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ACETALS AND ETHERS—XIII[1]

REACTION PRODUCTS OF 2-BUTENAL WITH ETHYLENE GLYCOL

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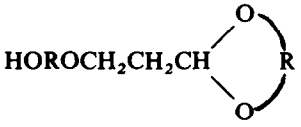
Abstract—The unsaturated cyclic acetal, 2-(1-propenyl)-1,3-dioxolane (**2**), has been found as an intermediate product in the *p*-toluenesulfonic acid catalysed reaction of 2-butenal with an excess of ethylene glycol. The final product consisted of 2-[2-(2-hydroxyethoxy)-propyl]-1,3-dioxolane (**3**), and a small amount of geometric isomers of *cis*- and *trans*-5-(2-hydroxyethoxy)-7-methyl-1,4-dioxepane (**4a** and **4b**, respectively).

Recently, we have shown[1] that the *p*-toluenesulfonic acid catalysed reaction of 2-propenal with an excess of 1,2- or 1,3-diols leads to formation of 2-[2-(hydroxyalkoxy)-ethyl]-1,3-dioxolanes and 1,3-dioxanes:



In this study the results of investigations on the 2-butenal (**1**) reaction with ethylene glycol are presented. The above reaction has been investigated under similar conditions, as described elsewhere.[1] By the analogy to the previous reaction, one can expect the formation of 2-[2-(2-hydroxyethoxy)-propyl]-1,3-dioxolane (**3**) as the only reaction product. This compound should be formed by acetalization of the CO group and by nucleophilic addition of a diol molecule to the activated —C=C— bond. Chromatographic analysis indicated the presence of an intermediate product, i.e. 2-(1-propenyl)-1,3-dioxolane (**2**; Fig. 1). This intermediate product underwent further conversions and it disappeared after a sufficiently long reaction time.

It turned out, however, that **3** is not exclusively the product of addition of two ethylene glycol molecules to 2-butenal. In the case, the reaction mixture was composed of **3** and a small amount of geometric isomers of *cis*- and *trans*-5-(2-hydroxyethoxy)-7-methyl-1,4-dioxepane (**4a** and **4b**; Scheme 1).

The presence of 5-alkoxy-1,4-dioxepanes along with

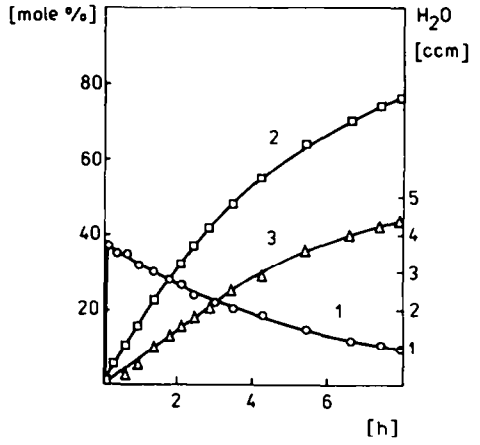
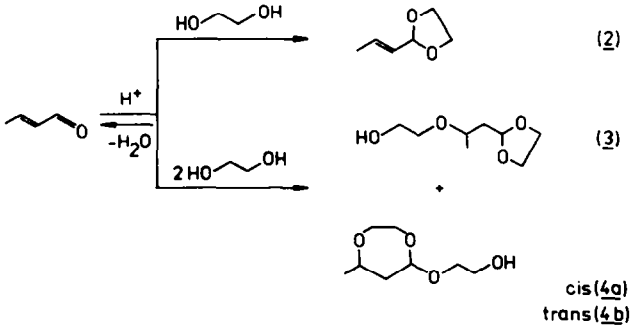


Fig. 1. Changes in the composition of the reaction mixture, 2-butenal/ethylene glycol, vs. reaction time. 1, 2-(1-propenyl)-1,3-dioxolane (**2**); 2, mixture (**3** + **4a** + **4b**); 3, reaction water released.

2-(β-alkoxyalkyl)-1,3-dioxolanes has been found by Mikhailov and Povarov[2-4] in the BF_3 catalysed reaction of 2-alkyl or 2-aryl-1,3-dioxolanes with vinyl-alkyl ethers. It has also been described by Mikhailov and Povarov,[3] that in the absence of solvent the 5-alkoxy-1,4-dioxepane derivatives undergo polymerization, but on the other hand the presence of solvent causes some partial rearrangement to 2-(β-alkoxyalkyl)-1,3-dioxolanes. The individual products have not been isolated from the reaction mixture. Their

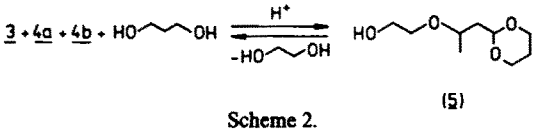


Scheme 1.

structure has been proven by the analysis of the 2,4-dinitrophenylhydrazone derivatives of the corresponding aldehydes as well as by the analysis of the individual aldehydes. The latter were obtained by the acidic hydrolysis of certain reaction mixtures.

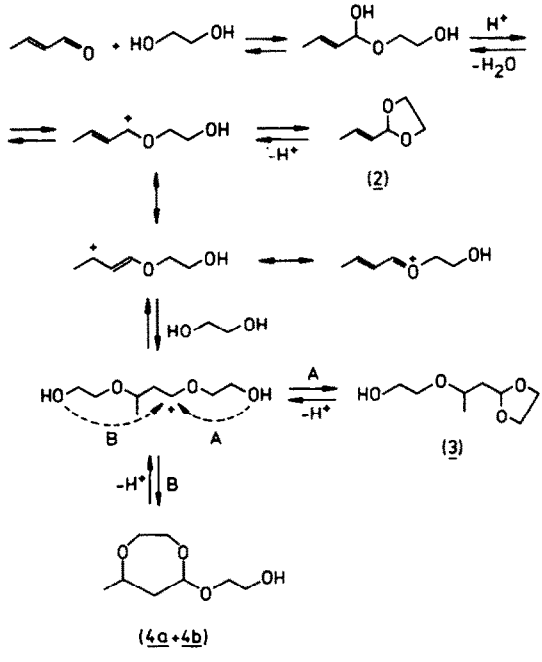
Recently, Lelandais *et al.*[5] presented a new and interesting method of synthesis of 2-methoxy-1,4-dioxacyclanes by anodic oxidation of cyclic ketals of β-ketocarboxylates on a graphite electrode.

All attempts to separate the compounds (**3** + **4a** + **4b**) were not satisfactory enough because of the similar properties of the compounds. A slight deformation of the chromatographic peak (GLC, Carbowax 20M) was the only evidence for the presence of **4a** + **4b** besides the main component (**3**). Thus, the identification of **3** and (**4a** + **4b**), as well as the evaluation of their contents in the reaction product, have been carried out indirectly. The mixture (**3** + **4a** + **4b**) was submitted to transacetalization with trimethylene glycol. 2-[2-(2-Hydroxyethoxy)-propyl]-1,3-dioxane (**5**) was found to be the only product. The reaction was carried out with an excess of trimethylene glycol under mild conditions to avoid any destruction of the ether bond (Scheme 2).



Scheme 2.

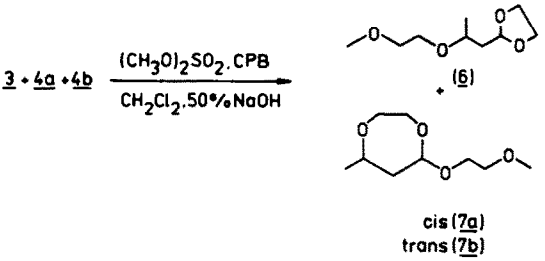
When the isolated **5** was subjected to the reversible transacetalization reaction in the presence of an excess of ethylene glycol, the starting mixture, i.e. (**3** + **4a** + **4b**) was obtained. It seems probable that the starting mixture is the equilibrium mixture of 5- and 7-membered ring compounds. Because its quantitative ratio is dependent on the relative ring stability, **3** is predominant in relation to (**4a** + **4b**). It is also probable that the formation of the mixture (**3** + **4a** + **4b**) in the reaction of 2-butenal with ethylene glycol proceeds according to Scheme 3.



Scheme 3.

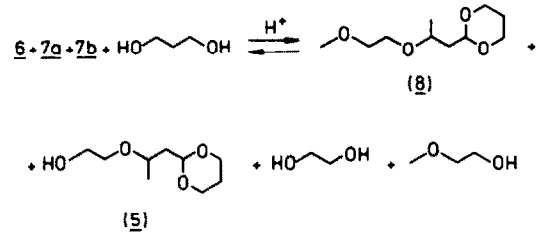
It is understandable that the transacetalization product of the mixture (**3** + **4a** + **4b**) with trimethylene glycol contains exclusively **5**. Its 6-membered 1,3-dioxane ring structure is very stable, thus the equilibrium between **5** and 5-(3-hydroxypropoxy)-7-methyl-1,4-dioxepane (another possible the transacetalization product) is strongly shifted towards **5**.

To identify the substituent at C-5 of (**4a** + **4b**), the mixture (**3** + **4a** + **4b**) was submitted to the conditions (PTC) with $(CH_3O)_2SO_2$ (Scheme 4).



Scheme 4.

Similar properties of the mixture components made the separation of the individual compounds **6**, **7a** and **7b** impossible. Its mixture composition was estimated from chromatographic peak areas, as follows: 20% of (**7a** + **7b**), τ_R = 35.6 min and 80% of **6**, τ_R = 41.2 min (XE60, T = 420 K). The assumption, that the degree of conversion of all mixture components, i.e. **3**, **4a** and **4b** is equal, leads to the conclusion that the composition of the mixture (**6** + **7a** + **7b**) may correspond to **3** and (**4a** + **4b**) contents in the initial mixture (**3** + **4a** + **4b**). Thus, the mixture (**6** + **7a** + **7b**) was subjected to the transacetalization reaction with an excess of trimethylene glycol (Scheme 5). Because the conditions did not

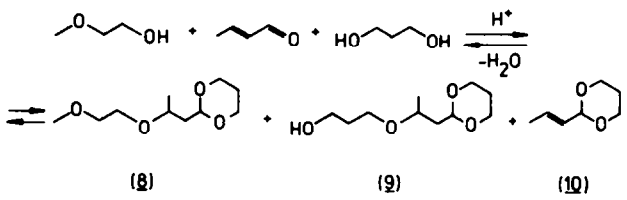


Scheme 5.

cause the ether bond destruction, the qualitative and quantitative mixture composition (GLC analysis) indicated that the presence of (**7a** + **7b**) in the initial mixture was confirmed by the presence of **5** and the methyl monoether of ethylene glycol. The reproduction of the molecule of methyl monoether of ethylene glycol under this condition could only be caused by breaking of the acetal bond. The components **5** and **8** were identified by a comparison with the authentic substances. 2-[2-(2-Methoxyethoxy)-propyl]-1,3-dioxane (**8**) was obtained in the reaction of 2-butenal with the mixture of trimethylene glycol and methyl monoether of ethylene glycol (Scheme 6).

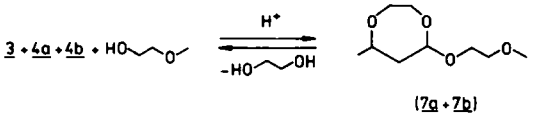
2-[2-(3-Hydroxypropoxy)-propyl]-1,3-dioxane (**9**) was identified as a by-product of the above reaction aside from the main component **8**. A slight amount of 2-(1-propenyl)-1,3-dioxane (**10**) was also found.

The mixture of geometric isomers of *cis*- and *trans*-5-(2-methoxyethoxy)-7-methyl-1,4-dioxepane (**7a** + **7b**) was obtained from the transacetalization product of the mixture (**3** + **4a** + **4b**) with an excess of methyl



Scheme 6.

monoether of ethylene glycol (Scheme 7). All attempts to obtain the individual isomers from the mixture (**7a** + **7b**) were not successful because of very similar compound properties. GLC analysis (XE60) indicated only the presence of two poorly separated peaks, among which the dominant compound showed a shorter retention time. The quantitative ratio of isomers could be evaluated approximately as 4:1. Figure 2 shows the ^{1}H-NMR spectrum of the isomer mixture (**7a** + **7b**). Since the spectrum is very complicated, its analysis provides only approximate data. Additionally IR spectra of the isomer mixture (**7a** + **7b**) does not show bands of OH and CO groups.



Scheme 7.

Compound **5** and the methyl monoether of ethylene glycol were the products of transacetalization of **7a** + **7b** with trimethylene glycol. The mixture (**3** + **4a** + **4b**) and methyl monoether of ethylene glycol were the products of transacetalization of **7a** + **7b** with ethylene glycol.

The presence of **5** in the reaction product of the mixture (**3** + **4a** + **4b**) with trimethylene glycol and the absence of **9** and **10** confirmed the assumption that the ether bond had not been broken. Similarly, **6** was identified in the reaction product **8** using an excess of ethylene glycol, whereas (**7a** + **7b**), **5** and **3** or the methyl monoether of ethylene glycol were not present.

EXPERIMENTAL

All starting materials were distilled before use. 2-Butenal was stabilized with hydroquinone (0.1%). The b.ps, read at the top of distillation column (glass packing, efficiency of *ca* 10TP) were not corrected. Chromatographic analyses were carried out using a gas–liquid chromatograph Giede 18.3.6. Metallic columns 0.004 × 2 m were filled with 20% Carbowax 20M on Chromosorb G/AW-DMCS (80/100 mesh), alkalized with 0.5% KOH or 15% Silicon XE60 on Chromosorb G/AW-DMCS (60/80 mesh). ^{1}H-NMR spectra were recorded on a Tesla BS 497 instrument having 100 MHz frequency of generator. The measurements were carried out for 10% solns in $CDCl_3$ using TMS as an internal standard.

Reaction of 2-butenal with ethylene glycol

A two-phase mixture containing 35.0 g (0.5 mol) of 2-butenal, 124.0 g (2 mol) of ethylene glycol, 200 ml of $CHCl_3$ and 0.6 g of *p*-toluenesulfonic acid monohydrate was vigorously stirred and boiled for 15 hr. Water removal was by means of a Dean–Stark adapter. Then, the homogenic mixture was cooled to room temp and neutralized with excess $NaHCO_3$. The neutralization products were filtered off and the filtrate was freed of $CHCl_3$. The residue was subjected to fractional distillation giving a small amount of 2-(1-propenyl)-1,3-dioxolane (**2**), the excess of glycol used and the mixture of **3** (the main component) and *cis*- and *trans*-**4a** + **4b**. B.p. 412.5 K/2.3 kPa, n_D^{293} 1.4528, d_{277}^{293} 1.0969. The overall yield of **3** + **4a** + **4b** was 74.9 g (85 mol %). The average molecular weight of **3** + **4a** + **4b**, determined by the oxime method,[6] was 175.3 ± 0.8 (calculated value for $C_8H_{16}O_4$ = 176.2).

Reaction of 2-butenal with the mixture of trimethylene glycol and methyl monoether of ethylene glycol

2-Butenal (21 g, 0.3 mol), trimethylene glycol (30.4 g, 0.4 mol), methyl monoether of ethylene glycol (76.1 g, 1 mol), *p*-toluenesulfonic acid monohydrate (0.6 g) were heated to boiling in 150 ml $CHCl_3$ for 15 hr. Water removal was by

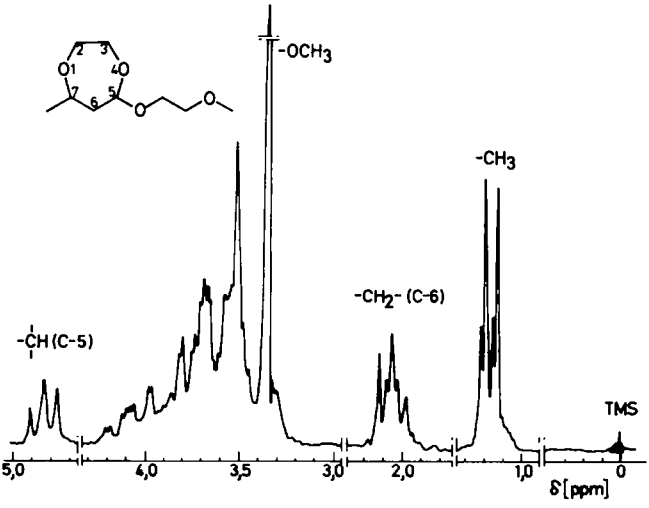


Fig. 2. ^{1}H-NMR spectrum of *cis*- and *trans*-5-(2-methoxyethoxy)-7-methyl-1,4-dioxepane mixture (**7a** + **7b**, $CDCl_3$, TMS = 0).

means of a Dean–Stark adapter. After cooling, the mixture was neutralized with excess $NaHCO_3$, the neutralization products were filtered, while $CHCl_3$ and the excess of methyl monoether of ethylene glycol along with a small amount of **10** were evaporated on a rotary evaporator. The residue was submitted to fractional distillation to give the following fractions: homogenic azeotrope of **8** and unreacted trimethylene glycol, b.p. 378–379 K/1.3 kPa; pure **8**, b.p. 398 K/1.3 kPa; **9**, b.p. 434.5 K/2.3 kPa, 9.2 g (15 mol %), n_D^{293} 1.4568, d_{277}^{293} 1.0563. Compound **8** was isolated from the azeotropic fraction by extraction with 7 × 10 ml of n-hexane. The n-hexane extracts were combined, the solvent was stripped and **8** was obtained by distillation. The overall yield of **8** was 46.0 g (75 mol % in relation to 2-butenal), n_D^{293} 1.4409, d_{277}^{293} 1.0194. Mol wts of **8** and **9** as determined by the oxime method were as follows: 203.7 ± 0.6 (calculated value for $C_{10}H_{20}O_4$ = 204.3), 204.9 ± 1 (calculated value for $C_{10}H_{20}O_4$ = 204.3). ^{1}H-NMR spectrum of **8** (TMS=O, J [Hz]): CH_3O— (3.37 ppm, s, 3H), —OCH_2CH_2O— (3.43–3.58 ppm, m, 4H), CH_3— (1.15 ppm, 6 Hz, d, 3H), —CH_2— in the α position (two non-equivalent protons) (1.82 ppm, 4.3, 7.7 and 14 Hz, m, 1H and 1.65 ppm, 6.6, 5.3 and 14 Hz, m, 1H), acetal methine proton at C-2 carbon atom of the ring (4.68 ppm, 4.3 and 6.6 Hz, dd, 1H) and characteristic signals of 1,3-dioxane ring protons. ^{1}H-NMR spectrum of **9** (TMS=O, J [Hz]): CH_3— (1.15 ppm, 6 Hz, d, 3H), acetal methine proton at C-2 carbon atom of the ring (4.67 ppm, 4.5 and 6 Hz, dd, 1H), HO— (3.15 ppm, s, 1H).

Reaction of O-methylation of mixture (**3** + **4a** + **4b**) *with* $(CH_3O)_2SO_2$

A two-phase mixture containing 35.2 g (0.2 mol) of the mixture (**3** + **4a** + **4b**) in 100 ml CH_2Cl_2 and 0.52 mol of 50% NaOH containing 0.5 g of cetylpyridinium bromide was vigorously stirred, and 30.3 g (0.24 mol) of $(CH_3O)_2SO_2$ was added dropwise during 1.5 hr at 300–305 K. After 8 hr of stirring, 4 ml conc NH_3 was added and the stirring continued for another 0.5 hr. The mixture was transferred to an extractor and shaken with 50 ml of H_2O. The organic layer was separated and the water layer was extracted with 3 × 15 ml of CH_2Cl_2. The combined organic phases were shaken with 2 × 10 ml of H_2O and dried over $MgSO_4$. The residue, after evaporation of CH_2Cl_2, was distilled twice to give 27.9 g (73.3 mol %) of the mixture (**6** + **7a** + **7b**), b.p. 391.2–392.2 K/1.4 kPa, n_D^{293} 1.4374, d_{277}^{293} 1.0355. The average mol wt of the mixture, determined by the oxime method, was 190.6 ± 1 (calculated value for $C_9H_{18}O_4$ = 190.2).

Reaction of transacetalization of mixture (**3** + **4a** + **4b**) *with trimethylene glycol*

35.2 g (0.2 mol) of mixture (**3** + **4a** + **4b**), 60.9 g (0.8 mol) of trimethylene glycol and several crystals of *p*-toluenesulfonic acid were maintained at room temp until the equilibrium of the reaction was reached (the course of the reaction was controlled by GLC). The mixture was neutralized with excess $NaHCO_3$, the neutralization products were filtered off, and the filtrate subjected to fractional distillation. In this way the fraction of **5**, 32.3 g (85 mol %), b.p. 412 K/1.4 kPa, n_D^{293} 1.4562, d_{277}^{293} 1.0770 was isolated. ^{1}H-NMR spectrum of **5** (TMS=O, J [Hz]): acetal methine proton at C-2 atom of the ring (4.71 ppm, 4.3 and 6 Hz, dd, 1H), —CH_2— in the α position in relation to C-2, two non-equivalent protons (1.87 ppm, 4.3, 8.0 and 14.3 Hz, m, 1H and 1.70 ppm, 4.7, 6.0 and 14.3 Hz, m, 1H); —CH— (3.71 ppm, 4.7, 6.0 and 8 Hz, m, 1H), CH_3— (1.29 ppm, 6 Hz, d, 3H), —OCH_2CH_2O— (3.60–3.80 ppm, m, 4H), HO— (3.02 ppm, s, 1H).

Reaction of transacetalization of mixture (**3** + **4a** + **4b**) *with methyl monoether of ethylene glycol*

35.2 g (0.2 mol) of mixture (**3** + **4a** + **4b**), 76.1 g (1 mol) of methyl monoether of ethylene glycol and several crystals of *p*-toluenesulfonic acid were maintained at room temp until equilibrium was reached. The mixture was neutralized with excess $NaHCO_3$. The neutralization products were filtered off and the excess of unreacted methyl monoether of ethylene glycol was evaporated. The residue was subjected to fractional distillation to give a fraction of *cis*- and *trans*-(**7a** + **7b**) as a homogenic azeotrope with ethylene glycol, b.p. 369.2–369.7 K/1.4 kPa. The azeotropic fraction was extracted with 7 × 10 ml n-hexane. The n-hexane layers were combined and the solvent was evaporated. The residue was subjected to fractional distillation to give 10.7 g (28 mol %) of mixture (**7a** + **7b**), b.p. 386.7–387 K/1.3 kPa, n_D^{293} 1.4429, d_{277}^{293} 1.0526. Mol wt of the mixture (**7a** + **7b**), determined by the oxime method, was 190.7 ± 0.6 (calculated value for $C_9H_{18}O_4$ = 190.2). Elementary analysis showed *C*, 56.7% and *H*, 9.6% (calc. $C_9H_{18}O_4$; C, 56.8 and H, 9.5%).

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