $BF_3.O(C_2H_5)_2$. The reaction mixture was cooled at 0-5°C for 10 h, and the crystals that separated were filtered. Yield 2.4 g of compound II, mp 158°C (from 3:1 ethanol–benzene mixture). Hydroxyacetone [4] was detected in the mother liquid by GLC (yield, 14%).

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