trioxide and two of arsono-acetic acid the polyarsenide, tetra-arseno-acetic acid, is obtained.

4. Water-soluble sodium salts of the above acids are readily prepared.
5. Analogous series derived from various halogen acids and halohydrins are now being synthesized in this Laboratory.

NEW HAVEN, CONNECTICUT

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

THE USE OF PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. IV. REDUCTION OF FURFURAL AND ITS DERIVATIVES[1]

BY W. E. KAUFMANN[2] WITH ROGER ADAMS

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The commercial development of furfural during recent years and its remarkable cheapness has led to many investigations for new uses. This communication describes the results obtained on the catalytic reduction of furfural and a number of its simple derivatives. The reduction is of interest not only because the products might be of practical importance, but also because there has been very little work done on the reduction of compounds of the furane series. Moreover, furfural itself is a different type of aldehyde from those which have thus far been reduced with the use of platinum oxide[3] as a catalyst and ferrous chloride as an activating agent.

The first work on the reduction of furfural was published in 1906 by Padoa and Ponti[4] who passed the vapors of furfural with hydrogen over a nickel catalyst at 190°. The primary product of the reduction was furyl alcohol. Further reduction always took place and from the mixture of reaction products it was possible to isolate methyl-2-furane, methyl-2-tetrahydrofurane and pentanol-2. It may thus be seen that rupture of the ring took place during reduction, though to only a very slight extent. The same authors reported that when they used a temperature of 270° the decomposition yielded in addition furane and carbon monoxide.

Law[5] studied the electrolytic reduction of furfural in the presence of alkali and acid but, with the exception of a small amount of furyl alcohol when the acid solution was used, only resins were obtained.

Pringsheim and Noth[6] reduced furfural by passing the vapors with hydrogen over

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[1] Part of the chloroplatinic acid used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.

[2] This communication is an abstract of a thesis submitted by W. E. Kaufmann in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers and Adams, **45**, 1071 (1923). (c) Adams and Shriner, **45**, 2171 (1923).

[4] Padoa and Ponti, *Atti. R. accad. Lincei*, **15**, [5] 610 (1906); *Gazz. chim. ital.*, **37**, [2] 105 (1907).

[5] Law, *J. Chem. Soc.*, **89**, 1517 (1906).

[6] Pringsheim and Noth, *Ber.*, **53**, 114 (1920).

iron as a catalyst at 200°. They observed the formation of the same products reported by Padoa and Ponti when nickel was used and in addition, furane and dihydrofurane. They concluded that in the reduction of furfural (1) the aldehyde group can be reduced to a methyl, (2) the aldehyde group may be eliminated entirely with the formation of furane or hydrogenated furanes, and finally (3) the ring is ruptured and the resulting products are hydrogenated.

More recently, the reduction of furfural has been undertaken by Wienhaus,[7] using charcoal impregnated with palladium chloride solution as a catalyst and reducing with hydrogen at ordinary temperatures and one atmosphere pressure. The reduction was carried out in the presence of water as well as without any solvent. There was thus obtained as a chief product tetrahydrofuryl alcohol, but in addition high-boiling products which the author supposed to be bimolecular compounds similar to those reported by Skita in the reduction of citral. These, however, were not investigated. The reaction was apparently quite unsatisfactory since it required 285 hours' time with 10 additions of fresh catalyst for the reduction of 48 g. of furfural. By the reduction of furyl alcohol the same author obtained a reaction mixture similar to that from furfural itself, thus indicating that furyl alcohol was the primary reduction product.

The reduction of furane and other derivatives besides furfural has been less extensively studied. Bourgignon[8] reported the reduction of furane with hydrogen and a nickel catalyst at 170°. A large portion of the furane was recovered unchanged and, in addition, a small amount of tetrahydrofurane and *n*-butyl alcohol.

Douris[9] reduced furyl ethyl carbinol with hydrogen and nickel catalyst at 175° and obtained as the chief product ethyl tetrahydrofuryl carbinol. As by-products were formed propyl-2-tetrahydrofurane, propyl-butyl ether, propyl-butadienyl ether, dipropyl ketone and a sirup which was not purified but which the author believed to be a glycol.

Yoder and Tollens[10] showed that by the action of sodium amalgam, pyromucic acid was not reduced. On the other hand, with this same reagent Hill and Wheeler[11] reduced furane-2,5-dicarboxylic acid readily to the tetrahydro derivative.

β-Furyl-acrylic acid has been reduced by Markwald with phosphorus and hydriodic acid to pimelic acid.[12]

Semler[13] reduced fural-acetophenone with sodium and alcohol to furyl-phenyl-propane. Apparently no reduction of the furane ring took place in this reaction.

Catalytic reduction with platinum or palladium catalyst has been used on a number of furfural derivatives. Wienhaus and Sorge[14] reduced pyromucic acid in the presence of platinum chloride and gum arabic to a product which they identified as tetrahydropyromucic acid. The reduction, just as with furfural itself, took place only very slowly and no yield was reported. Asahina and Shibata,[15] by means of hydrogen and platinum black in acetic acid, reduced methyl β-furyl-propionate to methyl β-tetrahydrofuryl-propionate. Windaus and Dalmer,[16] using hydrogen and platinum black, reduced β-furyl acrylic acid to β-tetrahydrofuryl-propionic acid. Finally, Bargellini and Marte-

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[7] Wienhaus, *Ber.*, **53**, 1656 (1920).

[8] Bourgignon, *Bull. soc. chim. Belg.*, **22**, 87 (1908).

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

[10] Yoder and Tollens, *Ber.*, **34**, 3462 (1901).

[11] Hill and Wheeler, *Am. Chem. J.*, **25**, 463 (1901).

[12] Markwald, *Ber.*, **21**, 1401 (1888).

[13] Semler, *Ber.*, **39**, 726 (1906).

[14] Wienhaus and Sorge, *Ber.*, **46**, 1927 (1913).

[15] Asahina and Shibata, *J. Pharm. Soc. Japan*, **423**, 391, 400 (1917).

[16] Windaus and Dalmer, *Ber.*, **53**, 2304 (1920).

giani[17] reduced fural-acetophenone with hydrogen and platinum or palladium black. They reported that only the ethylene double bond in the side chain was hydrogenated. Since quite different results were obtained in this investigation it may be mentioned that the method of these authors consisted merely in bubbling the hydrogen through a warm solution of the substance in alcohol without using pressure.

In this investigation the reduction of furfural, fural-acetone, fural-acetophenone, furoin, pyromucic acid, ethyl pyromucate and β-furylacrylic acid was studied. Alcohol was used as a solvent, and the catalyst employed was the platinum oxide[3] recently described and shown to be so active for the reduction of various types of organic compounds.

No difficulty was observed in the reduction of furfural when the proper conditions were used. The first experiments in this investigation consisted in determining the nature of the product obtained by the absorption of 1 molecular equivalent of hydrogen. It was found that a quantitative yield of furyl alcohol resulted, thus establishing without question that the initial point of attack of the hydrogen was the aldehyde group and that no other part of the molecule reacted until after the aldehyde group was completely reduced.

The other experiments were carried out to determine the nature of the products of reduction when as much hydrogen was absorbed as would be taken up. Instead of the absorption of three molecular equivalents of hydrogen, as would be expected if merely the aldehyde and the two double bonds of the furane ring were reduced, it was always found that more was absorbed, 3.2 to 4.3 molecular equivalents, the amount depending generally upon the type of catalyst used, the mode of reactivation and the length of time the reactions were allowed to proceed at the very end of the absorption. The reaction mixture obtained by the complete reduction of 12 runs of 50 g. each of furfural was worked up at one time. After distillation of the alcohol a brown oil resulted which weighed approximately 600 g., showing that no very volatile materials had been produced. The mixture was first carefully fractionated a number of times under diminished pressure until it separated into four main fractions, each boiling within a few degrees. These fractions were then redistilled independently and constant boiling products isolated. The first substance boiled at 137–139° at 751 mm. and proved by analysis and by its physical constants to be *n*-amyl alcohol. The second substance boiled at 176–177° at 751 mm. and was pure tetrahydrofuryl alcohol. Its constants agreed exactly with those described in the literature for this substance. The third substance boiled at 210.5–211.5° at 751 mm. By analysis and its formation of a diacetate it was shown to be a pentane glycol. It undoubtedly was pentanediol-1,2, a substance which has not been previously described. The fourth substance boiled at 239–241° at 751 mm. and was shown to be pentanediol-1,5. By analysis and by a comparison of its physical constants and those of its diacetate with

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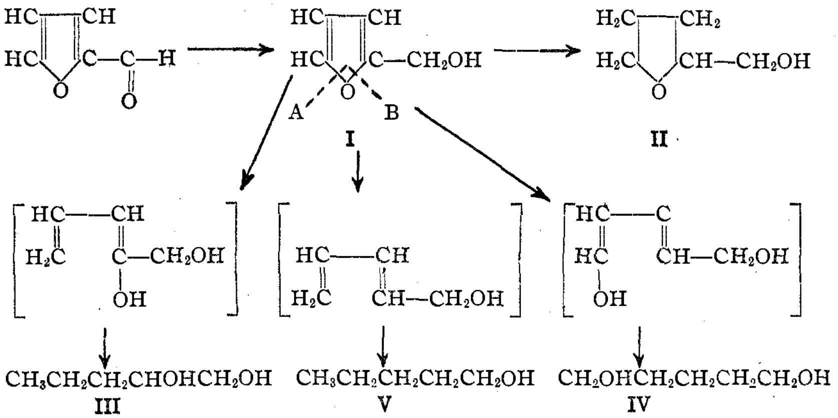
[17] Bargellini and Martegiani, *Gazz. chim. ital.*, **42**, [2] 417, 427 (1912).

the constants given in the literature for these substances, the compound was identified. Practically no residue was obtained. The four main fractions, from the lowest to the highest boiling weighed, respectively, 60 g., 222 g., 131 g. and 51 g. These figures do not represent the weight of pure materials obtained, but give some idea of the approximate proportion of each compound present in the mixture for one set of runs. The mechanism for the formation of these various products is best illustrated in the following chart.

Since the first molecular equivalent of hydrogen absorbed by the furfural gave a quantitative yield of furyl alcohol (I), it is obvious that the reduction of furyl alcohol itself must take place in a number of different ways. The main reaction is obviously simple hydrogenation of the double bonds in the furane ring with the formation of the tetrahydrofuryl alcohol (II). On the other hand, part of the reduction takes place between the oxygen of the furane and one or the other of the two carbons to which it is attached. By the reduction at Point A in Formula I, an intermediate substance is obtained which would immediately be reduced to pentanediol-1,2 (III). If the reduction took place at Point B in Formula I, an intermediate product would be formed which would reduce immediately to pentanediol-1,5 (IV). The *n*-amyl alcohol (V) may be formed either by the subsequent reduction of one of the glycols, possibly the pentanediol-1,2 or more probably by the direct reduction and elimination of oxygen from the furane ring of the furyl alcohol with immediate reduction of the intermediate product. The formation of the glycols or *n*-amyl alcohol certainly does not take place through the tetrahydrofuryl alcohol as an intermediate, since pure tetrahydrofuryl alcohol could not be reduced to the slightest extent under the conditions used for the reduction of furfural.



A comparison of the rupture of the furane ring by this reduction method and those previously employed is of interest. The opening of the furane ring at ordinary temperatures, as found in this investigation, is apparently much greater in amount than that which takes place by the use of other catalytic methods where high temperatures are employed. Moreover, the high temperature catalytic reductions gave a larger number of products and the number apparently varied with slight changes in conditions. Only the same four products of reaction were ever obtained in this work.

The character of the catalyst had a marked effect upon the speed of the reduction of the furfural. The results of the different experiments were of such general interest that a detailed discussion of the catalyst is necessary. In the previous paper it was shown that the platinum oxide made from spectroscopically pure chloroplatinic acid was a very inefficient catalyst toward the reduction of benzaldehyde. This same thing has been observed in the reduction of furfural; only by reactivation of the catalyst could the reduction be carried out at all, and then only very slowly. The presence of small amounts of ferrous chloride, however, caused the same marked increase in the activity of the catalyst as was shown in the case of benzaldehyde and heptaldehyde. In standard experiments on the reduction of these latter compounds, an increase in the amount of ferrous chloride, without changing the quantities of the other reagents, had practically no effect upon the speed of reduction after a certain minimum quantity had been added. In the reduction of furfural, however, this was not the case. With increasing amounts of ferrous chloride the speed of reduction increased to a point beyond which it decreased rapidly. No explanation of this fact has yet been found and a further study of the effect of ferrous chloride is necessary.

In the experiments to determine these facts, 25 g. of furfural, 75 cc. of alcohol and 0.5 g. of catalyst (sp. p.)[18] were used with various quantities of ferrous chloride. The most effective amount tried was 1.2 cc. of 0.1 *M* ferrous chloride. The results obtained using twice these amounts of reagents, namely 50 g. of furfural, 150 cc. of alcohol and 1 g. of platinum oxide with various amounts of ferrous chloride, were surprising. It was expected that for such a run as this, 2.4 cc. of 0.1 *M* ferrous chloride would activate the platinum so as to cause the reduction of this larger quantity to take place with the same speed as shown in the smaller run. This, however, was not the case. With 2.4 cc. of ferrous chloride, the reduction of the furfural did not take place as rapidly as in the smaller runs. On the other hand, if only 1.2 cc. of ferrous chloride was used, the same as in the smaller runs, the reduction proceeded just as rapidly. These results indicate that a certain amount of ferrous chloride can just as effectively activate small or large amounts of platinum catalyst. Further study of this relationship with other aldehydes is being made.

With these data available, it is not surprising that in a series of runs of

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[18] "Sp. p." is an abbreviation indicating that the catalyst was prepared from spectroscopically pure chloroplatinic acid.

25 g. of furfural, 75 cc. of alcohol, 0.5 g. of catalyst (sp. p.) and 1.2 cc. of 0.1 *M* ferrous chloride, it was found that when, after complete reduction of the furfural, the liquid was decanted and fresh quantities of furfural and alcohol were added, the addition of more ferrous chloride in the second run was unnecessary. In fact, when ferrous chloride was added, the reduction of the second portion of aldehyde was slower than the reduction of the first; without addition of ferrous chloride to the second run, the reduction was just as rapid as in the first run. The same conditions held true with the third run, using the same platinum catalyst. When ferrous chloride was added in the first run, also in the second and still again in the third, the reduction was much slower in the third than in the second run and it was quite obvious that the catalyst was being gradually rendered ineffective by further additions of ferrous chloride. On the other hand, with no further addition of ferrous chloride after the first run, the platinum catalyst proved to be practically as effective in the second, third, fourth and fifth runs. In all these experiments the amount of activity restored to the catalyst after reactivation with air or oxygen was proportional to that activity held initially by the catalyst in the presence of any given quantity of ferrous chloride.

It is noticeable that in these series of reductions where further addition of ferrous chloride tended to cause a diminution in the speed of reduction, the diminution in speed of absorption of the first two hydrogens to reduce the aldehyde group was much less than the diminution in speed of absorption of the succeeding two to three molecular equivalents of hydrogen. The larger amount of ferrous chloride, at the same time as it acts as a protection for the platinum catalyst from de-oxygenation, poisons the catalyst more readily in its activity toward the reduction of the ethylene double bonds than it does toward the reduction of the aldehyde group.

From these results it may be concluded that in the reduction of furfural, as soon as a sufficient amount of ferrous chloride has been added to activate the platinum catalyst, no more is necessary and this catalyst then remains exceedingly active in the reduction experiments, only an occasional reactivation with air or oxygen being necessary in order to reduce run after run of furfural without changing the catalyst. No attempt was made to find out how many portions of furfural could be reduced with the same catalyst under the conditions mentioned before the catalyst might become appreciably affected.

Many of the experiments in this investigation were carried out with platinum catalyst prepared from spectroscopically pure chloroplatinic acid. For the average laboratory, it would be a tedious matter to bring all the platinum to this state of purity before using it. Experiments were, therefore, conducted to determine whether similar results to those described above could not be obtained by using platinum oxide from the C. P. chloroplatinic acid of commerce. Such platinum oxide, without the addition of ferrous chloride, proved to be a more effective catalyst in the reduction of furfural than the oxide from spectroscopically pure chloroplatinic acid but the activity did not approach that obtained when a little ferrous chloride was present. The difference in the activity of the oxide from the two grades of chloroplatinic acid may be attributed to the presence of traces of iron or other effective impurities in the c. p. chloroplatinic acid of commerce. The results of several experiments show that by the addition of the proper amount of ferrous chloride to the platinum oxide from c. p. chloroplatinic acid of commerce, results could be obtained almost identical with those described by the use of platinum oxide from purest raw material.

It was pointed out in previous papers that the catalyst from the c. p. chloroplatinic acid of commerce, after it had been reworked[19] several times, gradually accumulated sufficient impurities so that it became quite active as a catalyst in the reduction of aldehydes without the necessity of adding ferrous chloride. Moreover, the effectiveness of such a catalyst obtained by frequent reworking remained constant after a maximum activity had been reached. Such a catalyst was used for the reduction of a large amount of furfural. Using 50 g. of furfural, 150 cc. of alcohol and 1 g. of such platinum oxide, it was possible to complete the reduction (3.3 to 3.6 molecular equivalents) within a reasonable time with about six reactivations of the catalyst with air with each 50 g. of furfural. As many as six successive runs of 50 g. each of furfural were made with the same catalyst and only a slight diminution in the speed of reduction was noted. The speed of this reduction was less than half that which was obtained by the use of platinum oxide with the addition of the proper amount of ferrous chloride. Although no similar experiments were carried out with this catalyst in which oxygen was used for reactivation, it is probable that the time of reduction could be cut in half by such a procedure, as indicated by the results discussed in the following paragraph.

The importance and usefulness of reactivating the platinum catalyst during reduction experiments have been emphasized by a number of investigators, as well as in the previous papers on the use of platinum oxide as a catalyst. The procedure, as usually carrried out, is merely to shake the catalyst with air for a few minutes. The advantage of using oxygen in place of air for the reactivation has not been sufficiently emphasized. Standard experiments with exactly the same quantities of reagents were carried out, the only difference being in the mode of reactivation of the catalyst. By the use of oxygen, the time for reduction was much less than when air was used.

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[19] The term "reworked" has been applied to that platinum oxide which was made from chloroplatinic acid formed after a number of cycles as follows: chloroplatinic acid to platinum black→use of the platinum black as a catalyst→solution of the platinum black to give chloroplatinic acid.

From the variety of reduction experiments which have been completed, the best results were obtained as follows. A mixture of 50 g. of furfural in 150 cc. of alcohol, 1 g. of catalyst (either from c. p. or sp. p. chloroplatinic acid) and 1.2 cc. of 0.1 *M* ferrous chloride was treated with hydrogen under 1 to 2 atmospheres' pressure (Table I). One molecular equivalent of hydrogen was absorbed in about an hour, and the reduction ran to completion with the absorption of about 3.3 to 4.3 molecular equivalents of hydrogen in about 4 hours. During the reduction the catalyst was thrice reactivated with oxygen. When the reduction was complete the solution was decanted from the platinum, the catalyst reactivated with oxygen and then 50 g. of furfural in 150 cc. of alcohol was added. The reduction proceeded in practically the same time as for the first 50 g. A third run was carried out in a similar manner and gave the same results without showing any appreciable devitalization of the catalyst. Unquestionably, still additional portions of 50 g. of furfural could have been reduced with the same catalyst without appreciable diminution in the speed of reduction.

Furfural is a different type of aldehyde than those studied in a previous paper by Carothers and Adams, in that it contains additional reducible groups. In the reduction of furfural a difference in the speed of absorption of the first molecular equivalent of hydrogen to convert the aldehyde group to the alcohol was observed as compared with the reduction of the ethylene double bonds in the furane ring. This was particularly noticeable in those experiments where the reduction was not too rapid, illustrated especially well in the series of runs where reworked platinum catalyst was used without the addition of ferrous chloride and where air was employed for reactivating the catalyst. The first portion of hydrogen was invariably absorbed rapidly, but usually one whole molecular equivalent was not absorbed before reactivation of the catalyst was desirable. It was especially noticeable that the last fraction of the first molecular equivalent of hydrogen was slowly absorbed, and that as soon as one molecular equivalent was completely absorbed a second reactivation was desirable. As soon as the absorption of the second molecular equivalent of hydrogen had started with the reactivated catalyst, the reduction proceeded again very rapidly. The significant point in these experiments is that just as long as any aldehyde is present the platinum catalyst is rapidly rendered inactive, but just as soon as all the aldehyde is reduced, the platinum catalyst is not devitalized and the reduction continues to proceed rapidly. It frequently happened in these experiments that after all but 5 to 10% of the first molecular equivalent of hydrogen had been absorbed, the last 5 to 10% could not be absorbed even over a long period of time, unless the catalyst was reactivated. After reactivation the absorption of this last small amount did proceed fairly rapidly, but during the process, devitalized the catalyst considerably so that reduction, after the first molecular equivalent of hydrogen had been absorbed, went more slowly than it should. When, however, the catalyst was always reactivated just after the complete absorption of the first molecular equivalent of hydrogen, regardless of when the previous reactivation had been made, the reduction of the ethylene linkages in the furane ring went very rapidly.

In all of the experiments described above no attempt was made to control the temperature. It was noted, however, that whenever the hydrogen was absorbed rapidly, there was a marked increase in the temperature of the reaction mixture. If the reduction slowed down appreciably, the reaction mixture might cool off but become warm again as soon as the platinum catalyst was reactivated. In the experiments in which the oxygen was used for reactivation and the maximum activity was obtained by using ferrous chloride, the reaction mixture remained at a temperature of 50–60° during the whole period of reduction, merely due to the heat of reaction.

A few experiments were carried out in order to determine whether furfural might be reduced without using a solvent, or using only a small amount of solvent. It was found that furfural alone with the catalyst was not reduced. Neither was it reduced in the presence of water sufficient in amount not to cause the formation of two layers. On the other hand, satisfactory results were obtained by dissolving the furfural in twice its volume of 50% alcohol. Since the preliminary experiments showed that the furfural in three volumes of 95% alcohol reduced very satisfactorily, this proportion was arbitrarily adopted.

In previous papers it has been mentioned that the brown platinum oxide could either be added to the reaction mixture and the reduction started, or the platinum oxide could first be added to the solvent, reduced to platinum black and then the reagents added and the reduction started. In all of the work with furfural the platinum oxide was reduced first to platinum black before the other reagents were added.

The reduction of furfural derivatives was carried out with platinum oxide obtained from chloroplatinic acid which had been reworked several times. The reactivation of the catalyst was carried out with air. All of the experiments were made before the study of furfural itself was completed, so that perhaps the best conditions were not used in every case. Nevertheless, the reductions took place in most cases with surprising ease. Apparently, the devitalizing of the catalyst which occurred in the reduction of furfural did not occur in the reduction of the majority of derivatives. Although the speed of reduction for each of these substances is given in the Experimental Part, it is not particularly significant, since the probability is that by varying the conditions somewhat according to those used for furfural, it could be increased markedly.

Pyromucic acid was reduced with the formation of tetrahydro-pyromucic acid as a chief product. Lower- and higher-boiling fractions were formed, however, the contents of which have not yet been determined. From analogy to the reduction of furfural it might be concluded that these fractions contain valerianic acid, α-hydroxy- and δ-hydroxy-valerianic acids.

The reduction of ethyl pyromucate took place only very slowly with the formation of a satisfactory yield of ethyl tetrahydro-pyromucate. It was obvious that very little decomposition of the ring took place as compared with the reduction of pyromucic acid.

The reduction of β-furyl-acrylic acid proceeded very rapidly with the absorption of three molecular equivalents of hydrogen to form β-tetrahydrofuryl-propionic acid. The by-product obtained in this reaction was small in amount, indicating the probable opening of the ring to only a very slight extent.

The reduction of furoin resembled closely the reduction of furfural owing, perhaps, to its similarity to furyl alcohol, the primary product in the reduction of furfural. By the absorption of 5 molecular equivalents, two glycols were obtained which, by analysis, proved to be stereo-isomeric dihydroxy-1,2-di-(tetrahydrofuryl)-1,2-ethanes. Besides these, some oily material resulted which was probably a complex mixture of polyhydroxy compounds such as might be formed by the rupture of one or both of the furane rings. The reduction was undoubtedly not complete when the hydrogenation was stopped.

The reduction of fural-acetone and fural-acetophenone took place with exceptional smoothness. A total of 4 molecular equivalents of hydrogen were absorbed before the reduction stopped; the first three were taken up very rapidly, reducing the aliphatic double bond and the two double bonds in the furane ring in each of the substances. The fourth molecular equivalent of hydrogen was absorbed comparatively slowly. When the reaction mixture was worked up after the first 3 molecular equivalents were absorbed, practically quantitative yields of pure ketone were obtained. When, however, 4 molecular equivalents were absorbed, the corresponding alcohol was obtained in quantitative yields. It has already been mentioned by previous investigators that fural-acetophenone could be reduced by hydrogen and platinum only to the saturated ketone. This is obviously incorrect.

Experimental Part

Materials.—The furfural used in this work was kindly donated by the Miner Laboratories of Chicago, Illinois. The authors wish to express their appreciation of this gift. The commercial material was purified merely by distillation under diminished pressure. It was then placed in brown bottles and kept until needed for use.

The pyromucic acid was prepared by the method of Frankland and Aston,[20] β-furyl-acrylic acid by the method of Gibson and Kahnweiler,[21] furoin by the method of

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[20] Frankland and Aston, *J. Chem. Soc.*, **79**, 515 (1901).

[21] Gibson and Kahnweiler, *Am. Chem. J.*, **12**, 314 (1890).

Fischer,[22] fural-acetone by the method of Claisen[23] and fural-acetophenone by the method of Semler.[24]

The spectroscopically pure chloroplatinic acid was made from ordinary C. P. chloroplatinic acid[25] of commerce by the method of E. Wichers.[26]

Reduction Experiments.—The apparatus used in the reduction was that described previously in this series of papers.[3]

The platinum oxide catalyst was made from chloroplatinic acid by the method described in the last paper.[3c] In all the experiments the platinum oxide was reduced to platinum black before the substance to be reduced was added. The procedure followed in each case was to add the platinum oxide to the reaction flask and wash it in carefully with a little water. There was then added sufficient alcohol to make the liquid about a 50% alcohol and then it was shaken with hydrogen under pressure until the platinum oxide turned black. This required from half a minute to a maximum of two or three minutes, providing the platinum oxide had originally been prepared in the proper way. The 50% alcohol which was present was allowed to remain in the bottle when the solution of alcohol for reduction was added.

The reductions were all carried out with hydrogen under a pressure of 1 to 2 atmospheres.

The reactivations of the catalyst were all carried out in a similar way. The bottle was evacuated, air or oxygen was passed in and the reaction mixture shaken for 10 minutes. The bottle was then again evacuated and filled with hydrogen before the reduction was continued. The first reactivation of the catalyst was invariably carried out an hour after the start of the reduction. Subsequent reactivations were made hourly in those experiments where the reductions proceeded rapidly, or every two or more hours in those experiments where the reductions were slow.

The procedure for working up the reaction mixture was very simple. As soon as the reduction was complete the bottle was allowed to stand for perhaps 30 minutes until the platinum settled. The solution was decanted or filtered, the alcohol distilled and the resulting residue fractionated under ordinary or diminished pressure.

Explanation of Table.—The total molecular equivalents of hydrogen which had been absorbed after definite periods of time are given in one column. The readings that were actually taken represented fall in pressure which was then converted to molecular equivalents of hydrogen. Since

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[22] Fischer, *Ber.*, **13**, 1334 (1880).

[23] Claisen, *Ber.*, **14**, 2468 (1881).

[24] Ref. 13, p. 729.

[25] The C. P. chloroplatinic acid in this investigation was the C. P. grade purchased from the Mallinckrodt Chemical Company. It contained traces of iron and other impurities.

[26] Wichers, THIS JOURNAL, **43**, 1268 (1921).

the drop in pressure varied between different limits, the molecular equivalents are approximate but are all within the general experimental error.

The asterisk (*) represents reactivation with oxygen, as described above. The reactivations were made at the ends of the time periods represented by the numbers directly before the signs, and also at beginning of each successive run (B, D, E) of a series.

Ten complete tables of exact experimental results which have led to the conclusions discussed in the introductory part of this paper could not be published on account of the necessity of conserving space in This Journal. If desired, copies of these tables may be procured by writing to the author (Adams).

Table I

Best Conditions for Rapid Reduction of Furfural

Columns A and B represent reduction with the same 1 g. of catalyst (C. P.), each run containing 50 g. of furfural in 150 cc. of alcohol (95%). Expts. C, D and E present a series of runs with the same 0.5 g. of catalyst (sp. p.) each run using 25 g. of furfural, in 75 cc. of alcohol (95%). To Run A only was added 1.2 cc. of 0.1 *M* ferrous chloride.

A		B		C		D		E	
Hrs.	Mol. equiv. H_2	Hrs.	Mol. equiv. H_2	Hrs.	Mol. equiv. H_2	Hrs.	Mol. equiv. H_2	Hrs.	Mol. equiv. H_2
		*				*		*	
1*	0.840	1*	1.04	1	1.040	1*	1.058	1*	1.058
2*	1.380	2*	1.900	2*	2.310	2*	2.443	2*	2.173
3*	2.580	3	3.060	3*	3.462	3	3.483	3	3.402
4	3.540								

Isolation of Products from Furfural Reduction.—The best results were obtained by distilling the crude material obtained from the reduction of six 50g. runs under ordinary pressure until all of the material boiling below 180° had passed over. This removed all the low-boiling products and most of the tetrahydrofuryl alcohol. The remainder was distilled under diminished pressure, and fractions were collected as follows: to 80°/3 mm., 80–95°/3 mm., 95–105°/3 mm., 105–118°/3 mm., 118–123°/3 mm. Three refractionations were then carried out under diminished pressure until most of the material had separated into fractions boiling up to 80°/3 mm., 95–105°/3 mm., and 118–123°/3 mm. These three fractions were then distilled under ordinary pressure and pure materials obtained as described below.

***n*-Amyl Alcohol** (V).—From each 600 g. of furfural only a very small amount of the fraction boiling at 130–145° was obtained. By careful fractionation, 5 g. was isolated which boiled at 137–139° (751 mm.); n_{D}^{15}, 1.4114; d_{20}^{20}, 0.8266. It had the characteristic odor of amyl alcohol and gave the proper constants and analytical results.

Analyses. Subs., 0.2757: CO_2, 0.6872; H_2O, 0.3282. Calc. for $C_5H_{12}O$: C, 68.18; H, 13.63. Found: C, 67.98; H, 13.32.

Undoubtedly the amount of this product formed was considerably greater than that actually isolated in a pure state.

Tetrahydrofuryl Alcohol (II).—From the material boiling at 145–180° a large fraction boiling at 174–180° was obtained which proved to be identical with the tetrahydrofuryl alcohol made and described in the literature. When pure it boiled at 177–178° (743 mm.); n_D^{19}, 1.4502; d_{20}^{20}, 1.0514.

Pentanediol-1,2 (III).—The fraction boiling at 95–105° (3 mm.) upon fractionation under ordinary pressure gave a large proportion boiling at 210.5–211.5° (751 mm.) or 99–100° (3 mm.); n_D^{19}, 1.4412; d_{20}^{20}, 0.9802.

Analyses. Subs., 0.3086: CO_2, 0.6493; H_2O, 0.3155. Calc. for $C_5H_{12}O_2$: C, 57.69; H, 11.53. Found: C, 57.38; H, 11.44.

This product was further identified as a glycol by conversion into the diacetate.

Pentanediol-1,2-diacetate.—The glycol was refluxed with a large excess of acetic anhydride for 3 hours. The reaction product was then fractionated under diminished pressure and yielded a practically quantitative amount of a diacetate boiling at 219–220° (748 mm.) or 103–104° (2 mm.); n_D^{20}, 1.4202; d_{20}^{20}, 1.0148.

Analyses. Subs., 0.3962: CO_2, 0.8341; H_2O, 0.2988. Calc. for $C_9H_{16}O_4$: C, 57.44; H, 8.51. Found: C, 57.42; H, 8.44.

Pentanediol-1,5; (Pentamethylene Glycol) (IV).—The high-boiling fraction of the original reaction mixture gave, upon distillation, constant-boiling fractions at 237–239° (751 mm.) or 119–120° (3 mm.); n_D^{20}, 1.4499; d_{20}^{20}, 0.9939. It was a practically water-clear liquid, miscible with water, alcohol and ether. Its constants agree with those of pentamethylene glycol prepared in a different manner. It gives a diacetate the constants of which agree with those previously found for this compound.

Analyses. Subs., 0.2349: CO_2, 0.4968; H_2O, 0.2383. Calc. for $C_5H_{12}O_2$: C, 57.69; H, 11.53. Found: C, 57.68; H, 11.36.

Pentanediol-1,5-diacetate.—This was prepared in exactly the same manner as the pentanediol-1,2-diacetate. It was a colorless liquid boiling at 241.5–243.5° (748 mm.) or 122–123° (3 mm.); n_D^{19}, 1.4261; d_{20}^{20}, 1.0296.

Analyses. Subs., 0.2765: CO_2, 0.5799; H_2O, 0.2099. Calc. for $C_9H_{16}O_4$: C, 57.44; H, 8.51. Found: C, 57.20; H, 8.50.

Furyl Alcohol (I).—From 200 g. of furfural reduced in 50 g. portions merely until one molecular equivalent of hydrogen had been absorbed, using the same 1 g. of catalyst, there was obtained 180 g. of practically pure furyl alcohol boiling at 168–170° (754 mm.); n_D^{20}, 1.4828; d_{20}^{20}, 1.1357.

Reduction of Furfural Derivatives

Catalyst (C. P.) was used in all the experiments on furfural derivatives and reactivations with air were employed. The experiments were completed before the distinct advantage of using oxygen for reactivation was found.

Pyromucic Acid to Tetrahydro-pyromucic Acid.—A sample of 25 g. of pyromucic acid in 100 cc. of alcohol (95%) was reduced with 0.5 g. of catalyst in about 4 hours. By fractionation of the reaction product tetrahydro-pyromucic acid was obtained to the extent of about 40% of the total reaction mixture. In addition, there were low- and high-boiling products present which are now being studied. Wienhaus and Sorge[14] did not in their work mention that any products besides tetrahydro-pyromucic acid were obtained. When pure, tetrahydro-pyromucic acid was water-clear and boiled at 131–132° (14 mm.); m. p., 21°; n_D^{19}, 1.4585; d_{20}^{20}, 1.1933.

Ethyl Pyromucate to Ethyl Tetrahydro-pyromucate.—The reduction of ethyl pyromucate took place much more slowly than the reduction of pyromucic acid. For the reduction of 25 g. of ethyl pyromucate in 75 cc. of 95% alcohol in the presence of 0.5 g. of catalyst, 45 hours was necessary with frequent reactivation of the catalyst with air. About 20 g. of crude reduction product was obtained from the reaction mixture and of this 13 g. boiled at a constant temperature of 82° (11 mm.); n_{D}^{18}, 1.4455; d_{20}^{20}, 1.0792. It had a pleasant, fruity odor, and was insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.4049: CO_2, 0.8620; H_2O, 0.3105. Calc. for $C_7H_{12}O_3$: C, 58.29; H, 8.39. Found: C, 58.06; H, 8.56.

β-Furyl-acrylic Acid to β-Tetrahydrofuryl-propionic Acid, $C_4H_7O—CH_2CH_2CO_2H$.—The reduction of 25 g. of β-furyl-acrylic acid in 75 cc. of 95% alcohol in the presence of 0.5 g. of catalyst was complete in about 2 hours. After fractionation 10 g. of pure β-tetrahydrofuryl-propionic acid was obtained boiling at 135–137° (4 mm.); n_{D}^{19}, 1.4562; d_{20}^{20}, 1.1155. It was obviously identical with the substance prepared by Windaus[16] and Dalmer. In addition to this main product was low- and high-boiling material which has not yet been identified.

Furoin to Dihydroxy-1,2-di-(tetrahydrofuryl)-1,2-ethane, $C_4H_7O—CHOHCHOH—C_4H_7O$.—A solution of 20 g. of pure furoin in 200 cc. of 95% alcohol was reduced with 1 g. of catalyst. The initial temperature in this experiment was about 35°, since furoin is not very soluble in cold alcohol, and even at the temperature mentioned a certain amount remained undissolved. The reduction proceeded rapidly and at the end of 6 hours, the catalyst having been reactivated with air only once, five molecular equivalents of hydrogen had been taken up. Apparently, further reduction was taking place but it was stopped at this point. Two such runs as these were made and the reaction products mixed before being worked up.

After filtering the platinum and evaporating the alcohol, a liquid was obtained from which a few crystals deposited on standing. The whole mixture, without removal of these crystals, was distilled under diminished pressure, when the major portion boiled from 145–200° (2 mm.). This distillate was a yellowish oil from which crystals deposited on standing. The crystals were filtered out and recrystallized from a very small amount of 95% alcohol. About 4 g. of the recrystallized product was thus obtained (Product A). The alcoholic filtrate from the recrystallization was added to the oil from which the crude crystals had been filtered and the alcohol removed from the mixture. There resulted 34 g. of yellow oil which on standing became semisolid. This was again fractionated under diminished pressure and two portions were collected, one boiling at 140–170° at 2 mm. and the other at 170–205° at 2 mm. The higher of these two fractions gradually solidified in the receiver. It weighed about 5 g. and contained a large percentage of Product A.

The fraction boiling from 140–170° (2 mm.) and weighing 26 g. was again fractionated and a constant-boiling fraction distilling at 147–148° (2 mm.) obtained. This solidified immediately to a pure white substance which melted at 75° (Product B). About 12 g. of this solid was obtained. No convenient method for recrystallizing it was found.

PRODUCT A.—Product A is a white crystalline solid, readily soluble in water and alcohol but only slightly soluble in ether, benzene or ethyl acetate. It can readily be crystallized from alcohol after which it melts at 167°.

Analyses. Subs., 0.2687: CO_2, 0.5843; H_2O, 0.2100. Calc. for $C_{10}H_{18}O_4$: C, 59.36; H, 8.98. Found: C, 59.30; H, 8.75.

PRODUCT B.—Product B is a white solid readily soluble in alcohol and water. It is more soluble in benzene, ether or ethyl acetate than Product A. It boils at 147–148° (2 mm.) after which it solidifies and melts at 75°.

Analyses. Subs., 0.2782: CO_2, 0.5982; H_2O, 0.2188. Calc. for $C_{10}H_{18}O_4$: C, 59.36; H, 8.98. Found: C, 58.64; H, 8.80.

Fural-acetone to Tetrahydrofuryl-1-butanone-3 and to Tetrahydrofuryl-1-butanol-3.—A solution of 55 g. of pure fural-acetone in 150 cc. of 95% alcohol was reduced in the presence of 1 g. of catalyst. The first molecular equivalent of hydrogen was absorbed in 20 minutes. The catalyst was reactivated and the second molecular equivalent of hydrogen was absorbed in 30 minutes. Again the catalyst was reactivated and the third molecular equivalent of hydrogen was absorbed in 70 minutes. The reduction in a number of experiments was stopped at this point. In other experiments the catalyst was again reactivated and the absorption carried on until a fourth molecular equivalent of hydrogen had been taken up. The absorption of this last molecular equivalent generally required between 8 and 15 hours with several reactivations of the catalyst. When the reduction was stopped after the absorption of 3 molecular equivalents, practically a quantitative yield of the ketone was obtained, and when four molecular equivalents were absorbed practically a quantitative yield of the alcohol was obtained.

Tetrahydrofuryl-1-butanone-3, $C_4H_7O—CH_2CH_2COCH_3$.—In the reduction of 55 g. of fural-acetone it was not difficult to obtain 40 g. of completely purified tetrahydrofuryl-1-butanone-3. The ketone was a water-clear liquid of pleasant odor, which gradually became yellowish on standing. It was insoluble in water but readily soluble in alcohol and ether. It boiled at 81° (2 mm.); n_D^{19}, 1.4459; d_{20}^{20}, 0.9815.

Analyses. Subs., 0.2055: CO_2, 0.5065; H_2O, 0.1763. Calc. for $C_8H_{14}O_2$: C, 67.55; H, 9.93. Found: C, 67.22; H, 9.60.

Tetrahydrofuryl-1-butanol-3, $C_4H_7O—CH_2CH_2CHOHCH_3$.—From 55 g. of fural-acetone 42 g. of absolutely pure alcohol could readily be obtained. It was a colorless, odorless liquid which did not become colored on exposure to air. It was practically insoluble in water but soluble in alcohol and ether. It boiled at 93–94° (2 mm.); n_D^{19}, 1.4546; d_{20}^{20}, 0.9774.

Analyses. Subs., 0.2182: CO_2, 0.5343; H_2O, 0.2244. Calc. for $C_6H_8O_2$: C, 66.61; H, 11.19. Found: C, 66.78; H, 11.51.

Fural-acetophenone to Tetrahydrofuryl-1-phenyl-3-propanone-3 and Tetrahydrofuryl-1-phenyl-3-propanol-3.—The reduction took place rapidly as in the case of the fural-acetone. It was possible to reduce 25 g. of pure fural-acetophenone in 75 cc. of alcohol with 0.5 g. of catalyst until three molecular equivalents of hydrogen had been absorbed in about 2 hours, with only one reactivation of the catalyst. The absorption of the fourth molecular equivalent of hydrogen required about 8 hours and two reactivations of the catalyst. The yields of ketone after three molecular equivalents of hydrogen had been absorbed, and of alcohol after four equivalents had been absorbed, were practically quantitative.

Tetrahydrofuryl-1-phenyl-3-propanone-3, $C_4H_7O—CH_2CH_2COC_6H_5$.—From 25 g. of fural-acetophenone 18 g. of perfectly purified ketone was obtained boiling at 153–154° (2 mm.); n_D^{20}, 1.4885; d_{20}^{20}, 1.0913. It was a practically colorless liquid, insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.3050: CO_2, 0.8577; H_2O, 0.2056. Calc. for $C_{13}H_{16}O_2$; C, 76.42; H, 7.90. Found: C, 76.69; H, 7.54.

Tetrahydrofuryl-1-phenyl-3-propanol-3, $C_4H_7O—CH_2CH_2CHOHC_6H_5$.—From 25 g. of fural-acetophenone about 21 g. of absolutely purified alcohol was obtained boiling at 167–168° at 2 mm.; n_D^{20}, 1.5245; d_{20}^{20}, 1.0601. It was a water-clear liquid, insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.2697: CO_2, 0.7490; H_2O, 0.2145. Calc. for $C_{13}H_{18}O_2$: C, 75.67; H, 8.80. Found: C, 75.74; H, 8.90.

Summary

1. The reduction of furfural in alcohol solution, using platinum oxide as a catalyst, has been studied. By the absorption of one molecular equivalent

of hydrogen, furyl alcohol is obtained in quantitative yields. When the reduction is carried further, 2.3 to 3.3 additional molecular equivalents of hydrogen are absorbed with the formation of a mixture of four products; tetrahydrofuryl alcohol, pentanediol-1,2, pentanediol-1,5 and *n*-amyl alcohol. The first of these is formed in largest amounts and the amounts of the others decrease in the order given.

2. It has been found that platinum oxide from spectroscopically pure chloroplatinic acid or C. P. chloroplatinic acid of commerce is a very ineffective catalyst toward the reduction. In the presence of small amounts of ferrous chloride, however, the reduction takes place very rapidly. A series of experiments using increasing amounts of ferrous chloride showed an increase in the speed of reduction up to a certain maximum beyond which larger amounts caused a diminution in speed. The larger amounts of ferrous chloride have a greater poisoning effect on the platinum as a catalyst toward the reduction of the ethylene linkages in the furane ring than toward the reduction of the aldehyde group.

3. The amount of ferrous chloride which afforded a maximum activity for a certain weight of platinum catalyst produced the same activity when double the amount of platinum and double the amount of reagents were used.

4. Platinum catalyst that has been redissolved and reprecipitated as oxide a number of times accumulates a certain amount of impurity so that it is active for the reduction of furfural without the addition of ferrous chloride. The activity of such catalyst, however, is much less than the activity in the presence of a little ferrous chloride.

5. The distinct advantage of using oxygen in place of air for reactivation of the catalyst has been demonstrated.

6. The best method for reducing furfural found in this research was by the use of 50 g. of furfural, 150 cc. of alcohol, 1 g. of catalyst and 1.2 cc. of 0.1 M ferrous chloride. Using hydrogen under 1 to 2 atmospheres' pressure the absorption of about 4 molecular equivalents of hydrogen took place in 4 hours. Three reactivations of the catalyst were made with oxygen during this period. This is in contrast to the reduction of furfural described by a previous investigator where 48 g. of furfural was used and 285 hours and 10 additions of fresh catalyst were required for the reduction.

7. By the use of the platinum oxide catalyst, furfural derivatives were readily reduced; pyromucic acid was converted to tetrahydro-pyromucic acid; ethyl pyromucate to ethyl tetrahydro-pyromucate; β-furyl-acrylic acid to β-tetrahydrofuryl-propionic acid; furoin to two stereo-isomeric dihydroxy-1,2-di-(tetrahydrofuryl)-1,2-ethanes; fural-acetone to tetrahydrofuryl-1-butanone-3 and to tetrahydrofuryl-1-butanol-3; fural-acetophenone to tetrahydrofuryl-1-phenyl-3-propanone-3 and tetrahydrofuryl-1-phenyl-3-propanol-3.

URBANA, ILLINOIS