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SYNTHESIS OF ACETYLENE TRIOLS

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Abstract

The data of studies aimed at obtaining biologically active compounds of the acetylene series are presented. Methods have been developed for the production of simple monoesters of acetylene triols, which include: condensation under the conditions of the Favorsky reaction of 1-alkoxy-pentine-2-ols with acetone in liquid ammonia at a temperature of (-30 – -35) °C in the presence of powdered caustic potassium. In this way, 6 new representatives of simple monoesters of acetylene triols were synthesized. It was found that the highest yield of the final product corresponds to an essential radical with methyl and ethyl groups. With an increase in the length of the alkyl radical, the yield of the final products decreases. To prove the composition and structure of the synthesized compounds, the reaction of splitting them into initial products- 1-alkoxy-pentine-2-ols and acetone when heated in the presence of K_2CO_3 (Favorsky reverse reaction), IR spectral data and elemental analysis were used. The test data of synthesized compounds are presented.

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Pharmacological studies of acetylene triols' monoethers obtained up to this point show that they exhibit hypotensive, antispasmodic, and hypotensive properties. Some of them reduce blood pressure [1-6].

Reagents and Equipment Used. The purity of all substances was controlled using thin-layer chromatography on plates in the following systems:

A. Diethyl ether + heptane (2:1)

B. Ethanol + benzene (1:9)

C. Chloroform D. Benzene + chloroform (5:1)

Chromatograms were developed with iodine vapors. The IQ spectra of synthesized compounds were recorded on a device (UR-10, UR-20, thin layer 10-15 microns). NMR spectra were recorded at 80 MHz on a Tesla-B-487 device, with GMDS as the reference in a CC14 solution.

Synthesis of the Main Substances. Synthesis of 1-alkoxy-4-pentyn-2-tyn (General Method): 7g of lithium metal and 1.5 liters of liquid ammonia were added to 100 ml of ether, and 0.8 mol of freshly distilled 1-alkoxy-2,3-epoxypropane was introduced and stirred for 2 hours. The mixture was stirred for an additional 6 hours in a low flow of acetylene. The reaction mixture was left to evaporate the excess ammonia.

To the acetylene alkoxy alcohol suspension, 200 ml of ether and a saturated solution of ammonium chloride (250 ml) were added and decomposed at 0°C. After 45 minutes of stirring, the ether layer was separated, and the aqueous layer was extracted with ether (2x 100 ml). The ether solution was dried with magnesium sulfate. After distillation of the solvent, the reaction product was fractionated under vacuum. The target products were identified by TLC in system B.

Synthesis of 1-ethoxy-4-pentyn-2-ol:

1.5 liters of liquid ammonia was placed in a three-necked flask equipped with a dropping funnel, gas outlet tube, and mechanical stirrer.

Acetylene was passed through with vigorous stirring for 2 hours. After stirring the mixture for 2 hours with low acetylene flow, 7g of finely cut lithium metal was added and stirred for another 30 minutes. Afterward, 100 ml of ether containing 81.6g (0.8 mol) of freshly distilled 1-ethoxy-2,3-epoxypropane was added, and the mixture was stirred for an additional 6 hours. The reaction mixture was left until ammonia evaporated completely. 200 ml of ether was added to the acetylene ethoxy alcohol suspension, and a saturated solution of ammonium chloride (250 ml) was decomposed at 0°C. After 45 minutes of stirring, the ether layer was separated and extracted with aqueous ether (2x 200 ml).

The ether extracts were dried with magnesium sulfate. After distillation of the solvent, the product was fractionated under vacuum. The boiling fraction at 72°C / 10 mm Hg was separated, yielding 86g (84%) with the following constants: n^{20}_D- 1.4420, d^{20}_D - 0.9601, MR_D found - 35.20, MR_D calc. – 35.63.

Example I. Synthesis of 6-methyl-1-ethoxyheptin-4-diol-2,6: 12.8g (0.1 mol) of 1-ethoxy-pentyn-4-ol-2 (XUL) and 5.8g (0.1 mol) of acetone were mixed in 50 ml of dry ether for 1.5 hours and then continued for another 9 hours. The reaction mixture was left until ammonia evaporated completely. The resulting complex was decomposed with water and extracted with ether. The ether extracts were dried with magnesium sulfate. After distillation of the solvent, the reaction products were fractionated under vacuum. 13.58g (73%) of 6-methyl-1-ethoxy-4-heptindiol was obtained. The product was identified by TLC in system B.

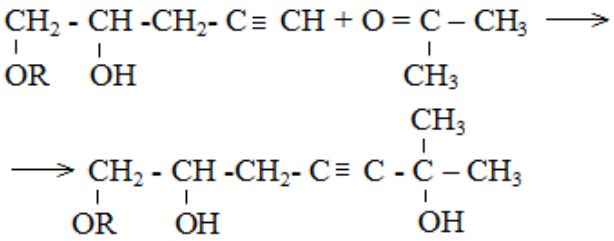
Boiling point: 126-8/2 mmHg, found: C – 64.81%, 64.93%; H – 10.05%, 9.99%. Calculated: C – 64.5%, H – 9.7%.

Decomposition of 6-methyl-1-ethoxy-4-heptindiol: 5g of ethoxyacetylene glycol and 0.5g of potassium were heated in a Favorskii flask under reduced pressure. The reaction products were collected in a receiver cooled with ice. During fractional distillation under vacuum, 0.6g of acetone with a boiling point of 54°C was separated. The remaining fraction was distilled under vacuum, yielding 1.2g of 1-ethoxy-4-pentyn-2-ol with a boiling point of 72/10 mm Hg, n^{20}_D - 1.4420. The yield of the product was insignificant.

The identification of decomposition products was carried out using IR absorption spectra.

Results and Their Analysis. Despite many studies on the synthesis and study of acetylene triols and their mono-, di-, and trie ethers, interest in new representatives of this compound class continues. During these works, we explored the possibility of obtaining monoethers of primary, secondary, and tertiary triols, as such compounds are rarely described in the literature and are of significant theoretical and practical interest.

By condensing 1-alkoxy-4-pentyn-2-ols with acetone, we obtained monoethers of primary-secondary-tertiary triols.



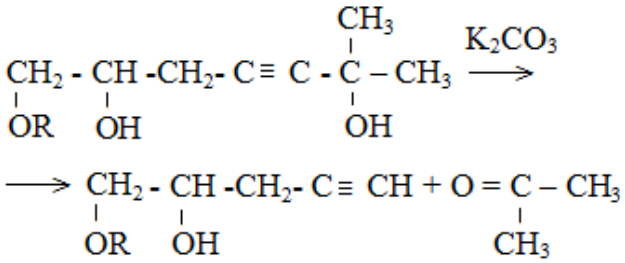
Here: R–C_2H_5, nC_3H_7, C_4H_9, C_6H_{13}, C_7H_{15}, $C_6H_5CH_2$.

The reaction was conducted at -35 to -40°C in liquid ammonia in the presence of potassium hydroxide powder. The increase in alkyl radical resulted in a decrease in the yield of the final product.

No additional products were observed. This shows the sufficient stability of the starting 1-alkoxy-4-pentyn-2-ols in an alkaline environment. The highest yield of the product was achieved with acetylene glycol: KOH: acetone in a 1:4:2 molar ratio. As a result, six acetylene triol monoethers were obtained.

A characteristic feature of acetylene alcohols, glycols, and triols (obtained by condensing acetylene-containing compounds with ketones) is their ability to decompose back into starting products [6], when heated in the presence of alkaline substances. This is one of the methods for proving the structure. Therefore, we decided to study the 6-methyl-1-alkoxy-4-heptin-2,6-diols under the reverse Favorskii reaction conditions using potassium as the alkaline agent.

For this purpose, the obtained compounds (1-V1) were heated under reduced pressure in the presence of small amounts of potassium.



Here: R – C_2H_5, nC_3H_7, C_4H_9, C_6H_{13}, C_7H_{15}, $C_6H_5CH_2$.

The structure of the separation products was determined by IR spectra and their correlation with the IR spectra of known compounds.

Furthermore, the structure of the obtained compounds was confirmed by elementary analysis and the recording of their IR absorption spectra. The IR spectra of acetylene triol monoethers showed absorption zones in the following frequency range: 3350-3400 cm^{-1} (stretching vibrations of OH groups), 2220 cm^{-1} (stretching vibrations of C≡C bonds), and 1110 cm^{-1} (stretching vibrations of C-O-C bonds).

The purity of the products was checked using thin-layer chromatography on silica gel.

The physical-chemical constants of the obtained compounds (1-V1) are provided in Table 1.

Table 1

Physicochemical properties of the obtained compounds

№ birikma	Compound	Exit, %	T.boil. °C(mm Hg)	found,%		formula	counted,%	
				C	H		C	H

1	2-methyl-7-etoxy-3-heptine-2,6-diol	73	126-8/2	64.81	10.05	$C_{10}H_{18}O_3$	64.5	9.7
11	2-methyl-7-propoxy-3-heptine-2,6-diol	67	130-2/2	65.80	9.80	$C_{11}H_{20}O_3$	66.00	10.00
111	2-methyl-7-butoxy-3-heptine-2,6-diol	56	136-8/2	67.20	10.55	$C_{12}H_{22}O_3$	67.30	10.30
1V	2-methyl-7-hexoxy-3-heptine-2,6-diol	54	157-8/2	69.59	11.05	$C_{14}H_{26}O_3$	69.40	10.80
V	2-methyl-7-heptoxy-3-heptine-2,6-diol	51	164-5/2	69.91	11.23	$C_{15}H_{28}O_3$	70.3	10.90
V1	2-methyl-7-benzoxy-3-heptine-2,6-diol	46	180-2/2	72.28	8.25	$C_{15}H_{18}O_3$	72.58	8.06

Conclusion. To study the reactivity of 1-alkoxy-4-pentyn-2-ols, the addition of acetone to alkoxypentynols under Favorskii reaction conditions led to the formation of new monoethers of primary, secondary, and tertiary acetylene triols. Optimal conditions for this reaction were determined.

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