"Dimethyldioxan" Obtained from Propylene Glycol and Sulphuric Acid Identified as 2-Ethyl-4-Methyl-1,3-Dioxolan

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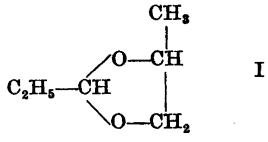
In the course of studies related to addition compounds of ethers we wanted to prepare 2,6- or 2,5-dimethyl-1,4-dioxan. According to Levene and Walti [1] the 2,6-compound is obtained when 1,2-propanediol is distilled with concentrated sulphuric acid. I.G. Farbenindustrie in a patent also states that dimethyl-1,4-dioxan is formed in this way without, however, indicating the positions of the methyl groups [2]. According to another patent, however, of The Standard Oil Development a structural isomeric compound, the cyclic acetal 2-ethyl-4-methyl-1,3-dioxolan (I) is formed under the conditions mentioned above [3].



I

When 1,4-dioxan is prepared by distilling ethylene glycol with sulphuric acid small quantities of a cyclic acetal, *viz.* 2-methyl-1,3-dioxolan, is known to be formed. It therefore appears possible that in the analogous reaction with 1,2-propanediol both dimethyldioxans and 2-ethyl-4-methyl-1,3-dioxolan are formed. The latter may be expected to result from the reaction between 1,2-propanediol and propionaldehyde in the presence of a water-attracting substance like sulphuric acid. Moreover 1,2-propanediol may partially be transformed into propionaldehyde under the conditions prevailing during the distillation process [4]. When fractionating the distillation product considerable quantities of an aldehyde were actually observed.

Levene and Walti believed the substance which they obtained when distilling bis(2-hydroxypropyl)ether with concentrated sulphuric acid to be identical with the substance they prepared from 1,2-propanediol. This was their reason for concluding that the latter is 2,6-dimethyl-1,4-dioxan. The identity of the two liquid products was established only by means of elementary analysis. However, since both dimethyldioxan and the acetal have the formula $C_6H_{12}O_2$ this result is not decisive. On distilling bis(2-hydroxypropyl) ether with sulphuric acid aldehyde was formed. It therefore does not appear impossible that the acetal is produced also under these conditions. The purity of the two products was also somewhat questionable, as the boiling interval reported for the substance obtained from 1,2-propanediol was 117—125°, for the substance obtained from the ether 110—119°.

We also have observed that the product obtained from 1,2-propanediol splits off aldehyde by hydrolysis even after repeated treatment with Tollens' reagent. We further observed that on addition of an acid solution of 2,4-dinitrophenylhydrazine to the substance a precipitate was formed, which was identified as the 2,4-dinitrophenylhydrazone of propionaldehyde. The maximum quantity of the hydrazone obtained by adding a sufficient quantity of 2,4-dinitrophenylhydrazine corresponded to 94 % of the theoretical value calculated under the assumption that the aldehyde is formed by complete hydrolysis of the cyclic acetal. From the products obtained by hydrolysis experiments with diluted acids both 1,2-propanediol and propionaldehyde could indeed be isolated. We have, on the other side, heated a mixture of 1,2-propanediol and propionaldehyde to 160° C in a sealed tube. The substance thus obtained turned out to be identical with the substance resulting from distillation of 1,2-propanediol with sulphuric acid. Their identity follows from the identity of their infrared absorption spectra. We may add that under similar conditions 2,4-dimethyl-1,3-dioxolan has been prepared from 1,2-propanediol and acetaldehyde [5].

According to I. R. investigations the purity of the acetal obtained by the method of I. G. Farbenindustrie for preparing dimethyldioxan is higher than the purity of the products obtained by the methods described by Levene and Walti and in the Standard Oil patent. The main difference is that in the I.G. Farbenindustrie process the 1,2-propanediol is added successively during the distillation. In this case the raw product will — after neutralisation and drying — distill below 117° C, the main part between 114—117° C. The distillation intervals for the purified products reported by Levene and Walti and in The Standard

Oil patent are 117—125° C and 116—121°, respectively.

From our experiments the conclusion must be drawn that *if* dimethyldioxans are formed when propylene glycol is distilled with sulphuric acid, the amounts are at least insignificant.

Experimental: Hydrolysis of the acetal. The acetal is sparingly soluble in water, but on heating with 1 % hydrochloric acid and shaking the acetal layer soon disappeared, propionaldehyde being evolved. The solution was kept for some time in an evacuated desiccator with phosphorus pentoxide and the remaining liquid distilled. The temperature rose rather rapidly to the boiling point of 1,2-propanediol. The distillate was viscous, miscible with water in all proportions and the taste sweet.

Reaction with 2,4-dinitrophenylhydrazine. 5 ml of concentrated sulphuric acid was added to 1.0 g of the reagent, then — drop by drop — 7.5 ml water and finally 25 ml ethanol (96 %). This solution was added to a solution of 0.250 g acetal in 10 ml ethanol (96 %). The precipitate (0.478 g) after repeated crystallisation from 96 % ethanol melted at 153.5°. The melting point showed no depression on addition of specially prepared propionaldehyde-2,4-dinitrophenylhydrazone. (Found: C 45.54; H 4.31; N 23.51. Calc. for $C_9H_{10}O_4N_4$: C 45.37; H 4.23; N 23.53).

The reaction between propionaldehyde and 1,2-propanediol. 17 g of propionaldehyde and 13 g of 1,2-propanediol were heated in a sealed tube to 160° during 68 hours. On fractionating it was found that the liquid distilling below 50° C consisted essentially of propionaldehyde. Between 50° and 86° a two-layer fraction was obtained. Subsequently the temperature rose rapidly to 160° C. The upper layer of the middle fraction was dried with anhydrous sodium sulphate before refractionating. After repeated fractionation the infrared absorption spectrum of the fraction 114—117° was compared with the spectrum of a corresponding fraction obtained from the distillation of 1,2-propanediol with sulphuric acid. The two fractions were found to consist of the same chief component, the contents of free propionaldehyde being somewhat different.

The molecular weight of the acetal prepared according to the I. G. Farbenindustrie patent was determined cryoscopically: Found 115.8, calc. 116.3.

Thanks are due to Mr. J. Lothe for taking the infrared spectra.

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A Preliminary Note on the Composition of the Non-hydratable Soyabean Phosphatides

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Degummed soyabean-oil, *i. e.* soyabean-oil from which the "mucilages" and the phosphatides have been removed by treatment with steam or hot water, still contains some phosphorus-containing compounds ordinarily referred to as non-hydratable phosphatides. The composition of these has never been fully established.

From a soyabean-oil extracted from american-grown beans and degummed by treatment with steam the non-hydratable phosphatides corresponding to more than 80 % of the remaining phosphorus-content have been isolated.

The nitrogen-content of the isolated phosphatides was only 0.3 %, whereas the ash-content normally was 21—22 %. The ash consisted mainly of Ca and Mg-phosphates, indicating that the isolated phosphatides were present as Ca and Mg-salts.

After converting the salts into free acids, the ether-soluble part, which contained about 75 % of the phosphorus, was fractionated using the countercurrent technique developed by Craig [1].

Fig. 1 shows the distribution-curves of weight, phosphorus, nitrogen and fatty acids obtained when using the solvent system: 62 volumes of carbon tetrachloride, 35 volumes of methanol and 3 volumes of water [2].