Dichloro-aceto-*p*-toluidide.—The same procedure was followed as for the *o*-toluidide and the reaction was entirely analogous. The product crystallized from alcohol in white, flaky plates, m. p. 153°, and sublimed readily, condensing in down-like, fluffy, white masses and long needles; m. p., 154°.

Rügheimer and Hoffmann,[8] made the toluidides of dichloro-acetic acid by heating the acid toluidine malonates with phosphorus pentachloride. Their description of the compounds corresponds to the products that I have prepared. They do not give a melting point for the *o*-toluidide, but do give 153° for dichloro-aceto-*p*-toluidide.

α-Naphthylamine dichloro-acetate was also prepared as directed by Wheeler and Smith. My product crystallized from water and alcohol in hard, grayish-violet crystals; m. p., 136°. Wheeler and Smith by similar treatment obtained *α*-naphthylamine trichloro-acetate; m. p., 173° (decomp.).

Summary

The behavior of dichloro-acetic acid with aromatic amines is entirely normal, giving amine salts or aryl substituted amides of dichloro-acetic acid, according to temperature and duration of heating. In no case is there any indication of the formation of trichloro-acetic acid or its derivatives.

AMHERST, MASSACHUSETTS

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

PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. VIII. THE REDUCTION OF ALKYL FURYL CARBINOLS[1]

BY J. S. PIERCE[2] WITH ROGER ADAMS

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In a recent paper by Kaufmann and Adams[1d] the reduction of furfural by means of hydrogen and platinum black made from platinum oxide was studied. It was found that the initial product was furyl carbinol. This upon further reduction yielded four products: tetrahydrofuryl carbinol, pentane-diol-1,2, pentane-diol-1,5 and *n*-amyl alcohol. The first substance made up the largest proportion of the reaction mixture while the last was obtained in only small amounts. In the article describing this work, a review of the previous researches on the reduction of furane and its de-

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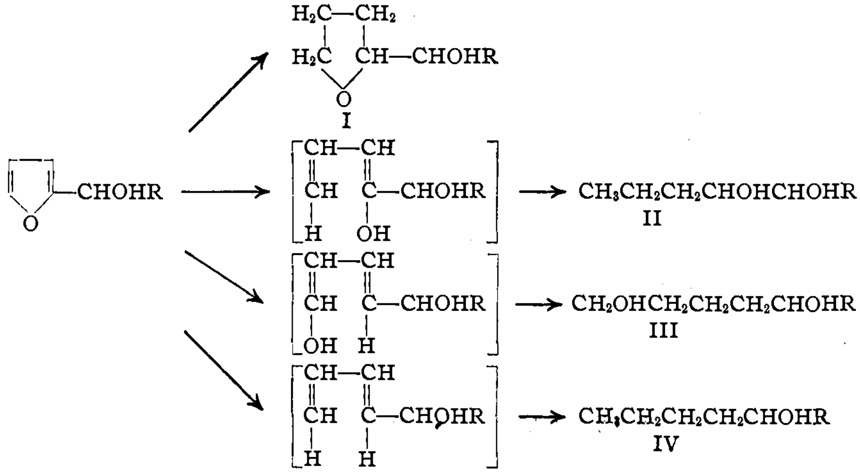
[8] Rügheimer and Hoffmann, *Ber.*, **18**, 2987 (1885).

[1] For previous papers in this field see (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers and Adams, *ibid.*, **45**, 1071 (1923). (c) Adams and Shriner, *ibid.*, **45**, 2171 (1923). (d) Kaufmann and Adams, *ibid.*, **45**, 3029 (1923). (e) Carothers and Adams, *ibid.*, **46**, 1675 (1924). (f) Shriner and Adams, *ibid.*, **46**, 1683 (1924). (g) Carothers and Adams, *ibid.*, **47**, 1047 (1925).

[2] This communication is an abstract of a portion of a thesis submitted by J. S. Pierce in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

rivatives was given.[3] Owing to the ease with which the furane ring was opened in the reduction of furfural and the facility with which good yields of the products mentioned above were obtained, further research has been carried out on the reduction of certain alkyl furyl carbinols. These substances correspond in every way to the intermediate product, furyl carbinol, which is the primary reduction product of furfural.

The reduction of both ethyl- and *n*-butyl-furyl carbinols ran smoothly. An absorption of 2.5 to 3.0 molecular proportions of hydrogen took place and there was produced in every case rather large amounts of alkyl tetrahydrofuryl carbinols (I), smaller amounts of 1,2-glycols (II) and 1,5-glycols (III) and very small amounts of monatomic alcohols (IV)



The isolation of the various products of reduction was more complicated than in the reduction of furfural. This is due to the fact that stereoisomers are possible for the alkyl tetrahydrofuryl carbinols as well as for the 1,2-glycols. As the isomeric alkyl tetrahydrofuryl carbinols were both liquids it was questionable whether a single product was obtained or a mixture of isomers. In the case of 1,2-glycols, however, it was found that one isomer was obtained as a solid, the other as an oil, and consequently it was possible to obtain the solid isomer in a pure state. No method was found for isolating the oily isomer pure.

It was found in the reduction of furfural that ferrous salts were necessary in order to have the reduction take place rapidly. The same was found to be true in the reduction of ethyl-furyl carbinol unless it was very carefully purified. In the case of the butyl-furyl carbinol, however, ferrous salt actually retarded somewhat the speed of reduction. This may be ex-

[3] See also Scheibler, Sotscheck and Friese, *Ber.*, **57**, 1443 (1924). The reduction of a furane nucleus in a benzofurane is described by Stoermer [*Ber.*, **57**, 72 (1924)] who converted acetyl coumarone by sodium and alcohol into *o*-(γ-hydroxybutyl)phenol.

plained by the fact that traces of furfural, which boils only 20° lower than ethyl-furyl carbinol, were still present in the ethyl derivative and, therefore, impeded the reduction if ferrous salt was not present. This difficulty did not arise in the case of the butyl derivative.

The question as to whether the reduction of furane derivatives by means of platinum black and hydrogen to yield open-chain compounds is general for all furane derivatives has not been determined. It seems more probable that the stability of the ring depends to a certain extent on the character of the substituting group in the furane nucleus. Judging from the fact that furyl carbinol, alkyl furyl carbinols, furoin and pyromucic acid all yield open-chain compounds very readily upon reduction, it would seem that the presence of an hydroxyl group on the alpha carbon may be especially effective in weakening the stability of the furane ring.

Phenyl-furyl carbinol is also readily reduced, presumably to give analogous products. Owing to the difficulty of obtaining pure phenylfuryl carbinol the crude product was used in the reduction experiments. Such a complex mixture of products resulted that pure individual compounds were not isolated.

Experimental Part

Ethyl-furyl Carbinol.—Ethyl-furyl carbinol was produced by the action of ethylmagnesium bromide upon furfural.[4] During the reaction the mixture was stirred constantly, and the reaction product was decomposed with a saturated solution of ammonium chloride. After two fractionations, a constant-boiling product was obtained; b. p., 75–80° at 1.3 mm., 86–89° at 18 mm.; n_D^{21}, 1.476; d_4^{20}, 1.044.

Reduction of Ethyl-furyl Carbinol.—The apparatus used was the same as that employed by Voorhees and Adams.[1a] The platinum oxide was made according to the method of Adams and Shriner.[1c] The procedure was similar to that used by Kaufmann and Adams[1d] in the reduction of furfural. In a typical run, 0.5 g. of catalyst, 5 cc. of water, 15 cc. of alcohol were shaken with hydrogen for two minutes, at the end of which time platinum oxide was reduced. A solution of 25 g. of ethyl-furyl carbinol in 65 cc. of alcohol was then added and the reduction carried out in the usual way. It was found that activation of the catalyst with oxygen every hour (10 minutes' shaking) was desirable. In preparing large quantities, the same catalyst was used for several runs.

The time required for the reduction (absorption of 2.5 to 2.7 molecular equivalents of hydrogen) of such a run was approximately nine hours. When, however, 1 cc. of freshly prepared 0.1 *M* ferrous sulfate solution was added before reducing the platinum oxide to platinum black, five to six hours were required with only three activations.

When the ethyl-furyl carbinol was carefully purified from sodium bisulfite solution so as to free it from traces of furfural, it was possible to reduce

[4] Douris, *Compt. rend.*, 157, 722 (1913).

the product in five hours with three or four activations without the addition of any ferrous sulfate.

The alcoholic solutions of several reduction mixtures were combined and the solvent distilled. Upon fractionation of 380 g. of crude reduction product, about 5 g. of low-boiling liquid (up to 75° at 23 mm.) was obtained. The rest of the material, fractionated five times at a low pressure, distilled in several distinct fractions, about 192 g. boiling from 75° to 83° (1 mm.), 18 g. boiling from 83° to 94° (1 mm.), 61 g. boiling from 94° to 108° (1 mm.), 21 g. boiling from 108° to 117° (1 mm.), 46 g. boiling from 117° to 135° (0.6 mm.). A small residue of about 4 g. boiled at approximately 145° (0.6 mm.).

Heptanol-3 (IV).—The low-boiling fraction (up to 75°, at 23 mm.) consisted of a mixture of heptanol-3 and ethyl-tetrahydrofuryl carbinol. As the amount was too small, the heptanol-3 was not isolated in a pure state. It had the typical odor, however, of this alcohol, and the physical constants, in general, indicated that this was the product.

Ethyl-tetrahydrofuryl Carbinol (I).—The second fraction was distilled once, after which it boiled at 181–189° (751 mm.), and on several further fractionations it boiled at 182–186° (745 mm.). It was a colorless liquid with a very slight odor. The other constants (n_D^{20}, 1.4485; and d_4^{20}, 0.9903) as well as the boiling point agree fairly well with those given in the literature for this substance.[4]

It was noticed, however, in a number of experiments in the preparation of this product that the ethyl-tetrahydrofuryl carbinol always boiled over a rather wide range. It seems probable, therefore, that the substance that was obtained in this investigation, as well as by the previous investigator, was perhaps not a pure compound, but more likely a mixture of the two possible isomeric forms. An attempt was made by the reaction with phenyl isocyanate and with 3,5-dinitrobenzoyl chloride to separate these two forms, but without success. Moreover, the acetates could not be separated by distillation.

ETHYL-TETRAHYDROFURYL CARBINOL ACETATE.—This product was obtained by refluxing ethyl-tetrahydrofuryl carbinol for several hours with two molecular equivalents of acetic anhydride and then by distilling the product under reduced pressure; b. p., 97–99° (18 mm.); n_D^{22}, 1.4362; d_4^{20}. 1.0110. It is a colorless liquid with a fruity odor. The constants agree almost exactly with those given in the literature.[4]

Heptanediol-3,4 (II)(Solid).—In the second main fraction of the distillation, a crystalline solid commenced to separate in the receiving flask. When the fraction was taken as described, it became almost semi-solid. The solid was filtered by suction from the oil and then recrystallized from petroleum ether, forming white crystals; m. p., 96–96.5°. The product is soluble in water and organic solvents. From the 61 g. of the main fraction, about 15.5 g. consisted of solid material. There was also obtained a certain amount of solid material from the intermediate fraction, which boiled higher.

Anal. Subs., 0.1815: CO_2, 0.4245; H_2O, 0.1997. Calcd. for $C_7H_{16}O_2$: C, 63.59; H, 12.20. Found: C, 63.81; H, 12.31.

Heptanediol-3,4-di-*p*-nitrobenzoate.—This compound was formed by the action of *p*-nitrobenzoyl chloride upon an aqueous alkaline solution of heptanediol-3,4. It formed light yellow pyramids from a mixture of ethyl acetate and alcohol. It melted when pure at 157.5–158.5°.

Anal. Subs., 0.5100: 22.65 cc. of 0.1070 *N* H_2SO_4. Calcd. for $C_{21}H_{22}O_8N_2$: N, 6.5. Found: 6.7.

Heptanediol-3,4 (II) (Liquid).—A large amount of oil was obtained after filtering off the solid diol-3,4. This boiled at 205–210° (737 mm.); n_D^{26}, 1.4420; d_4^{20}, 0.9457. It was a colorless liquid soluble in practically all organic solvents and slightly soluble in water. Of the materials boiling over the range mentioned above, there was obtained about 31 g. At —8° it became very viscous but did not solidify. Several attempts were made to produce solid derivatives that could be more readily purified, such as the *p*-nitrobenzoyl or 3,5-dinitrobenzoyl derivatives. The products, however, were oils. The probability is that the material at hand was not absolutely pure, due to the fact that traces of the solid isomer probably remained dissolved in the liquid isomer and could not be fractionated from it. In fact, there was obtained a very small amount of solid reaction product when the compound was allowed to react with *p*-nitrobenzoyl chloride. This reaction product, however, proved to be the di-*p*-nitrobenzoyl derivative of the solid glycol. An analysis of the liquid showed that it was a glycol.

Anal. Subs., 0.1586: CO_2, 0.3670; H_2O, 0.1701. Calcd. for $C_7H_{16}O_2$: C, 63.59; H, 12.20. Found: C, 63.13; H, 12.00.

Heptanediol-1,5 (III).—From the main high-boiling fraction produced in the original distillation, there was obtained 27 g. of material boiling at 126–128° (1.8 mm.); n_D^{22}, 1.4571; d_4^{20}, 0.9705. The product is a colorless, practically odorless oil essentially insoluble in water but soluble in organic solvents.

Anal. Subs., 0.1736: CO_2, 0.4080; H_2O, 0.1861. Calcd. for $C_7H_{16}O_2$: C, 63.59; H, 12.20. Found: C, 64.10; H, 12.00.

Heptanediol-1,5-di-*p*-nitrobenzoate.—This was formed by the same method as that for producing the di-*p*-nitrobenzoyl derivative of heptanediol-3,4. It formed light yellow needles from alcohol; m. p., 82–83°.

Anal. Subs., 0.3800: 17.26 cc. of 0.1070 *N* H_2SO_4. Calcd. for $C_{21}H_{22}O_8N_2$: N, 6.5. Found: 6.8.

***n*-Butyl-furyl Carbinol.**—This substance was produced by the action of butylmagnesium bromide upon furfural according to the same procedure as that for the production of ethyl-furyl carbinol; yield, about 84%.

By distilling immediately, 169 g. of pure product or 55% of the calculated amount was obtained from 258 g. of crude product. When the crude product was allowed to stand for three weeks before distillation, the yield of pure material was only 37%. The pure substance is a colorless oil boiling at 100–102° (2 mm.); n_D^{24}, 1.4720; d_4^{20}, 0.9914.

Anal. Subs., 0.1430: CO_2, 0.3667; H_2O, 0.1145. Calcd. for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 69.96; H, 8.96.

Reduction of *n*-Butyl-furyl Carbinol.—The reduction of 25 g. of butyl-furyl carbinol with 0.5 g. of catalyst took place in about two hours with the absorption of 2.6 molecular equivalents of hydrogen. One activation was used in the reduction. The addition of ferrous sulfate to the reaction mixture did not hasten the reduction; in fact it required a longer time for the reduction to be completed. Several runs were always made with the same sample of catalyst.

From 400 g. of butyl-furyl carbinol was obtained 408 g. of crude reduction product. A low-boiling fraction was removed at 20 mm. pressure and the rest was fractionated thrice in a modified Claisen flask[5] at a pressure of 1–3 mm. A low-boiling fraction was obtained and then 187 g. of a fraction

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[5] Noyes, THIS JOURNAL, **39**, 2718 (1917).

boiling at about 98° (1 mm.). A fraction boiling at about 116° (0.9 mm.) contained mostly isomeric 1,2-diols, and a fraction boiling at about 141° (1.8 mm.) was mostly 1,5-diol.

Dibutyl Carbinol.—From the lowest-boiling fractions from 639 g. of crude reaction product, there was obtained 4.5 g. of a clear, colorless liquid boiling at 178–189°. It had the characteristic odor of a secondary alcohol and undoubtedly was an impure sample of dibutyl carbinol. Although it was not pure material, it indicated that at least traces of dibutyl carbinol were present.

Butyl-tetrahydrofuryl Carbinol.—The first main fraction in the distillation of the crude product was redistilled, and a colorless liquid was obtained boiling at 99–100° (0.5 mm.); n_D^{21}, 1.4493; d_4^{20}, 0.9428. Although it is possible that two isomeric forms were present, the boiling point could readily be obtained constant, which was not the case with the ethyl-tetrahydrofuryl derivative.

Anal. Subs., 0.1634: CO_2, 0.4090; H_2O, 0.1724. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.29; H, 11.81.

BUTYL-TETRAHYDROFURYL CARBINOL ACETATE.—This substance was a colorless oil with a fruity odor and boiled at 120–124° (18 mm.); n_D^{22}, 1.4396; d_4^{20}, 0.9682.

Anal. Subs., 0.1994: CO_2, 0.4782: H_2O, 0.1786. Calcd. for $C_{11}H_{20}O_3$: C, 65.96; H, 10.07. Found: C, 65.42; H, 10.02.

Nonanediol-4,5 (Solid).—The second main fraction of the distillation of the crude material solidified to a semisolid mass. Upon filtration with suction, white crystals were obtained which, after purification from petroleum ether, melted at 124–125°. About 27 g. of this white solid was produced and about 8.5 g. was obtained from the next higher intermediate fraction. This substance had a sweet taste.

Anal. Subs., 0.1936: CO_2, 0.4758; H_2O, 0.2103. Calcd. for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.05; H, 12.16.

Nonanediol-4,5-di-*p*-nitrobenzoate.—This substance was produced in the same way as the di-*p*-nitrobenzoate of heptanediol-3,4. It was purified from a mixture of ethyl acetate and alcohol and formed yellow crystals; m. p., 125–126°.

Anal. Subs., 0.5350: 22.38 cc. of 0.1070 *N* H_2SO_4. Calcd. for $C_{23}H_{26}O_8N_2$: N, 6.1. Found: 6.3.

Nonanediol-4,5 (Liquid).—The filtrate from the solid diol was distilled under diminished pressure. There was obtained 12 g. of a colorless liquid boiling at 120–121° (1.6 mm.); n_D^{22}, 1.4476.

It was impossible to obtain a fraction that did not contain small amounts of the solid isomer.

Nonanediol-1,5.—The third main fraction after distillation yielded 15 g. of a colorless liquid boiling at 145–147° (2.7 mm.); n_D^{24}, 1.4560; d_4^{20}, 0.9370; it was a colorless, practically odorless oil.

Anal. Subs., 0.1863: CO_2, 0.4637; H_2O, 0.2108. Calcd. for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.90; H, 12.66.

Nonanediol-1,5-di-*p*-nitrobenzoate.—This substance was formed in the same way as the other di-*p*-nitrobenzoates. It formed yellow needles from alcohol; m. p., 55.5–56°.

Anal. Subs., 0.4687: 19.44 cc. of 0.1070 *N* H_2SO_4. Calcd. for $C_{23}H_{26}O_8N_2$: N, 6.1. Found: 6.2.

Summary

The catalytic reduction of alkyl furyl carbinols by means of platinum black from platinum dioxide and hydrogen yields a mixture consisting of

(a) isomeric alkyl tetrahydrofuryl carbinols, (b) isomeric alkyl-*n*-propyl 1,2 glycols, (c) alkyl 1,5-glycols, (d) alkyl butyl carbinols.

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[CONTRIBUTION FROM THE NEW YORK SUGAR TRADE LABORATORY]

THE SPECIFIC ROTATION OF INVERT SUGAR AND THE CLERGET DIVISOR

BY F. W. ZERBAN

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During an investigation at present in progress in this Laboratory and involving the analysis of sugar mixtures, we had occasion to refer to Vosburgh's paper on the same subject.[1] This author showed that, contrary to the opinion held generally,[2] the specific rotation of invert sugar at a given concentration is not the sum of the specific rotations of glucose and fructose at their partial concentrations, but one-half of the sum of the specific rotations of the two sugars at the total sugar concentration. Browne has already pointed out the significance of Vosburgh's conclusions for practical sugar analysis.[3]

Vosburgh did not formulate from his results an equation for the specific rotation of invert sugar, nor did he make any comparisons with the values obtained by former investigators. Since the specific rotation of invert sugar is not only an important physical constant, but also forms the basis of the Clerget divisor, it was decided to make use of Vosburgh's data for the purpose just mentioned.

If we reduce Vosburgh's equation for the specific rotation of fructose,[4] which he established for the temperature of 25°, to the standard temperature of 20°, by using his temperature correction formula,[4] we obtain

$$[\alpha]_D^{20} = -(91.33 + 0.164\,c - 0.00086\,c^2) \qquad (1)$$

By combining this equation, according to Vosburgh's rule, with that for the specific rotation of glucose, given by Tollens[5] and recalculated by Browne[6] to the basis of c instead of p,

$$[\alpha]_D^{20} = 52.50 + 0.0227\,c + 0.00022\,c^2 \qquad (2)$$

we get the following equation for invert sugar, valid between 2.6 and 20 g. per 100 cc.

$$[\alpha]_D^{20} = -(19.415 + 0.07065\,c - 0.00054\,c^2) \qquad (3)$$

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[1] Vosburgh, THIS JOURNAL, **43**, 219 (1921).

[2] Compare Landolt, "Das optische Drehungsvermögen," Friedrich Vieweg und Sohn, Braunschweig, **1898**, 2d ed., pp. 214–216.

[3] Browne, *Louisiana Planter*, **67**, 44 (1921).

[4] Vosburgh, THIS JOURNAL, **42**, 1697 (1920).

[5] Tollens, *Ber.*, **17**, 2238 (1884).

[6] Browne, *J. Ind. Eng. Chem.*, **2**, 526 (1910).