hexyl-phenol. The properties of these compounds have been determined. Cyclohexyl-phenol, which has been prepared previously, was obtained by two new methods.

2. Cyclohexyl-phenol was not found to have any germicidal properties in water solution because of its limited solubility. Cyclohexyl-resorcinol gave a phenol coefficient of 24–27.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SELECTIVE REDUCTION OF FURFURACROLEIN BY MEANS OF PLATINUM-OXIDE PLATINUM BLACK AND HYDROGEN. XVI[1]

BY R. H. BRAY[2] WITH ROGER ADAMS

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In a previous paper it was shown that aldehydes[3] could not be reduced to alcohols with hydrogen and platinum-oxide platinum black unless some promoter such as a ferrous salt was present. As these promoters for the reduction of aldehydes are poisons toward the reduction of olefins, the study of the reduction of α,β unsaturated aldehydes,[4] in particular cinnamic aldehyde and citral, resulted in the discovery that by using a ferrous salt, together with a small amount of zinc salt, it was possible to reduce quantitatively the aldehyde group to a primary alcohol without affecting the olefin linkages. Cinnamyl alcohol and geraniol, respectively, were produced.

Furfural[5] was like other aldehydes and the catalytic reduction with platinum-oxide platinum black and hydrogen would not take place unless ferrous salt or some such promoter was present. The primary product was furyl carbinol formed upon the absorption of one molecular equivalent of hydrogen. If the reduction was allowed to go until no more absorption of hydrogen took place, ordinarily slightly over four molecular equivalents of hydrogen were absorbed, and there resulted a mixture of tetrahydrofuryl carbinol, pentane-diol-1,2, pentane-diol-1,5, and a small amount of *n*-amyl alcohol, the latter three substances being produced by scission of the ring.

In the present investigation the work on selective reduction has been

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[1] (a) For previous papers in this field, see Adams, Cohen and Rees, THIS JOURNAL, **49**, 1093 (1927) (footnote 1) for references to the first thirteen articles; (b) also Hiers and Adams, *ibid.*, **49**, 1099 (1927).

[2] This communication is an abstract of a portion of a thesis submitted by R. H. Bray in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

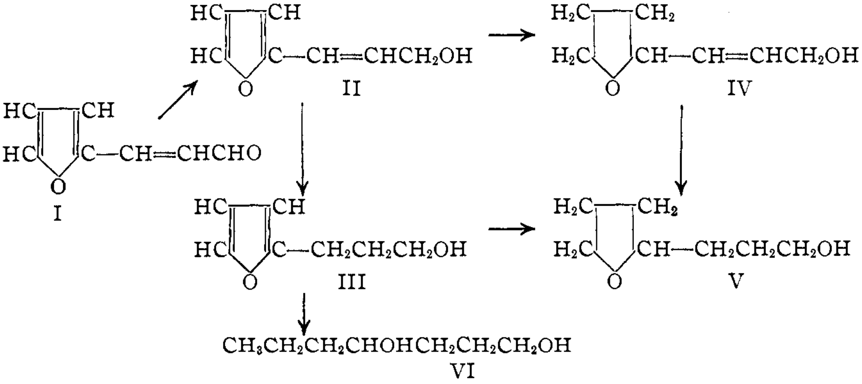
[3] (a) Carothers and Adams, *ibid.*, **45**, 1071 (1923); (b) **46**, 1675 (1924).

[4] (a) Tuley and Adams, *ibid.*, **47**, 3061 (1925); (b) Adams and Garvey, **48**, 477 (1926).

[5] Kaufman and Adams, THIS JOURNAL, **45**, 3029 (1923).

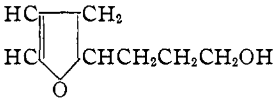
extended to furfuracrolein (I) which combines certain conditions present in furfural and in α,β unsaturated aldehydes. This compound, as might be expected, could not be reduced unless a promoter was present. The presence of ferrous sulfate caused the absorption of hydrogen to take place although, as in the case of the cinnamic aldehyde, the reaction did not stop after one molecular equivalent had reacted, but more hydrogen was absorbed to a maximum of 4.3–4.4 molecular equivalents. If the reaction mixture was distilled after one molecular equivalent of hydrogen was absorbed no pure product was obtained. When a small amount of zinc acetate, in addition to the ferrous salt was present, however, the absorption of hydrogen stopped completely after one molecular equivalent reacted and a single product resulted—furylallyl alcohol (II).

An attempt was made to isolate pure products after two molecular equivalents of hydrogen had been absorbed, using merely the ferrous salt to promote the reaction, but the results were unsuccessful. After the absorption of three molecular equivalents of hydrogen, two pure products could be separated from the reaction mixture by distillation, furylpropyl alcohol (III) and tetrahydrofurylallyl alcohol (IV), the former in the larger quantities. Finally, after all of the hydrogen was absorbed which would react, a good yield of tetrahydrofurylpropyl alcohol (V) resulted, with small amounts of a heptane-diol (VI), which was probably the 1,4-isomer.

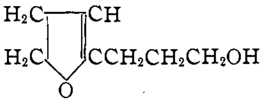


Obviously the mechanism consists first in the absorption of hydrogen to reduce the aldehyde group. This is followed by the reduction either of the olefin groups in the furane nucleus or of the olefin linkage in the side chain. Since the yield of tetrahydrofurylallyl alcohol was much smaller than that of the furylpropyl alcohol, the tendency for the aliphatic olefin linkage to reduce is greater than of the ring olefin linkages. The furylpropyl alcohol is then reduced for the most part to the tetrahydro derivatives, but a little of it, as with furylcarbinol, is reduced with splitting of the oxygen ring and formation of a diol.

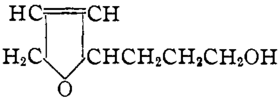
It was assumed that tetrahydrofurylallyl alcohol is actually the substance which was obtained and not one of the possible isomers. Although there are five isomeric compounds which agree with the analyses, the *cis* or *trans* form of the tetrahydrofurylallyl alcohol and three isomeric dihydrofuryl propyl alcohols (VII, VIII, IX), the extreme difficulty in isolation of a dihydrofuryl derivative by any method of reduction of a furane derivative renders the latter compounds very unlikely products.



VII



VIII



IX

Whether the compound in hand is the *cis* or *trans* modification of tetrahydrofurylallyl alcohol has not been determined.

The heptane diol isolated is probably the 1,4-isomer, as can be seen by comparing its constants and those of its derivatives with the 1,7-isomer prepared by another method.[6]

TABLE I

PHYSICAL CONSTANTS OF GLYCOLS

	Heptane-diol 1,4	Heptane-diol 1,7
Glycol	B. p., 126.5–128.5° (4 mm.); 240–245° (750 mm.); n^{25}_{D}, 1.4510; d^{20}_{20} 0.9559	B. p., 262° (atm.)
Diacetate	B. p., 113–113.5° (1 mm.); 249–252° (748 mm.); n^{25}_{D}, 1.4268; d^{20}_{20} 0.9934; d^{0}_{0}, 1.0135	B. p., 274° (atm.); d^{0}_{0}, 1.0219
Phenylurethan	Oil	M. p., 134°
α-Naphthylurethan	M. p., 81–82°	

The lower boiling point would indicate the 1,4-isomer, since in isomeric straight-chained glycols the one with the hydroxyl groups closer together invariably boils lower. Moreover, the indices of refraction of glycols increase as the hydroxyl groups are situated further apart. The values are of the same order for 1,2-glycols, for 1,5-glycols, etc., regardless of the number of carbon atoms in the molecule. From the data given below, therefore, the indications are for the 1,4-isomer.

TABLE II

INDICES OF REFRACTION OF GLYCOLS

Compounds	n_d
Pentane-diol 1,2[a]	1.4412
Pentane-diol 1,5[a]	1.4499
Heptane-diol 3,4[b]	1.4420
Heptane-diol new	1.4510
Heptane-diol 1,5[b]	1.4571
Nonane-diol 4,5[b]	1.4476
Nonane-diol 1,5[b]	1.4560

[a] Ref. 5.

[b] Pierce and Adams, THIS JOURNAL, **47**, 1098 (1925).

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[6] R. Dionneau, *Ann. chim.*, [9] **3**, 248 (1915).

Acetates and α-naphthylurethan derivatives of the various compounds isolated were prepared and identified.

Experimental

Materials.—The platinum oxide was prepared according to the method of Adams and Shriner[7] from C. P. chloroplatinic acid.

The furfuracrolein was prepared by the method of Konig and Hey[8] by condensation of furfural with acetaldehyde. In order to purify the product, fractional distillation under diminished pressure was found much more satisfactory than steam distillation followed by crystallization. It was absolutely necessary that the material be freshly distilled before the reduction was started or else the reaction took place only very slowly or not at all.

Reduction of Furfuracrolein (I).—In a typical run 0.2 g. of platinum oxide, 0.00002 mole of ferrous sulfate, 100 cc. of alcohol and 24.4 g. of furfuracrolein were used. The platinum oxide was reduced to platinum black in half of the alcohol, then the ferrous sulfate, the furfuracrolein and the rest of the alcohol were added. The reduction was carried out under 2.5–3 atmospheres' pressure with hourly reactivations with air or oxygen for the first seven hours and then occasional reactivations thereafter. The time for the complete reduction, during which 4.2–4.4 molecular equivalents of hydrogen were absorbed, was approximately 24 hours.

In the preparation of furylallyl alcohol, 0.00003 mole of zinc acetate and 0.0002 mole of ferrous sulfate were used in place of the amount of ferrous sulfate in the typical run just described. The reduction was thus slowed down and it practically stopped after one molecular equivalent of hydrogen had been absorbed. The time for this reduction was about 9.5 hours as compared with 4.5 hours for the absorption of one molecular equivalent when no zinc salt was added.

The products were isolated by means of fractional distillation under diminished pressure. The alcohols with unsaturated side chains always yield a certain amount of red, resinous residue when distilled, indicating partial decomposition or polymerization.

Furylallyl Alcohol (II).—Upon the reduction of 24.4 g. of furfuracrolein in presence of iron and zinc salts as described above until one molecular equivalent of hydrogen was absorbed, 19 g. of pure product was isolated. The furylallyl alcohol boils at 108–110° at 4 mm.; n_D^{27}, 1.5520; d_{20}^{20}, 1.1439. Upon distillation it decomposes somewhat and always leaves a high-boiling residue. On standing it turns yellow, then red and finally thickens. By the action of acetic anhydride no ester was obtained, as decomposition apparently took place.

Anal. Subs., 0.1480: CO_2, 0.3668; H_2O, 0.0890. Calcd. for $C_7H_8O_2$: C, 67.72; H, 6.50. Found: 67.61; 6.73.

α-Naphthyl Urethan of Furylallyl Alcohol.—The α-naphthyl urethan derivative was prepared according to the directions of Bickel and French[9] from the alcohol and α-naphthyl isocyanate. The product crystallizes from ligroin in white rosets. When pure it melts at 93–93.5°.

Anal. Subs., 0.1000: 4.60 cc. of 0.0714 *N* NaOH. Calcd. for $C_{18}H_{15}O_3N$: N, 4.78. Found: 4.60.

Furylpropyl Alcohol (III).—From a reduction of furfuracrolein using ferrous sulfate and stopping the reaction after approximately 3 molecular equivalents of hydrogen were absorbed, there was obtained by fractionation two products. One, the lower-distilling,

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[7] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[8] Konig and Hey, *Frdl.*, **13**, 110 (1923).

[9] Bickel and French, THIS JOURNAL, **48**, 747 (1926).

which proved to be furylpropyl alcohol, boils at 90–91° at 4 mm.; 201–208° at 747 mm.; n_D^{25}, 1.4760; d_{20}^{20} 1.0613. The yield was approximately 50 per cent. of the calculated amount. The product gradually turns yellow on standing.

Anal. Subs., 0.1584: CO_2, 0.3859; H_2O, 0.1158. Calcd. for $C_7H_{10}O_2$: C, 66.63, H, 7.99. Found: 66.46, 8.18.

α-Naphthyl Urethan of Furylpropyl Alcohol.—It forms white crystals from ligroin, m. p., 49°.

Anal. Subs., 0.1500: 7.06 cc. of 0.0714 *N* NaOH. Calcd. for $C_{18}H_{19}O_3N$: N, 4.71. Found: 4.71.

Furylpropyl Acetate.—A mixture of 10 cc. of alcohol and an excess of acetic anhydride was refluxed for 3.5 hours. The pure ester boils at 92° at 2 mm.; 217–218° at 747 mm.; n_D^{25}, 1.4553; d_{20}^{20} 1.0601. It turns yellow on standing.

Anal. Subs., 0.1410: CO_2, 0.3299; H_2O, 0.0927. Calcd. for $C_9H_{12}O_3$: C, 64.26; H, 7.19. Found: 63.83, 7.36.

Tetrahydrofurylallyl Alcohol (IV).—The higher-boiling material obtained after separating the furylpropyl alcohol proved to be tetrahydrofurylallyl alcohol. It boils at 100–101° at 4 mm.; n_D^{25}, 1.4675; d_{20}^{20}, 1.0317. The yield of pure product was approximately 10 per cent. It turns red on standing. It was impossible to obtain solid derivatives with α-naphthyl isocyanate, phenyl isocyanate, or 3,5-dinitrobenzoyl chloride.

Anal. Subs., 0.1613: CO_2, 0.3853; H_2O, 0.1360. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: 65.17, 9.43.

Tetrahydrofurylallyl Acetate.—The acetate boils at 90–91° at 2 mm.; n_D^{25}, 1.4468; d_{20}^{20}, 1.0374. It turns yellow-orange on standing.

Anal. Subs., 0.1168: CO_2, 0.2710; H_2O, 0.0845. Calcd. for $C_9H_{14}O_3$: C, 63.50; H, 8.29. Found: 63.30, 8.10.

Tetrahydrofurylpropyl Alcohol (V).—When the reductions in the presence of a little ferrous sulfate were run to completion with the absorption of 4.2–4.4 molecular equivalents of hydrogen, the chief product of reaction was tetrahydrofurylpropyl alcohol in yields of about 60 per cent. It boils at 106–107° at 2 mm.; 221° at 747 mm.; n_D^{25}, 1.4540; d_{20}^{20}, 1.0032. The higher-boiling fraction was a heptane-diol described below.

Anal. Subs., 0.1158: CO_2, 0.2732; H_2O, 0.1126. Calcd. for $C_7H_{14}O_2$: C, 64.57; H, 10.84. Found: 64.36, 10.88.

3,5-Dinitrobenzoate of Tetrahydrofurylpropyl Alcohol.—By warming molecular equivalents of the alcohol and 3,5-dinitrobenzoyl chloride on a water-bath, then adding water, the ester was obtained which, on purification from dil. alcohol, melts at 65.5–66°.

Anal. Subs., 0.2000: 17.2 cc. of 0.0714 *N* NaOH. Calcd. for $C_{14}H_{16}O_7N_2$: N, 8.64. Found: 8.60.

Tetrahydrofurylpropyl Acetate.—This product boils at 99° at 2 mm.; 228.5–229° at 750 mm.; n_D^{25}, 1.4380; d_{20}^{20}, 1.0207.

Anal. Subs., 0.1983: CO_2, 0.4546; H_2O, 0.1673. Calcd. for $C_9H_{16}O_3$: C, 62.75; H, 9.37. Found: 62.54, 9.44.

Heptane-diol 1,4 (VI).—The high-boiling fraction from the complete reduction of furfuracrolein proved to be a heptane-diol and was obtained in about 10 per cent. yields. It boils at 126.5–128.5° at 4 mm.; 240–245° at 750 mm.; n_D^{25}, 1.4510; d_{20}^{20}, 0.9559. It is completely miscible in water.

Anal. Subs., 0.1894: CO_2, 0.4423; H_2O, 0.2039. Calcd. for $C_7H_{16}O_2$: C, 63.58; H, 12.20. Found: 63.71, 12.05.

α-Naphthyl Urethan of Heptane-diol.—This product on crystallization from ligroin melts at 81–82°.

Anal. Subs., 0.1000: 5.60 cc. of 0.0714 *N* NaOH. Calcd. for $C_{29}H_{30}O_4N_2$: N, 5.95. Found: 5.60.

Heptane-diol Diacetate.—The substance boils at 113–113.5° at 1 mm.; 249–252° at 748 mm.; n^{25}_{D}, 1.4268; d^{20}_{20}, 0.9934; d^{0}_{0} 1.0135.

Anal. Subs., 0.1019: CO_2, 0.2280; H_2O, 0.0876. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.28. Found: 61.05, 9.62.

Summary

1. The reduction of furfuracrolein in alcohol solution was carried out using platinum-oxide platinum black as a catalyst and a little ferrous sulfate as a promoter. After the absorption of 3 molecular equivalents of hydrogen, there was isolated furylpropyl alcohol and tetrahydrofurylallyl alcohol. After absorption of 4.2–4.4 molecular equivalents of hydrogen, the maximum amount taken up, there was obtained tetrahydrofurylpropyl alcohol and a heptane-diol.

2. An attempt to isolate products after the absorption of one molecular equivalent or two molecular equivalents of hydrogen was unsuccessful. If the reduction was carried out in the presence of ferrous sulfate and zinc acetate, however, the reduction stopped automatically after one molecular equivalent of hydrogen had been absorbed and pure furylallyl alcohol was readily obtained.

3. The acetates of many of the alcohols were prepared and the α-naphthyl urethans of some of them.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORY OF THE DEPARTMENT OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN. A CORRECTION TO THE ARTICLE OF THIS TITLE BY SMITH, BOORD, ADAMS AND PEASE

BY HENRY DE LASZLO[1]

RECEIVED JUNE 8, 1927 PUBLISHED AUGUST 5, 1927

The ultraviolet absorption spectra of a large number of colorless aliphatic and aromatic compounds have been studied by Henri and his coworkers. One of the main results of this very careful examination was that while benzene possesses some very well marked bands in the region λ2600 Å.–λ2400 Å., the saturated cyclic and open-chain aliphatic hydrocarbons are transparent in this portion of the spectrum. Even decahydronaphthalene[2] absorbs only from 2300 Å. downwards. The intro-

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[1] Research Associate, Department of Physics, Massachusetts Institute of Technology.

[2] De Laszlo, *Proc. Roy. Soc.* (London), **111A,** 376 (1926).