HYDROLYSIS OF SOME BISACETALS OF DIALDEHYDES

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We studied the complete hydrolysis of the bis-diethylacetal of β -ethoxyglutaric dialdehyde (I) earlier [1] and arrived at the conclusion that the reaction proceeds complexly, forming a mixture of glutaconic dialdehyde (II), β -ethoxyglutaric dialdehyde (III), and 2,4,6-triethoxytetrahydropyran (IV):



Moreover, (IV) was isolated from the reaction mixture in 12-15% yield. The question of the ratio of (II) and (III) was not solved. The sodium salt of the enol form (II) was successfully isolated in 60-70% yield by treating the mixture with a sodium hydroxide solution; it was therefore assumed that the basic component of the mixture is (II). To solve the problem of the composition of the mixture after hydrolysis of (I), we conducted some supplementary investigations. The hydrolysis product of (I) in the presence of traces of phosphoric acid was neutralized with chalk, and then extracted with ether; the residue after drying and distillation of the ether was introduced into a reaction with carbethoxymethylenetriphenylphosphorane under the usual conditions of the Wittig reaction. As a result, a complex ester was obtained, which corresponded to the diethyl ester of 4-ethoxyoctadiene-2,6-dioic-1,8 acid (V), in about 80% yield [if we assume the initial hydrolyzate as pure (III)]. The structure of (V) was supplementarily confirmed by its infrared and ultraviolet spectra (absence of a system of conjugated double bonds)

HOCCH₂CH (OC₂H₅) CH₂CHO
$$\xrightarrow{2(C_6H_5)_3P=CHCOOC_2H_5}$$

(III)
C₂H₅OOCCH=CIICH₂CH (OC₂H₅) CH₂CH=CIICOOC₂H;
(**V**)

In addition we condensed the hydrolyzate of (I) with nitromethane and, as a result, obtained a product corresponding to 2,6-dihydroxy-4-ethoxynitrocyclohexane (VI)



Of the possible mixture of isomers, we isolated only one crystalline isomer in the individual state, with m.p. $103-105^{\circ}$, in about 50% yield. A condensation of a similar type was recently described by Lichtenthaller [2] for glutaric dialdehyde itself. Finally, by taking the ultraviolet spectrum of the hydrolyzate, we determined that the absorption intensity in the region characteristic of conjugated unsaturated aldehydes is extremely low: 225 mµ (ε 270), 265-275 mµ (ε 310). Thus, it can be considered demonstrated that when (I) is hydrolyzed in the presence of

phosphoric acid, (III) is formed as the main product. The formation of the sodium salt of the enol form (II), noted earlier when the hydrolyzate was treated with sodium hydroxide, should be explained by splitting out of the ethoxy group in (III) under the action of alkali.

 $\begin{array}{c} \text{HOCCH}_2\text{CH} (\text{OC}_2\text{H}_5) \oplus \text{CH}_2\text{CHO} & = \frac{\text{NaON}}{\alpha_2\text{H}_5\text{OH}} \text{ NaOCH}_{2}\text{CHCH} \oplus \text{CHOHO} \\ \end{array}$

Just after the publication of our work [1], the article [3] appeared in print, in which the authors conducted the hydrolysis of the bis-dimethylacetal of o-methoxyglutaric dialdehyde in the presence of hydrochloric acid at 56°, and concluded on the basis of the formation of the sodium salt of the enol (II) that glutaric dialdehyde arises under these conditions. In the light of the data described above, this conclusion seemed doubtful. As a verification, we conducted the hydrolysis of (I) in the presence of mineral acids (hydrochloric and sulfuric); after neutralization, extraction with ether, drying, and removal of the ether, the residue was subjected to a spectroscopic study. In not one case did the absorption intensity (ε) at 225 and 265-275 mµ exceed 110-310, although these hydrolyzates also gave sodium salts of the enol form (II) in high yields. From this it can be concluded that in the presence of strong acids hydrolysis of (I) gives chiefly β -ethoxyglutaric dialdehyde (III).

Continuing our past work [1], we were also interested in the possibility of selective hydrolysis of the diacetal type $(C_2H_5O)_2CH[CH_2CH(OC_2H_5)]_nCH_2CH(OC_2H_5)_2$, n = 2 (VII), n = 3 (VIII), at one of the acetal groups, as well as the possibility of hydrolysis of (VII) and (VIII) with cleavage of the ethoxy groups and the formation of dialdehydes of the type HOCCH₂(CH = CH)_nCHO or HOC(CH = CH)_nCH₂(CH = CH)_mCHO. However, it was found that hydrolysis of the bis-diacetals (VII) or (VIII) with an equivalent amount of water in the presence of phosphoric or p-toluene-sulfonic acid takes place nonselectively, and after distillation of the reaction mixture, only the products of complete hydrolysis of the diacetals (VII) or (VIII) with splitting out of the ethoxy groups (boiling with a solution of p-toluenesulfonic acid with distillation of the alcohol, boiling with an aqueous-dioxane solution in the presence of sulfuric acid with distillation of the alcohol, boiling with an aqueous-dioxane solution in the presence of sulfuric acid with distillation of the alcohol, boiling with a negative results. In all these cases, resins were formed, from which no individual products could be isolated. Under milder conditions, complete splitting out of the ethoxy groups was formed.

In one of the works of Baumgarten [4], it was noted that the bis-dimethylacetal of glutaconic aldehyde is selectively hydrolyzed, forming a monomethylacetal of the type of (IX); however, the structure of the product was not confirmed. In the light of our studies on the selective hydrolysis of diacetals [5-7], such a reaction direction seemed to us to be the less probable of the two possible:

(CH₃O)₂ CHCH₂CH=CHCH (OCH₃)₂ \downarrow (CH₃O)₂CHCH₂CH=CHCHO (CH₃O₂)CHCH=CHCH₂CHO (X) (IX)

In view of this, we conducted the hydrolysis of the bis-dimethylacetal of glutaconic dialdehyde with an equivalent amount of water in the presence of phosphoric acid and showed that the monoacetal (X) is formed in this case. This was confirmed by the ultraviolet spectrum and a comparison of the 2,4-dinitrophenylhydrazone (X) with a known sample, kindly provided us by S. M. Makin.

EXPERIMENTAL

<u> β -Ethoxyglutaric Dialdehyde (III)</u>. A mixture of 26 g (I) and 40 ml of 0.25% phosphoric acid was intensively mixed with heating on a water bath until the formation of a homogeneous solution. The mixture was thoroughly extracted with ether, the ether solution dried, and after distillation we obtained 7.8 g of β -ethoxyglutaric dialdehyde (III) with b.p. 80-82° (2 mm); n²¹D 1.4387; contains an admixture of 10-15% 2,4,6-triethoxytetrahydropyran.

Diethylester of 5-Ethoxynonadiene-2,7-dioic-1,9 Acid (V). A 7.2 g portion of the (III) produced above was boiled for 14 h with 24.4 g of carbethoxymethylenetriphenylphosphorane in 100 ml of absolute benzene. The mix-ture was evaporated under vacuum at 70-80°. In the distillation we isolated 7 g of a substance with b.p. 120-124° (0.09 mm); $n^{18.5}$ D 1.4690, which corresponds in composition to the ester (V). Found: C 62.97, 63.08; H 8.57, 8.54%. C₁₂H₂₄O₅. Calculated: C 63.36; H 8.51%. Infrared spectrum: 1687 cm⁻¹.

2,6-Dihydroxy-4-ethoxynitrocyclohexane (VI). A 3.7 g portion of the product of saponification of (I) was heated with 6.1 g of nitromethane, 0.5 g of potassium carbonate, and 15 ml of water almost to boiling. After cooling, the mixture was extracted with ether, dried, and after removal of the ether, 3 g of a crystalline product was obtained, which corresponded in composition to (VI), m.p. 103-105° (from benzene). Found: C 46.82, 46.80; H 7.55, 7.58; N 6.54, 6.62; C_2H_5O 21.87, 21.71%. $C_8H_{15}O_5$. Calculated: C 46.82; H 7.35; N 6.83; C_2H_5O 21.95%. Found: active H 2.98, 3.05. Calculated (2OH, 1CHNO₂), active H 3.

5,5-Dimethoxypentene-2-al (X). A mixture of 3.6 g of the bis-dimethylacetal of glutaconic dialdehyde and 0.34 ml of water (containing 3% phosphoric acid) was heated on a boiling water bath with distillation of the methanol. After the distillation of methanol ceased, chalk was added, the reaction mass was mixed for 1 h, and extracted with ether. In the distillation we isolated 2.1 g of a product with b.p. 95-99° (9 mm); n¹⁸D 1.4565; λ_{max} (in alcohol) 220 mµ (ϵ 11,320). The 2,4-dinitrophenylhydrazone was produced by the action of a solution of 2,4-dinitrophenylhydrazine acetate in alcohol, m.p. 132-133°; λ_{max} (in alcohol) 373 mµ; gave no depression in a mixed melting point test with a known sample of the 2,4-dinitrophenylhydrazone of 5,5-dimethoxypentene-2-al.

SUMMARY

1. The basic product of the hydrolysis of the bis-diethylacetal of β -ethoxyglutaric dialdehyde is β -ethoxy-glutaric dialdehyde.

2. The hydrolysis of the bis-dimethylacetal of glutaconic dialdehyde with an equivalent amount of water gives 5,5-dimethoxypentene-2-al.

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