SYNTHESIS OF HOMOLOGS OF 1,4-DIOXANE AND 1,4-DIOXENE

I. F. BEL' SKII, S. N. KHAR' KOV, Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN

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Abstract

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I. F. BEL’ SKII, S. N. KHAR’ KOV, Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN

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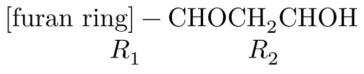
The most widespread method for preparing substituted 1,4-dioxanes is the interaction of chloro- or dichlorodioxanes with a Grignard reagent ([1,3]). Astle and Jacobson ([4]) synthesized a series of alkyl- and aryldioxanes by the interaction of α-glycols with olefin oxides. Individual homologs of 1,4-dioxane have been obtained by heating 1,2- and 1,5-diols with various dehydrating agents, for example with cationites ([5]). Most of these methods are multistage and make it possible to obtain alkyldioxanes in insignificant yields.

Methods for synthesizing homologs of 1,4-dioxene are, up to the present time, almost completely lacking, although 1,4-dioxene itself is quite readily obtained from 2,3-dichlorodioxane and an alkylmagnesium bromide ([6]). In essence, the number of alkyldioxenes is limited to two homologs (5-methyldioxene and 2,6-dimethyldioxene), obtained by Bell ([7]) in the catalytic dehydration of dialkyl glycols.

Earlier in our work it was shown that compounds of the furan series containing in the side chain a functional group ($\mathrm{C{=}O, OH, NH_2, COOH, COOR}$), upon catalytic hydrogenation in the vapor phase, are readily converted into compounds of other classes; moreover, the nature of the transformations depends on the relative arrangement of the furan ring and the functional group in the side chain. In particular, aliphatic bifunctional compounds or heterocycles of various structures with oxygen or nitrogen atoms in the ring may be obtained. In this way homologs of furan ([8]) and tetrahydrofuran ([9]), pyrrole and pyrrolidine ([10]), as well as tetrahydropyran ([11]), were synthesized.

In the present work we have investigated the catalytic transformations of monofurfuryl ethers of 1,2-glycols containing a hydroxyl group in the 4-position relative to the furan ring. For this purpose we synthesized furan ether alcohols of the general formula



$$\text{[furan ring]} - \underset{R_1}{\mathrm{CH}}\mathrm{OCH_2}\underset{R_2}{\mathrm{CH}}\mathrm{OH}$$

(where $R_1 = \mathrm{H}, \mathrm{C_2H_5},\ R_2 = \mathrm{H}, \mathrm{CH_3}$), which were then hydrogenated in a flow system over Pt–C at 140, 180, and 220°. The main reaction proceeding under these conditions is hydrogenolysis of the 1,5 C–O bond, as a result of which, depending on the temperature, either homologs of 1,4-dioxene or homologs of 1,4-dioxane are obtained:

$$\text{(I)} \xrightarrow[\text{Pt–C}]{\mathrm{H_2}} [\mathrm{C_3H_7{-}C(=O){-}CH(R_1)OCH_2CH(R_2)OH}] \xrightarrow{-\mathrm{H_2O}} \text{(II)} \xrightarrow{\mathrm{H_2}} \text{(III)}$$

$$\downarrow \mathrm{H_2}$$

$$\text{(IV)} \xrightarrow{\mathrm{H_2}} \qquad \text{(V)}$$

where $R_1 = \mathrm{H}, \mathrm{C_2H_5}$, $R_2 = \mathrm{H}, \mathrm{CH_3}$.

At 140–180° homologs of 1,4-dioxene (II) are formed, whereas at 220° homologs of 1,4-dioxane (III) are obtained, in yields of 38–70% and 25–80%, respectively.

In addition to temperature, a factor favoring the formation of 1,4-dioxenes is the selective decrease in catalyst activity with time. The activity of the catalyst decreases with respect to the hydrogenation of alkyldioxenes to alkyldioxanes, whereas with respect to hydrogenolysis of the furan ring at the C–O bond, no 1.5-fold decrease in activity was observed even after 200 hours of catalyst operation. During hydrogenation of furfuryl ether alcohols over Pt–C, a side reaction occurs—the cleavage of the ether bond in the side chain, as a result of which furan homologs (IV) and the products of their hydrogenolysis—aliphatic ketones (V)—are formed. From 1-furyl-2-oxa-butanol-4 and 1-furyl-4-methyl-2-oxa-butanol-4, sylvan (2–14%) and pentanone-2 (2–12%) are formed, while from 1-furyl-1-ethyl-2-oxa-butanol-4, respectively, α-propylfuran (35–42%) and heptanone-4 (10–18%) are formed. These data show that the presence of an alkyl radical adjacent to the oxygen atom in the side chain sharply increases the extent of hydrogenolysis of the ether bond. Raising the temperature also promotes cleavage of the ether bond in the side chain, and at 270° this reaction becomes the main one. Thus, for example, 1-furyl-2-oxa-butanol-4 at this temperature is almost completely converted into pentanone-2. Thus, as a result of the study carried out, it was established that hydrogenation of monofurfuryl ethers of 1,2-glycols over Pt–C leads, depending on the temperature, to the formation of the corresponding homologs of 1,4-dioxene or 1,4-dioxane.

Experimental Part

Synthesis of the starting substances. Monofurfuryl ethers of 1,2-glycols were obtained by the reaction of the alcoholates of furfuryl alcohol and ethylfurylcarbinol with ethylene- and propylenechlorohydrins and had the following properties: 1-furyl-2-oxa-butanol-4: b.p. 110° (10 mm), d_4^{20} 1.1327; n_D^{20} 1.4839. Yield 70%. 1-Furyl-4-methyl-2-oxa-butanol-4: b.p. 116° (20 mm), d_4^{20} 1.0840;

n_D^{20} 1.4756. Yield 70%. 1-Furyl-1-ethyl-2-oxa-butanol-4: b.p. 117° (13 mm), d_4^{20} 1.0639; n_D^{20} 1.4770. Yield 50%.

Conditions for carrying out the experiments and methods of analysis. Hydrogenation of monofurfuryl ethers of 1,2-glycols was carried out over platinized carbon (5% Pt) in a flow system at normal pressure and at temperatures of 140, 180, and 220°. The starting substance was fed into the reaction tube at a space velocity of 0.1 h^{-1}. Individual substances isolated from the reaction products by distillation on a rectification column were identified by determination of physical constants, by elemental and spectral analysis data, and also by gas-liquid chromatography. An LKhM-5 IOKh chromatograph with a thermal-conductivity detector was used.

A column 2.5 m long and with an internal diameter of 6 mm was used, packed with Tween-80 (20%) deposited on diatomite, and a column with polyethylene glycol succinate (20%) applied to Chromosorb W. Helium was used as the carrier gas; it was passed through the column, thermostated at 100°, at a rate of 85 ml/min.

Hydrogenation of monofurfuryl ethers of 1,2-glycols over Pt—C at 140 and 180° leads to the formation of homologs of 1,4-dioxene, and at 220°—to homologs of 1,4-dioxane.

Their properties are given in Table 1.

Hydrogenation of homologs of 1,4-dioxene to the corresponding homologs of 1,4-dioxane. The presence of a double bond in the alkyldioxenes was proved by Raman spectra, in which a very intense band was observed in the region 1685—

Table 1

Properties of homologs of 1,4-dioxane and 1,4-dioxene

No.	Formula	Yield, %	B.p., °C/mm	d_4^{20}	n_D^{20}	Found C, %	Found H, %	Found MR	Calculated C, %	Calculated H, %	Calculated MR	Empirical formula
1	C_3H_7-substituted 1,4-dioxane	75	155-156/750	0.9388	1.4290	64.66 64.51	10.70 10.60	35.74	64.57	10.80	35.61	$C_7H_{14}O_2$
2	C_3H_7-substituted 1,4-dioxene	70	154/7[illegible]	0.9671	1.4440	65.54 65.5[illegible]	9.73 9.63	35.06	65.59	9.44	35.14	$C_7H_{12}O_2$

No.	Formula	Yield, %	B.p., °C/mm	d_4^{20}	n_D^{20}	Found C, %	Found H, %	Found MR	Calculated C, %	Calculated H, %	Calculated MR	Empirical formula
3	C_3H_7- and CH_3-substituted 1,4-dioxane	80	67–67.5/18	0.9155	1.4265	66.69 66.79	11.28 11.14	40.40	66.62	11.21	40.23	$C_8H_{16}O_2$
4	C_3H_7- and CH_3-substituted 1,4-dioxene	70	161–162/760 59/17	0.9395	1.4382	68.10 68.1[illegible]	10.[illegible]8 10.13	39.74	67.57	9.92	39.76	$C_8H_{14}O_2$
5	C_2H_5- and C_3H_7-substituted 1,4-dioxane	25	61–62/6	0.9252	1.4370	68.42 68.[illegible]	11.57 11.40	44.80	68.31	11.46	44.85	$C_9H_{18}O_2$
6	C_2H_5- and C_3H_7-substituted 1,4-dioxene	38	60–61/8	0.9446	1.4480	69.39 69.[illegible]	10.17 10.21	40.27	69.19	10.32	40.38	$C_9H_{16}O_2$

1690 cm^{-1}. In the spectra of the hydrogenation products this band disappeared, and bands characteristic of the 1,4-dioxane ring appeared.

Hydrogenation of the alkyldioxenes was carried out over a skeletal Ni—Al catalyst in tetrahydrofuran medium at 80–100° and an initial hydrogen pressure of 100 atm. As a result, the corresponding homologs of 1,4-dioxane were obtained in yields of 80–85%.

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