[Contribution from the Quaker Oats Company Research Laboratories]

BY-PRODUCTS FROM HYDROGENATION OF FURFURYL ALCOHOL

SAMUEL SWADESH and A. P. DUNLOP

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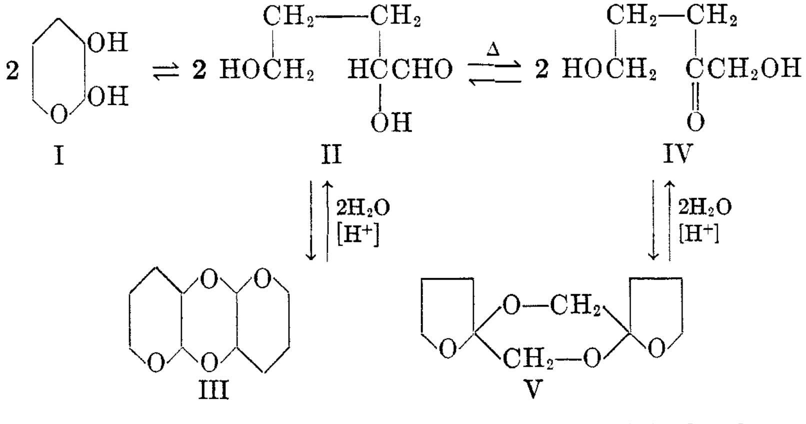
The commercial production of tetrahydrofurfuryl alcohol by the hydrogenation of furfuryl alcohol over Raney nickel results in the formation of a number of by-products. In practice, these are separated by fractional distillation, being recovered as a low-boiling fore-run and a high-boiling residue. From these fractions it has been possible to isolate and identify all of the compounds attributable to hydrogenolysis (1) or hydrolytic ring cleavage (2). However, these side reactions do not account for all of the by-products, and it is the object of this paper to discuss yet another type of reaction which may contribute to the complexity of the hydrogenation process.

On careful fractional distillation of the high-boiling residue, a small quantity of a white, crystalline solid was observed to separate from the fraction boiling in the range of the 1,5-pentanediol component. Recrystallization showed it to be a pure compound, $C_{10}H_{16}O_4$, which had not been previously described. Tests for carboxyl, hydroxyl, carbonyl, and ester groups gave negative results, and there was no evidence for unsaturation. Following a mild acid hydrolysis, positive tests were obtained for hydroxyl and carbonyl, and it was possible to prepare both a hydrazone and an osazone. Results of the analysis of these two derivatives could be explained if the hydrazone and osazone were assumed to be the corresponding derivatives of an oxopentanediol, in which one of the hydroxyl groups is alpha to the carbonyl. Assuming that the oxopentanediol was II or IV, we postulated formula III or V to account for the experimental findings of our white, crystalline solid. Mild acid hydrolysis would be expected to split such tricyclic diacetals into two molecules of II or IV.



During a discussion shortly thereafter, Prof. C. D. Hurd disclosed to us that he and Mr. O. E. Edwards had, in the course of their work, isolated a compound which behaved surprisingly similar to our crystalline solid. A mixed melting point determination confirmed their identity. Hurd and Edwards (3) have now reported their compound which was obtained by thermal dehydration of 2,3-dihydroxytetrahydropyran (3,4-didesoxyaldopentose), I, which is the cyclic form of 2,5-dihydroxyvaleraldehyde, II. However, they propose 2,5-bis(trimethyleneoxy)-1,4-dioxane, V, and not III, as the structure of their crystalline solid,[1] and the mechanism of its formation from I as proceeding *via* the isomeric compounds II and IV. This follows from the fact that a keto- rather than an aldopentose is formed on mild hydrolysis of the crystalline compound. While the osazone of the hydrolysate is identical with that obtained from I, the hydrazones from these sources are not identical, but isomeric (3).

While the mechanism indicated above explains the formation of the new compound, V, from I, it does not explain the occurrence of V in the products of hydrogenation of furfuryl alcohol. Under the conditions of the latter process, the formation of any of the precursors of V (I, II or IV) is considered to be extremely unlikely. However, if one were to interpose certain intermediate steps in the conversion of IV into V, a relationship of the origin of V from thermal dehydration of IV and from hydrogenation of furfuryl alcohol, VI, can be shown. If we postulate 4,5-dihydrofurfuryl alcohol, VII, (through dehydration of IVa, the cyclic form of IV) as an intermediate in the formation of V from IV, we can account for the occurrence of the same intermediate during the hydrogenation process. Schniepp and others (5, 6) have shown that methylfuran can undergo 4,5-dihydrogenation and that this is probably an intermediate in the complete hydrogenation to methyltetrahydrofuran. If we assume a similar course in the hydrogenation of furfuryl alcohol, the resulting intermediate would be 4,5-dihydrofurfuryl alcohol, VII.

As a vinyl ether possessing a primary hydroxyl group, VII might be expected to dimerize to X, and this on intramolecular addition of the hydroxyl group across the remaining double bond would result in the formation of the new compound, V. Addition of VI to VII might also give V by way of IX and X as illustrated.

This suggested mechanism may also account for a number of the as yet unidentified by-products in the high-boiling residue obtained in the manufacture of furfuryl alcohol. Thus, any of the hydroxylic compounds present in the reaction mixture[2] is capable of adding across the reactive double bond of either VII or X to give individual new compounds. Some of these possibilities are shown in the above diagram (VII + VIII = XI and X + ROH = XII). Furthermore, hydrogenolysis and/or hydrolysis of any of these compounds would give rise to yet additional by-products. It will be of interest to reexamine the high-boiling residue in the light of these considerations.

In a similar manner, it is possible to explain the observation of Adkins (1) of

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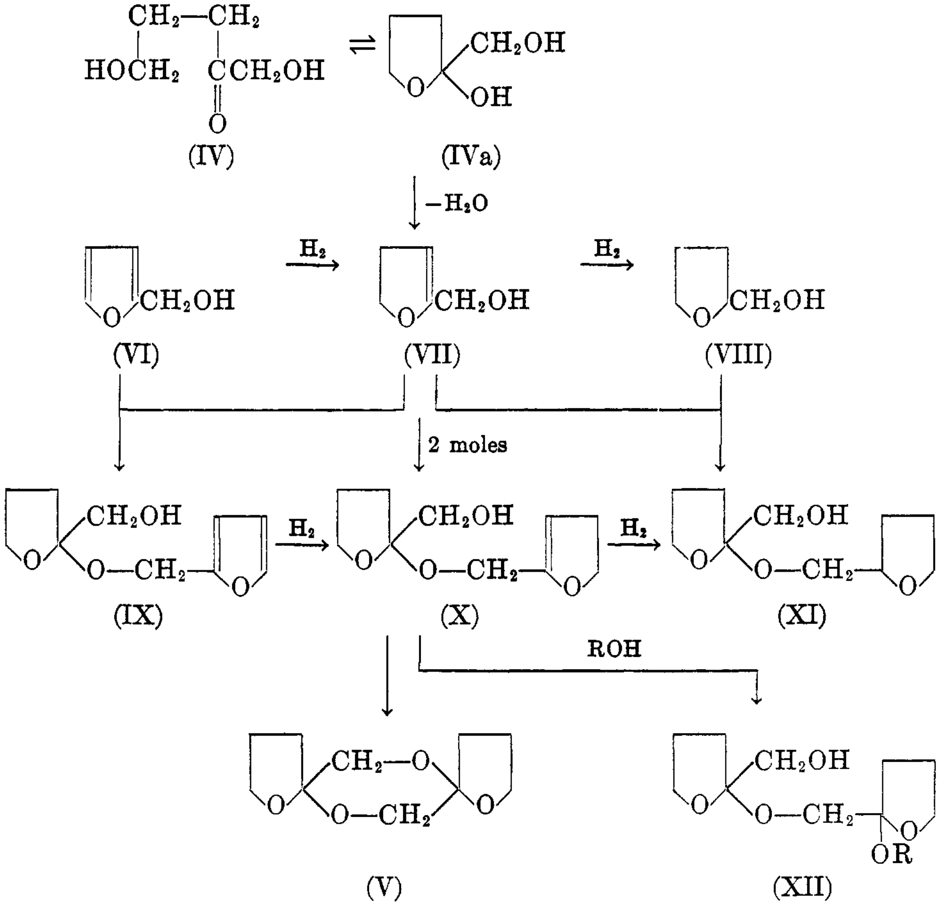
[1] Among other products they obtained were tetrahydrofurfural, and a higher-melting crystalline solid which may have the structure III.

[2] These are quite numerous, and include not only the saturated and unsaturated furan alcohols, but also a variety of pentanols (*e.g.* 1-ol, 2-ol, 1,2-diol, 1,4-diol, 1,5-diol, and 1,2,5-triol).



the occurrence of 1,9-dioxa-5-spirononane as a product of the hydrogenation of furylacrolein over Raney nickel. 4,5-Dihydrogenation of either the furylpropanol or furylpropenol intermediate, and subsequent intramolecular addition of the hydroxyl group across the double bond of the vinyl ether so formed, would produce the spirane.

EXPERIMENTAL

2,5-Bis(trimethyleneoxy)-1,4-dioxane (V). Fractional distillation of a 3.78-liter sample of high-boiling residue from commercial tetrahydrofurfuryl alcohol manufacture (hydrogenation of furfuryl alcohol over Raney nickel) gave 517 grams of a fraction boiling in the range of 1,5-pentandiol (130–131°/11 mm.). The solid phase was filtered off and washed with ether; yield, 118 grams, approximately 3% of the residue sample, or 0.8% of the original crude hydrogenation product. The solid was recrystallized four times from ether before a constant melting sample (101.4–101.8° using an Anschütz thermometer) was obtained. Hurd and Edwards (3) report 103° as the melting point of their sample of V and found no depression in melting point[3] when mixed with a sample of our compound.

Anal. Calc'd for $C_{10}H_{16}O_4$: C, 59.99; H, 8.06; Mol. wt., 200.

Found: C, 59.84; H, 8.09; Mol. wt. (cryoscopically in benzene), 200.

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[3] Private communication.

1,5-Dihydroxy-4-pentanone (IV). This compound was not isolated as such but its osazone and hydrazone derivatives were prepared.

2,4-Dinitrophenylosazone of IV. Refluxing 0.2 g. of V, 0.4 g. of 2,4-dinitrophenylhydrazine, 0.5 ml. of conc'd HCl, and 25 ml. of ethanol for 15 minutes, cooling and recrystallizing the precipitate from nitrobenzene gave the osazone melting at 235–236° with decomposition [reported (4) as 242°].

Anal. Calc'd for $C_{17}H_{16}N_8O_9$: C, 42.86; H, 3.39; N, 23.53.
Found: C, 44.13; H, 3.33; N, 23.11.

2,4-Dinitrophenylhydrazone of IV. A solution of 0.2 g. of V. in 5 ml. of 0.1 *N* HCl was warmed for 15 minutes after which 0.4 g. of 2,4-dinitrophenylhydrazine and 25 ml. ethanol were added and the mixture boiled under reflux for 15 minutes. On cooling, the solution was filtered and an equal volume of water added to the filtrate. The hydrazone was recrystallized by solution in ethanol followed by dilution with water. The melting point was 155–155.5° [reported (3) as 164–165°, when immersed at 140°].

Anal. Calc'd for $C_{11}H_{14}N_4O_6$: C, 44.29; H, 4.73; N, 18.79.
Found: C, 45.01; H, 4.77; N, 18.57.

SUMMARY

A component of the by-products from the hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol has been identified as 2,5-bis(trimethyleneoxy)-1,4-dioxane and is identical with one of the compounds obtained by Hurd and Edwards on pyrolysis of 3,4-didesoxyaldopentose.

A mechanism is proposed for the formation of the compound during the hydrogenation of furfuryl alcohol. The mechanism may also account for a number of the as yet unaccounted for components of the by-products.

CHICAGO 16, ILL.

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