

DIHYDRO PYRAN DERIVATIVES

II.* BIS(3,4-DIHYDRO-2-PYRANYL) ETHERS OF GLYCOLS

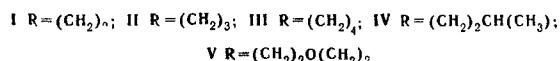
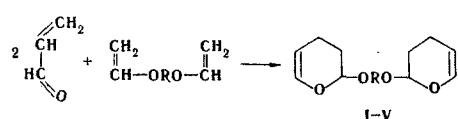
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A number of glycol bis(3,4-dihydro-2-pyranyl) ethers were synthesized by diene condensation of glycol divinyl ethers with acrolein. The physiological activity of the products was tested.

The literature contains only patent information regarding the preparation of a simple bis(3,4-dihydro-2-pyranyl) ether, and the reaction conditions are not indicated [2].

A number of previously unknown glycol bis(3,4-dihydro-2-pyranyl) ethers were obtained by diene condensation of glycol divinyl ethers with acrolein. The reaction proceeds in 4-5 h in the absence of a solvent and a catalyst at 150-160°C via the scheme



The characteristics of I-V are presented in Table 1. Their structure was proved by IR spectroscopic data, the results of elementary analysis, and by chemical transformation.

The bands at 1654 and 3065 cm^{-1} in the IR spectra of I-V indicate, respectively, the presence of $\text{C}=\text{C}$ and $=\text{CH}$ bonds in the dihydropyran rings. The vibrations of the $\text{C}-\text{O}-\text{C}$ groupings appear at 1180 and 1215 cm^{-1} . The absorption bands of an aldehyde group are absent.

The corresponding glycol bis(tetrahydro-2-pyranyl) ethers (V) were obtained by hydrogenation of the synthesized compounds in alcohol in the presence of Raney nickel. Absorption bands at 1654 and 3065 cm^{-1}

*See [1] for communication I.

TABLE 1. Glycol Bis(3,4-dihydro-2-pyranyl) Ethers

Com- ound	R	bp, °C (mm)	MR_D		Empirical formula	Found, %		Calc., %	Yield, %
			d_4^{20}	n_D^{20}		found	calc.		
I	$(CH_2)_2$	105 (3)	1.1098	1.4824	$C_{12}H_{18}O_4$	63.8	8.1	63.7	8.0
II	$(CH_2)_3$	141 (9)	1.0824	1.4790	$C_{13}H_{20}O_4$	65.0	8.4	65.0	8.4
III	$(CH_2)_4$	120 (2)	1.0717	1.4803	$C_{14}H_{22}O_4$	66.1	8.7	66.1	8.7
IV	$(CH_2)_2CH(CH_3)$	141 (7)	1.0661	1.4771	$C_{14}H_{22}O_4$	66.1	8.8	66.1	8.7
V	$(CH_2)_2O(CH_2)_2$	133 (2)	1.1117	1.4820	$C_{14}H_{22}O_5$	61.9	8.1	62.2	8.2

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are absent in the IR spectra of VI; this indicates the completeness of the hydrogenation and again confirms the proposed structure of I-V. As a result of tests on I-V for physiological activity it was ascertained that they are moderately or slightly toxic for white mice ($LD_{50} = 0.7\text{--}1.5$ g/kg). Increased excitability of the test animals was noted in some cases. In the rest of the animals, their behavior remained without special signs, and their reflexes were retained; no effect on the cardiovascular system and respiration was observed.

EXPERIMENTAL

The IR spectra of microlayers of the compounds were recorded with a UR-20 spectrometer (with NaCl and LiF prisms).

The glycol divinyl ethers used as the dienophiles were obtained by direct vinylation of the appropriate glycols with acetylene under pressure in an autoclave in the presence of alkaline catalysts [3].

Ethylene glycol divinyl ether had bp 126° (748 mm) and n_D^{20} 1.4350. Trimethylene glycol divinyl ether had bp 143° (760 mm) and n_D^{20} 1.4332. Tetramethylene glycol divinyl ether had bp 167° and n_D^{20} 1.4398. 1,3-Butylene glycol divinyl ether had bp 54° (17 mm) and n_D^{20} 1.4348. Diethylene glycol divinyl ether had bp 89° (13 mm) and n_D^{20} 1.4465. Freshly distilled acrolein [bp 52–53° (720 mm), n_D^{20} 1.3998] containing 1% hydroquinone as a polymerization inhibitor was used.

Ethylene Glycol Bis(3,4-dihydro-2-pyranyl) Ether (I). A 0.25-liter rotating steel autoclave was charged with 11.4 g (0.1 mole) of ethylene glycol divinyl ether and 11.2 g (0.2 mole) of acrolein, and the mixture was heated for 4 h at 150°. The mixture was removed from the autoclave and distilled, initially at atmospheric pressure [during which 1.1 g of acrolein (bp 52°, n_D^{20} 1.4007) was isolated] and then in vacuo to give 14.1 g (62.4%) of I.

Compounds II–V were similarly synthesized.

Diethylene Glycol Bis(tetrahydro-2-pyranyl) Ether (VI). A long-necked hydrogenation flask was charged with 6.8 g (0.025 mole) of V, 30 ml of ethanol, and a catalytic amount of Raney nickel. A total of 1.2 liters of hydrogen was introduced with vigorous stirring. The mixture was filtered, the ethanol was removed from the filtrate by distillation, and the residue was fractionated in vacuo to give 5.8 g (84.6%) of VI with bp 154° (4 mm), d_4^{20} 1.0755, and n_D^{20} 1.4649. Found: C 61.4; H 9.7%; MR_D 70.51. $C_{14}H_{26}O_5$. Calculated: C 61.3; H 9.6%; MR_D 70.67.

LITERATURE CITED

1. M. G. Voronkov, A. S. Atavin, V. I. Lavrov, V. K. Stankevich, and I. D. Kalikhman, Khim. Geterotsikl. Soenin., 330 (1974).
2. C. E. Smith, D. C. Norton, and S. A. Ballard, US Patent No. 2,514,168 (1950); Chem. Abstr., 44, 8377 (1950).
3. M. F. Shostakovskii and P. V. Tyupaev, Organic Syntheses, Vol. 2, Wiley.