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ALCOHOLYSIS OF 4-PROPENYL-1,3-DIOXANE

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The methanolysis of 4-substituted 1,3-dioxanes proceeds via the formation of mixed acetals, 1,3-diols, and products of the intra- and intermolecular dehydration of the latter [1-4]. The composition of the reaction products depends on the nature of the dioxane: monoalkyl-substituted dioxanes give mainly the corresponding diols [1, 3, 5, 6], while dialkyl-substituted dioxanes give both diols and also their monomethyl ethers [2, 3, 7, 8], unsubstituted alcohols, dienic hydrocarbons with conjugated double bonds [2, 3, 9], and compounds with a tetrahydrofuran structure [10].

The alcoholysis of 4-alkenyl-substituted dioxanes has never been studied. Their involvement in the reaction in question may provide information about the connection between the nature of the dioxane and the routes by which it is converted during alcoholysis. We have studied the reaction scheme of 4-propenyl-1,3-dioxane (I) with methanol, ethanol and propanol, and the products formed.

It might be expected that 4-hexen-1,3-diol (II) would be the major product or one of the products of the methanolysis of (I), but the reaction goes in the direction leading to the formation of 2-methyl-5,6-dihydropyran (III) and two isomeric hydroxy ethers, viz., 3-methoxy-4-hexen-1-ol (IVa) and 5-methoxy-3-hexen-1-ol (Va), while (II) and its intramolecular-dehydration products could not be detected.

The yield of the products varies over a quite narrow range (Table 1) when the methanolysis of (I) is carried out under different conditions. The total yield of the hydroxy ethers is 60-70% and that of the pyran is 30-40%.

The kinetic curves for the accumulation of the reaction products formed by methanolysis of (I) (Fig. 1) give us reason to suppose that (III), (IVa), and (Va) are formed directly from the dioxane, by-passing the formation of the hexenediol. Nevertheless, we tested experimentally the possibility of (IVa) being formed by reaction of (II) with methanol. The experiments showed that solvolysis of (II) with methanol does indeed give the

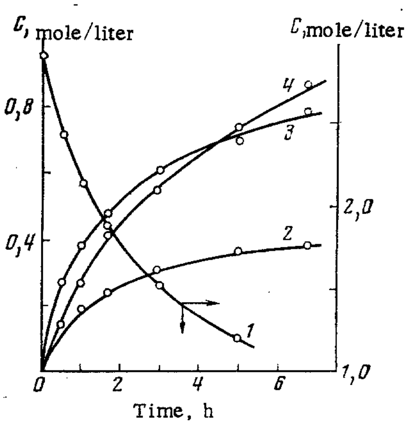

Fig. 1. Kinetic curves for the accumulation of products of the reaction of 4-propenyl-1,3-dioxane with methanol: 1) (I); 2) (IVa); 3) (Va); 4) (III). Temperature 70°C, $[(I)]_0 = 3.0$, $[CH_3OH]_0 = 14.6$ moles/liter, $[H_2SO_4] = 2.9\%$.

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TABLE 1. Methanolysis of 4-Propenyl-1,3-dioxane (I) under Various Conditions

Reaction conditions				Conversion of (I), %	Yield of products, % of theor.		
T., °C	(I):CH_3OH molar ratio	H_2SO_4, %	time, min		(III)	(IVa)	(Va)
70	1:5	2,0	35	18,4	26,8	25,0	48,2
70	1:5	2,0	60	27,6	31,0	22,6	45,2
70	1:5	2,0	100	37,0	35,1	21,0	43,0
70	1:5	2,0	180	49,0	38,2	20,8	41,6
70	1:5	2,0	300	60,6	41,8	20,1	38,0
70	1:5	2,9	180	52,2	33,0	24,0	44,0
70	1:5	4,0	180	71,1	50,0	17,6	32,4
70	1:3	2,9	180	53,0	53,5	17,6	28,7
70	1:10	2,9	180	65,2	37,1	21,0	41,5
50	1:5	2,9	180	14,5	19,6	28,1	51,0
60	1:5	2,9	180	31,3	29,0	24,5	46,1

expected (IVa), as well as (Va), which is presumably formed by allylic rearrangement of (IVa). Carrying out the reaction at 50°C in the presence of 2.5% of H_2SO_4 gave the following results:

Time, min	0	10	20	30	60
(IVa), mole/liter	—	0,15	0,21	0,25	0,26
(Va), mole/liter	—	0,35	0,48	0,57	0,60
(II), mole/liter	0,90	0,40	0,20	0,07	0,04

In order to check our hypothesis about the formation of (Va) from (IVa), we investigated the behavior of the latter under the conditions employed for methanolysis of (I). The experiments confirmed the possibility of the allylic rearrangement of (IVa) into (Va) and confirmed that an equilibrium is established between the isomeric hydroxy ethers (70°C, 2.3% H_2SO_4)

Time, min	0	10	30	60	80
(IVa), mole/liter	0,90	0,65	0,40	0,29	0,29
(Va), mole/liter	—	0,25	0,50	0,60	0,61

We also investigated this equilibrium in the direction from (Va) to (IVa) under the same conditions as in the previous experiment

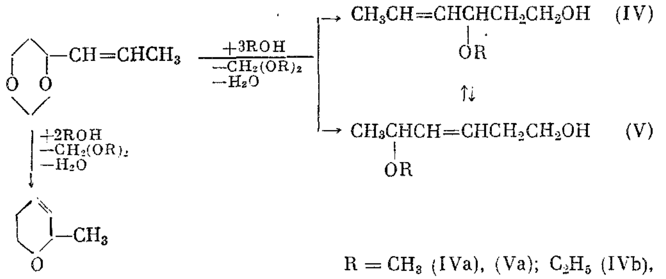
Time, min	0	10	30	50	80
(IVa), mole/liter	—	0,15	0,28	0,30	0,31
(Va), mole/liter	0,90	0,75	0,62	0,59	0,59

It follows from the results obtained that (IVa) and (Va) are capable of undergoing mutual interconversion; the (IVa):(Va) molar ratio in the equilibrium mixture at 70°C is ~1:2.

Thus, on the basis of the data discussed above, the hydroxy ethers are evidently formed in parallel directly from (I) during its methanolysis. At the same time, (Va) may also be formed consecutively by allylic rearrangement of (IVa). The most probable route for the formation of (III) during methanolysis of (I) is intramolecular rearrangement of (I) with elimination of formaldehyde. This hypothesis is confirmed by the fact that heating (I) in acidified sulfolane for 6 h gives (III) in a yield of 61.2% based on the (I) introduced.

Ethanol and propanol react with (I) similarly to methanol, giving (III) and the corresponding hydroxy ethers.

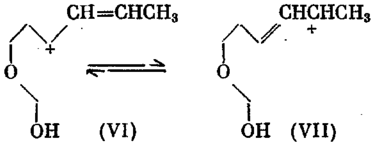
On the basis of all the data obtained we can postulate the following reaction scheme for the alcoholysis of (I):



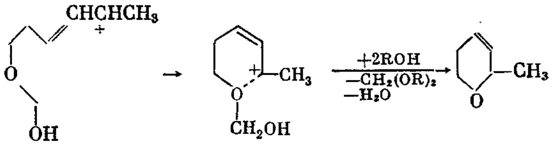
(III)

R = CH_3 (IVa), (Va); C_2H_5 (IVb), (Vb); C_3H_7 (IVc), (Vc)

According to the available literature data, the methanolysis of alkyl-substituted dioxanes proceeds with ring-opening across the $C^2—O^1$ bond [1, 11, 12]. The peculiar behavior of (I) in its reactions with alcohols may be due to the fact that the dioxane ring in this case is possibly opened across the $O^3—C^4$ bond, forming an allylic cation (VI) which is stabilized by the π electrons of the adjacent double bond and readily undergoes isomerization [13]



Reaction of (VI) and (VII) with alcohols then leads, via intermediate hemiformals, to the isomeric hydroxy ethers. In addition, carbonium ion (VII) cyclizes to form the pyran



EXPERIMENTAL

Compound (I) was synthesized as in [14] by condensation of piperylene with formaldehyde: bp 177.5°C; d_4^{20} 0.9837; n_D^{20} 1.4444.

Chromatographic analysis was carried out with an LKhM-8MD instrument with a column (2 m × 3 mm) containing 13% dimethylsiloxane rubber on INZ-600. The carrier gas was H_2 (60-200 ml/min).

The PMR spectra were recorded in CCl_4. The chemical shifts are given on the δ scale, ppm.

Methanolysis of (I). A mixture of 390 g of (I), 475 g of methanol and 51.9 g of H_2SO_4 (d = 1.83) was heated at 60-65°C for 4 h. Methylal was withdrawn from the reaction zone as it was formed. The mixture was neutralized with gaseous NH_3, filtered to remove salts, and distilled at atmospheric pressure and under vacuum, to give 31 g of (I) (92% conversion), 120 g of (III) (43.7%), 52.1 g of (IVa) (14.3%), and 108 g of (Va) (29.6%). Compound (III) [15]: bp 103°C; d_4^{20} 0.8791; n_D^{20} 1.4334. Compound (IVa): bp 40-41°C/3 mm; d_4^{20} 0.9242, n_D^{20} 1.4428; unsaturation 0.99; PMR spectrum 1.68 d (CH_3CH); found C 64.69, H 10.52, OH 13.5, CH_3O 24.0%, MR 37.28; $C_7H_{14}O_2$; calculated C 64.61, H 10.77, OH 13.7, CH_3O 23.8%, MR 37.34. Compound (Va): bp 56-57°C/3 mm; d_4^{20} 0.9249; n_D^{20} 1.4458; unsaturation 0.97; PMR spectrum 1.19 d (CH_3CHO); found C 64.51, H 10.51, OH 13.6, CH_3O 23.7%, MR 37.47; $C_7H_{14}O_2$); calculated C 64.61, H 10.77, OH 13.7, CH_3O 23.8%, MR 37.34.

Ethanolysis of (I). A mixture of 240 g of (I), 280 g of abs. ethanol and 12.7 g of H_2SO_4 (d = 1.83) was heated at 70°C for 5 h. Analogous treatment of the reaction mixture and distillation gave 30 g (21.0%) of (III), 52.1 g (24.7%) of (IVb), and 78.5 g (38.4%) of (Vb). Compound (IVb) [16]: bp 53-54°C/4 mm; d_4^{20} 0.9067; n_D^{20} 1.4398; unsaturation 0.99; PMR spectrum 1.64 d ($CH_3CH=$); found C. 66.51, H 11.00, OH 11.5%, MR 41.83; $C_8H_{16}O_2$; calculated C 66.67, H 11.11, OH 11.8%, MR 41.99.

Compound (Vb): bp 69-70°C/4 mm; d_4^{20} 0.9089; n_D^{20} 1.4190; unsaturation 0.98; PMR spectrum 1.11 d (CH_3CHO); found C 66.55, H 10.92, OH 11.6%, MR 41.67; $C_8H_{16}O_2$; calculated C 66.67, H 11.11, OH 11.8%, MR 41.99.

Propanolysis of (I). A mixture of 238 g of (I), 447 g of n-propanol and 14.8 g of H_2SO_4 (d = 1.83) was refluxed at 70°C for 5 h. The mixture was worked up as usual and distilled to give 34.1 g (18.7%) of (III), 38.8 g (13.2%) of (IVc), and 91 g (31.0%) of (Vc). Compound (IVc): bp 75-76°C/5 mm; d_4^{20} 0.9023; n_D^{20} 1.4442; unsaturation 0.98; PMR spectrum 1.63 d ($CH_3CH=$); found C 68.23, H 11.21, OH 10.6%, MR 46.52; $C_9H_{18}O_2$; calculated C 68.35, H 11.39, OH 10.8%, MR 46.64. Compound (Vc): bp 90-91°C/5 mm; d_4^{20} 0.9064; n_D^{20} 1.4460; unsaturation 0.97; PMR spectrum 1.12 d (CH_3CHO); found C 68.17, H 11.19, OH 10.7, MR 46.49; $C_9H_{18}O_2$; calculated C 68.35, H 11. 39, OH 10.8%, MR 46.64.

Preparation of (III) from (I). A mixture of 98.5 g of (I), 3.5 g of H_2SO_4 (d = 1.83) and 100 ml of sulfolane was heated in the still of a rectification column for 6 h, while withdrawing (III) as it was formed together with water. The distillate was dried and redistilled to give 46.1 g (61.2%) of (III) with constants similar to those described above.

The kinetic experiments on the methanolysis of (I) were conducted in thermostatted glass ampules with a capacity of 3 ml. The ampules were rapidly cooled to −18°C at fixed intervals, opened, and their contents neutralized with gaseous NH_3 and analyzed by GLC. The reactions of (II) (synthesized from (I) as in [17]), (IVa), and (Va) in methanol solution were studied similarly.

CONCLUSIONS

1. Alcoholysis of 4-propenyl-1,3-dioxane in the presence of H_2SO_4 gives 2-methyl-5,6-dihydropyran and the monoalkyl ethers of 4-hexene-1,3-diol and 3-hexene-1,5-diol, although the diols themselves are not detected in the reaction products.

2. The reaction products are formed directly from the dioxane, by-passing the formation of the diols. This unusual reaction path is explained on the assumption that ring-opening takes place across the O^3-C^4 bond during the alcoholysis of 4-propenyl-1,3-dioxane, resulting in the formation of an allylic cation.

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SYNTHESIS OF UNSATURATED AMINES BY REACTION OF BUTADIENE WITH PRIMARY AMINES IN THE PRESENCE OF PALLADIUM COMPLEXES

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The amination of 1,3-dienes with primary or secondary amines in the presence of Pd-containing catalysis is nonselective and results in a complex mixture of oligomers [1, 2]. With the object of finding ways to regulate the addition of 1,3-dienes to primary amines, we have investigated the effect of various activators

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