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CATALYTIC HYDROGENATION AND HYDROGENOLYSIS OF FURAN COMPOUNDS

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INTRODUCTION

In 1897 Sabatier discovered the catalytic hydrogenation of organic compounds. Subsequently the most diverse classes of such compounds have been examined, and catalysts have been found possessing the necessary activity, stability, and specificity.

The hydrogenation of furan compounds by Sabatier's method on a nickel catalyst[1,2] did not yield satisfactory results, and therefore liquid-phase hydrogenation was employed almost exclusively in subsequent work on furan compounds. Adams platinum, Raney nickel, copper chromite, and several other catalysts were widely used for the liquid-phase hydrogenation of furan derivatives. It was soon found, however, that the furan ring can be smoothly hydrogenated to a tetrahydrofuran ring also in the vapour phase if special catalysts are employed for this purpose, such as osmium on asbestos (Zelinskii, Shuikin), palladium and foraminate Ni–Al (Shuikin and his collaborators). The hydrogenation of furan compounds is also of practical value, mainly owing to the possibility of opening the ring and passing from compounds of the furan series to those of other classes. Thus from 2-substituted homologues of furan it proved possible to obtain aliphatic ketones and alcohols, and the limits of applicability of this method were considerably extended after the discovery of "conjugate" hydrogenolysis of the furan ring.

Starting from furfuraldehyde the synthesis of furylacraldehydes and furfurylidene ketones on the one hand, and of 2-acyl-5-alkylfurans on the other, can be accomplished in an extremely simple manner. Both of these groups of furan compounds are valuable starting materials for the catalytic synthesis of aliphatic, heterocyclic, and carbocyclic compounds. 2-Acyl-5-alkylfurans can be directly converted by vapour-phase hydrogenation into 1,5-diketones and homologues of tetrahydropyran, of cyclohexanone, and of phenol. Furylacraldehydes and furfurylidene ketones are converted, on hydrogenation and reductive amination, into furan alcohols and furan amines, in which the functional groups are in position 3 with respect to the furan ring. Catalytic hydrogenation of furan alcohols and amines of this structure in the vapour phase forms di- and tri-substituted homologues of tetrahydrofuran and of pyrrolidine, which are products of the intramolecular cyclisation of the alkane-1,4-diols and 4-aminoalcohols formed as intermediates. All this shows that the problem of the catalytic hydrogenation of furan compounds has acquired fresh importance, for the development of new methods, convenient in practice, of synthesising organic compounds of the aliphatic, heterocyclic, and carbocyclic series. In several cases these methods not only supplement the old methods of organic synthesis, but are also more feasible in practice, because of their simplicity and the availability of the furan starting materials. The successful development of improved industrial methods for obtaining furfuraldehyde from raw materials containing pentosans provides the main conditions for the evolution of organic synthesis on the basis of furan compounds.

1. HYDROGENATION OF 2-ALKYL- AND 2-ALKENYL--FURANS

The first investigation of the catalytic hydrogenation of the furan ring was carried out by Padoa and Ponti in 1906,[1] and in 1908 Bourguignon[2] examined the hydrogenation of furan by Sabatier's method. When furan was passed over a nickel catalyst at 170° a mixture was formed of tetrahydrofuran (12%), butan-1-ol (8%), and lower hydrocarbons which were not investigated, while 34% of the furan remained unchanged.

In 1923 Kaufmann and Adams[3] employed a platinum catalyst for the liquid-phase hydrogenation of several functional derivatives of furan (furfuraldehyde, furfuryl alcohol, etc.), and found that under these conditions the process takes place without side reactions, and can be controlled to obtain partly or completely hydrogenated products.

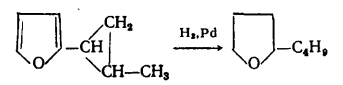
Then it was found that in the presence of Raney nickel the furan ring is hydrogenated quite satisfactorily at moderate temperatures[4]; thus an 80% yield of tetrahydrofuran was obtained from furan at 50°.[5]

Adkins and Connor[6], and then Lazier[7] used chromite catalysts (mainly copper chromite) for the liquid-phase hydrogenation of furan and several of its derivatives, obtaining either tetrahydrofuran derivatives or products of the hydrogenolysis of the furan ring.

Zelinskii and Shuikin[8] investigated the hydrogenation of sylvan [methylfuran (Ed. of Translation)] in the presence of osmium on asbestos in a flow system at 80°–82°, and obtained a quantitative yield of tetrahydrosylvan. The smooth hydrogenation of furan to tetrahydrofuran was accomplished in the presence of the same osmium catalyst at 65°–70°.[9]

An excellent catalyst for the hydrogenation of the furan ring proved to be palladium oxide mixed with palladium black. Starr and Hixon[10] obtained a quantitative yield of tetrahydrofuran by the hydrogenation of furan at a pressure of ~7 atm.

Shuikin *et al.* made a detailed study[11,12] of palladium as catalyst for the hydrogenation of the furan ring. Furan and its mono- and di-alkyl derivatives (the 2-methyl, 2-ethyl, 2-propyl, 2,5-dimethyl, and 2-ethyl-5-methyl derivatives) were hydrogenated over a palladium catalyst at 150° and ordinary pressures in a flow system. Only the corresponding mono- and di-alkyltetrahydrofurans were obtained. Shuikin and Daiber[13] found that the hydrogenation of 2-furylcyclopropane and 1-fur-2′-yl-2-methylcyclopropane by a flow method in the presence of palladium on asbestos at ordinary pressures yielded interesting results. At 140° the former gave 2-propyltetrahydrofuran, and at 150° the latter yielded 2-butyltetrahydrofuran:



Thus the cyclopropane ring underwent cleavage with extraordinary ease under conditions producing smooth hydrogenation of the double bonds in the furan ring.

Shuikin *et al.*[14] investigated the hydrogenation of 2-benzylfuran on platinum and palladium catalysts. Liquid-phase hydrogenation at room temperature in the presence of platinum on charcoal or of platinum black yielded 2-benzyltetrahydrofuran (the main reaction product) and 1-phenylpentan-2-ol. Hydrogenation of 2-benzylfuran by a flow method in the presence of platinum and palladium on asbestos at 230° resulted in the complete opening of the furan ring with the formation of 1-phenylpentan-2-ol and a small amount of n-pentylbenzene.

A palladium catalyst was extensively used by Yur'ev and his coworkers[15-17] for the hydrogenation of various furan compounds. Mixtures of 2-alkyl- and 2-alkenyl-furans,

methyl pyromucate [methyl furan-2-carboxyate (Ed. of Translation)], and 2,4-dimethylfuran were hydrogenated in the presence of palladium on asbestos at 150°–160° in a flow system. The yields of the corresponding tetrahydrofuran derivatives were not less than 70%.

Nickel catalysts prepared in various ways showed high activity in effecting hydrogenation of the furan ring. Foraminate nickel catalysts, approaching palladium and osmium in their properties, found especially wide use. Shuikin and Bunina [18] showed that a foraminate nickel catalyst prepared by the incomplete extraction of aluminium from an Ni–Al alloy can successfully replace osmium and palladium catalysts for the hydrogenation of the furan ring. In the presence of this catalyst furan and sylvan were hydrogenated at 100°–140° and 120° respectively to give high yields of the tetrahydro-derivatives. It was noted that raising the reaction temperature to 170° produced a thorough breakdown of the furan with the formation of volatile products. Burnette [19] also employed a foraminate nickel catalyst, from which only 6–8% of the aluminium had been removed, for the hydrogenation of sylvan by a flow method. At 200° the main product was tetrahydrosylvan (yield 50%), and appreciable amounts of ring-cleavage products, pentan-2-one and pentan-2-ol, were obtained. Paul [20] studied the hydrogenation of mixtures of the 2-furyl derivatives of propene and propane, butene and butane, and pentene and toluene (ω-) in the presence of Raney nickel. Hydrogenation was carried out in the liquid phase at 110°–118° under a hydrogen pressure of 65–85 atm. The yield of the corresponding tetrahydrofurans varied from 68% for 2-butyltetrahydrofuran to 91% for 2-benzyltetrahydrofuran.

Yur'ev *et al.* [21] hydrogenated furan, over nickel deposited on aluminium oxide, at 123°–160° and an initial pressure of 60 atm in an autoclave. An 86% yield of tetrahydrofuran was obtained. A 95% yield of this product was obtained in the presence of nickel on kieselguhr when this was employed by Katsuno [22] for the liquid-phase hydrogenation of furan at high pressures of hydrogen.

Boles [23] hydrogenated furan, sylvan, and dimethylfuran on catalysts containing Ni, Cu, or Mo. At 190°–200° and 60–80 atm, 90–95% yields of the corresponding tetrahydrofurans were obtained.

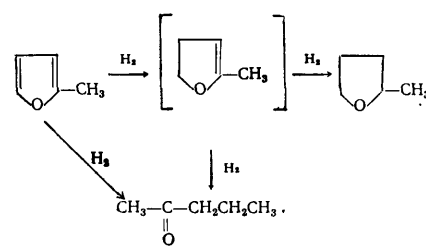
The aim of all these investigations was to discover catalysts and reaction conditions such that furan compounds would be hydrogenated to the maximum extent into their tetrahydro-derivatives. However, apart from this type of hydrogenation, the furan ring can undergo cleavage at the C–O and C–C bonds. The predominant or sole occurrence of one of these reactions depends on the conditions, mainly of temperature and on the nature of the catalysts. A rise in temperature favours ring cleavage. The use of different catalysts is even more effective than temperature for achieving selective hydrogenation of the furan ring. The properties of catalysts can be compared if the other reaction conditions are kept the same, since it has been established that the same catalyst can effect hydrogenation of the furan ring in different ways depending on whether reaction takes place in the liquid or in the gas phase. For example, various furan derivatives are smoothly hydrogenated to the corresponding tetrahydrofurans in the liquid phase over an Adams platinum catalyst. Similarly palladium also exhibits excellent catalytic properties for the liquid-phase hydrogenation of the furan ring [10]. However, these two catalysts differ markedly in their behaviour towards hydrogenation and hydrogenolysis of the furan ring in the vapour phase. Under these conditions palladium retains its property of specifically catalysing hydrogenation of the furan ring [11], whereas in the vapour phase over platinum at 275° the furan nucleus undergoes solely hydrogenolysis.

Hydrogenolysis of the furan ring results in the conversion of furan compounds into aliphatic compounds, and in this respect is of great practical value. In 1947 Bremner [24] stated in a patent that it was possible to obtain alcohols by the hydrogenation of furan and its alkyl and aryl derivatives at temperatures above 120° (preferably at 200°–300°) and hydrogen pressures exceeding 100 atm in the presence of catalysts containing silver, copper, or silver or copper chromite deposited on an inert carrier, kieselguhr or pumice. It was stated that the yields of the alcohols were increased by adding small amounts of an acid or of a salt thereof to the reaction mixture. Thus the hydrogenation of furan in the presence of $CuCr_2O_4.BaCr_2O_4$ at 220° and 100 atm in an autoclave gave tetrahydrofuran (30%) and n-butanol (70%). In the same way the homologues of furan yielded pentan-1-ol, pentan-2-ol, and hexan-2-ol.

Further investigation showed that hydrogenolysis of the furan ring could be more usefully carried out in the vapour phase. Bremner *et al.* [25] reported that hydrogenolysis of sylvan with the formation of pentan-2-one takes place when the sylvan is passed through a tube containing a Cu–ZnO catalyst at 325°. Ethylfuran gives ethyl propyl ketone under these conditions.

Wilson [26] investigated the conditions for obtaining tetrahydrosylvan and pentan-2-one by the vapour-phase hydrogenation of sylvan over a nickel catalyst. At 100° tetrahydrosylvan (yield 86%) is formed, and at 185° pentan-2-one (75%). The latter product is formed also on other catalysts, but in lower yields and at higher temperatures (340°–350°). Thus on copper chromite 52% of pentan-2-one and a little pentan-2-ol are formed, on a Co–Cu catalyst ~ 60% of pentan-2-one, and on an Fe–Cu catalyst mainly tetrahydrosylvan with only ~ 10% of the ketone.

Wilson considers that the formation of pentan-2-one from sylvan does not involve an intermediate stage of tetrahydrosylvan formation, since a mixture of the latter with hydrogen passed over a nickel catalyst at 250° yielded no ketone at all, but considerable formation of gas was observed; at 100° tetrahydrosylvan remained unchanged. On this basis Wilson suggested the following scheme of successive reactions



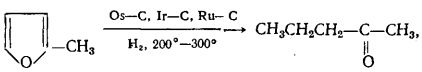
Thus he assumes that fission of the C–O bond is possible both in the sylvan ring and in that of dihydrosylvan.

Platinum deposited on carbon proved to be a good catalyst for the vapour-phase hydrogenolysis of the furan ring. Hydrogenation of 2-alkylfurans (where the alkyl group is methyl, ethyl, propyl, butyl, or pentyl) in the vapour phase at atmospheric pressure and 275° over Pt–C involves selective hydrogenolysis at the 1,5 C–O bond (not adjacent to the alkyl radical), with formation of the corresponding aliphatic ketones (pentan-2-one, hexan-3-one, heptan-4-one, octan-4-one, and nonan-4-one) in yields of 90–95%. [27]

Under the same conditions hydrogenolysis in 2-ethyl-5--methylfuran takes place in both ways, with the formation of heptan-2-one and heptan-3-one, and also a small amount of heptane[28]. A foraminate Pt–Al catalyst exhibited properties similar to those of platinised carbon. On this catalyst sylvan undergoes hydrogenolysis in the vapour phase at 275°, being smoothly converted into methyl propyl ketone[29]. The difference between palladium and platinum is also marked at this temperature. Both palladised carbon and also a foraminate Pd–Al catalyst act as specific catalysts for the hydrogenation of the double bonds in the furan ring over quite a wide temperature range. For example, sylvan and 2-ethyl-5-methylfuran are hydrogenated, in the vapour phase over palladium catalysts at 275°, to the corresponding homologues of tetrahydrofuran in yields of 75–80%.[29]

A comparative study of the catalytic properties of the Group VIII metals was made by investigating the hydrogenation of sylvan in the vapour phase over osmium, iridium, ruthenium, and rhodium precipitated on carbon[30].

The results for the hydrogenation of sylvan on Os–C, Ir–C, and Ru–C at 200°–300° show that these catalysts are completely devoid of the ability to reduce the furan ring, but effect exclusively hydrogenolysis of the ring at the 1,5 C–O bond with the formation of methyl propyl ketone, the yield of which depends on the temperature and the speed at which the substance is passed over the catalyst:



On Ir–C at 200° and with a flow velocity of 0.1 h^{-1} sylvan yields ~60% of methyl propyl ketone, but at 275° with the same flow velocity it is practically all converted into the ketone. On Os–C and Ru–C at 275° and with other conditions the same, the degree of conversion of sylvan into pentan-2-one is 40% and 85% respectively. In no case has tetrahydrosylvan been isolated at this temperature. An exception is provided by the rhodium catalyst, on which at 200° both hydrogenation of the furan ring (40%) and hydrogenolysis of the ring at the 1,5 C–O bond (60%) take place.

The results obtained enable some general conclusions to be reached. All these catalysts containing Group VIII metals deposited on carbon can be divided into two groups according to their action on the furan ring in vapour-phase hydrogenation at normal pressure:

1. Catalysts of the platinum type (Pt, Os, Ir, Ru) possess a feebly developed capacity (or practically none at all) for hydrogenating the double bonds in the furan ring. On these catalysts at 200°–300°, only hydrogenolysis of the ring at the 1,5 C–O bond takes place.

2. Catalysts of the palladium type (Pd, Rh) are able smoothly to hydrogenate the double bonds in the furan ring over quite a wide temperature range. They are able to effect hydrogenolysis of the ring, though to no great extent, only at elevated temperatures.

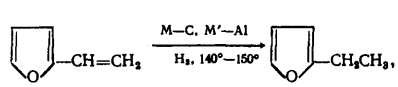
The hydrogenation of sylvan in the vapour phase has been investigated also on Ni–Zn and Cu–Al foraminate catalysts[29,31]. These showed the same activity and selectivity as platinum: in contact with them at 250°–300° sylvan is split only at the C–O bond not adjacent to the methyl group, and is quantitatively converted into methyl propyl ketone. Nickel deposited on zinc, cadmium, and beryllium oxides also has a similar effect on the furan ring on vapour-phase hydrogenation. At 250°–300° the ring undergoes hydrogenolysis solely at the ether bond remote from the alkyl side-group, the reaction going just as smoothly on Ni–ZnO as on a platinum catalyst, but not quite as well on Ni–CdO and Ni–BeO.[31]

All these catalysts, while being so very effective for the hydrogenolysis of the furan ring, show very little activity in effecting hydrogenation of the cyclic double bonds. Thus sylvan on Pt–C and foraminate Ni–Zn at 150° is hydrogenated to tetrahydrosylvan to the extent of only 20–25%, the remainder of the catalysate consisting of hydrogenolysis products of the furan ring, pentan-2-one and pentan-2-ol.[31,32]

Thus three groups of catalysts have been investigated under conditions of the vapour-phase hydrogenation of the furan nucleus at ordinary pressures: (1) metals deposited on carbon: Pt–C, Pd–C, Os–C, Ir–C, Rh–C, and Ru–C; (2) foraminate catalysts: Pt–Al, Pd–Al, Ni–Zn, and Cu–Al; (3) nickel on oxides: Ni–ZnO, Ni–CdO, and Ni–BeO.

Among all these it is only the palladium catalysts (Pd–C and foraminate Pd–Al) which exhibit a clearly marked ability to hydrogenate the furan to the tetrahydrofuran ring in the vapour phase at normal pressure; this ability is shown in lesser degree by rhodium on carbon. All the rest are typical hydrogenolysis catalysts for the furan ring, and in the case of the 2-alkylfurans they effect hydrogenolysis in only one way, at the C–O bond remote from the alkyl radical. A double bond in the side chain of various furan derivatives is hydrogenated at lower temperatures than is the furan ring. Thus there is a considerable difference in optimum temperatures for hydrogenation of a side-chain double bond in furan compounds and hydrogenolysis of the furan ring. Therefore all catalysts which are active in the hydrogenolysis of the furan ring and inactive towards hydrogenation thereof exhibit a high selectivity with respect to a side-chain olefinic bond on vapour-phase hydrogenation at atmospheric pressure. The flow velocity is also important, apart from the temperature, since a decrease in speed will favour the secondary reaction of hydrogenolysis of the furan ring.

The hydrogenation of 2-vinylfuran has been investigated in the vapour phase at normal pressure on Group VIII metals deposited on carbon[30] and over foraminate catalysts[29]. The temperature of hydrogenation was 140°–150°, and the flow velocity 0.1 h^{-1}. Under these conditions 2-vinylfuran was converted into 2-ethylfuran in 95–100% yield



where

$$M = Pt, Os, Ir, Ru, Rh;\ M' = Pt, Cu.$$

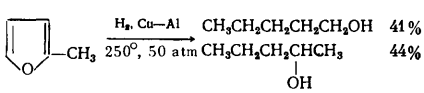
Nickel deposited on the oxides of zinc, cadmium, and beryllium has almost identical properties. At 150°–175° 2-propenylfuran was hydrogenated to 2-propylfuran in 90–95% yield[31]. Thus provided that certain temperature conditions are observed, many catalysts can be used for the selective hydrogenation of a double bond in the side chain of furan compounds.

Bremner[33] accomplished the selective hydrogenation of the double bond in the hydrogenation of 2-vinylfuran on Raney nickel or on nickel deposited on carriers in the presence of ammonia or diethylamine. At 80° and 50 atm a 90% yield of 2-ethylfuran was obtained. In the absence of ammonia, the main product of hydrogenation under the same

conditions was 2-ethyltetrahydrofuran. Bremner also found that the hydrogenation of 2-vinylfuran in the presence of nickel on kieselguhr at 65° and 250 atm gives 2-ethylfuran practically exclusively. Hydrogenation of the furan ring begins at pressures above 250 atm.

Interesting results were obtained in an investigation of the effect of the hydrogen pressure on the direction of hydrogenation of the furan ring by a flow method. Sylvan was hydrogenated at 50 atm in a flow system over platinised carbon, foraminate Ni–Zn, and foraminate Ni–Al catalysts [34].

As mentioned above, on these catalysts at atmospheric pressure and 250°–300° sylvan is completely hydrogenolysed at the C–O bond remote from the methyl group, with the smooth formation of methyl propyl ketone. In contrast, its hydrogenation on Pt–C at 275° and an increased pressure of hydrogen (50 atm) gives as the main product tetrahydrosylvan (75%) with considerably smaller amounts of pentan-2-one (20%) and pentan-2-ol (5%). The use of elevated pressures in the hydrogenation of sylvan on a foraminate Ni–Zn catalyst also favours hydrogenation of the furan nucleus and represses hydrogenolysis, but this effect is less marked than on a platinum catalyst. Over foraminate Ni–Zn at 250°–260° and 50 atm sylvan forms 35–40% of tetrahydrosylvan, 20–25% of pentan-2-one, and ~40% of pentan-2-ol. In the hydrogenation of sylvan over a foraminate Cu–Al catalyst, raising the pressure influences the course of hydrogenation of the furan nucleus in a different way from that found with Pt–C and foraminate Ni–Zn. On the Cu–Al at 50 atm the furan ring is hydrogenated to the extent of only 5–8%. Thus in this case a rise in pressure has a very slight influence towards hydrogenation of the furan ring. On the other hand, hydrogenolysis at elevated pressures and 250° takes place here in both possible ways, as a result of which sylvan is converted predominantly into pentan-1-ol and pentan-2-ol:



The relative amounts of alcohols formed depend on the pressure: at 25 atm 33% of pentan-1-ol and 54% of pentan-2-ol are formed, but at 50 atm the corresponding quantities are 41% and 44%. Thus, depending on the nature of the catalyst, raising the pressure in the hydrogenation of 2-alkylfurans in a flow system favours hydrogenation of the furan ring or increases the degree of hydrogenolysis of the furan nucleus at the ether bond adjacent to the alkyl group.

Conjugate Hydrogenolysis of the Furan Ring

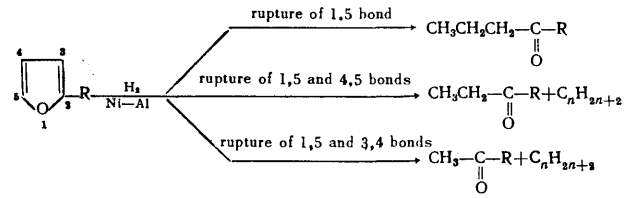
Among catalysts investigated for the hydrogenation of furan compounds, the foraminate Ni–Al catalyst occupies a special position. As already mentioned above, this catalyst hydrogenates the furan ring in both the liquid and the vapour phase. In this respect it resembles palladium catalysts, and is sharply distinguished from foraminate Ni–Zn, which exhibits very little ability to hydrogenate the furan ring. But the most important property distinguishing foraminate Ni–Al from all other catalysts and making it valuable from the point of view of synthesis is its ability to effect the so-called "conjugate" hydrogenolysis of the furan ring. An investigation [35,36] of the hydrogenation of 2-alkyl- and 2-alkenyl-furans in the vapour phase at normal pressure on a foraminate Ni–Al catalyst showed the following:

1. The hydrogenolysis products of 2-alkyl- and 2-alkenyl-furans are mainly secondary alcohols and the corresponding ketones. Primary alcohols are either almost completely absent from the reaction products, or else are present in very small amounts.

2. The hydrogenolysis of 2-alkyl- and 2-alkenyl-furans yields on the one hand alcohols and ketones containing the same number of carbon atoms as the original furan compound, and on the other alcohols and ketones in which the carbon chain is shorter by one or two C-atoms compared with the number of carbon atoms in the original alkylfuran.

3. Furan and tetrahydrofuran rings display a fundamental difference in their ability to undergo hydrogenolysis under identical conditions of hydrogenation. The latter ring is more stable than the furan ring, and undergoes hydrogenolysis in a different way.

All these experimental facts can be explained on the assumption that on a foraminate Ni–Al catalyst the furan ring undergoes hydrogenolysis both at C–O and at C–C bonds. It is obvious that separate rupture of cyclic C–C bonds does not occur (this would lead to the formation of ethers), but simultaneous, or so-called "conjugate", fission of C–O and C–C bonds takes place, as a result of which a 2-alkylfuran molecule yields a molecule of an aliphatic alcohol or ketone and a molecule of an aliphatic hydrocarbon



When homologues of furan are hydrogenated over foraminate Ni–Al, all the ketones containing a carbon chain which is one C-atom shorter are alkan-3-ones, while ketones containing two C-atoms less than the original 2-alkylfuran molecule are alkan-2-ones. In general the formation of alcohols and ketones having such a structure is possible only as a result of hydrogenolysis of carbon–carbon bonds in the furan ring.

The influence of temperature on conjugate hydrogenolysis was also examined, and it was found that a rise in temperature increases the degree of hydrogenolysis of the furan ring, substantially changing the direction of the reaction. At temperatures not exceeding 120°–130°, smooth hydrogenation of the furan to a tetrahydrofuran nucleus is possible in the vapour phase over foraminate Ni–Al. With rise in temperature conjugate hydrogenolysis of the furan ring becomes increasingly predominant, alcohols and ketones being formed at the lower temperatures, but only ketones at the higher temperatures. It was also established that a change in temperature affects the direction of conjugate hydrogenolysis of the furan ring. At 175° the ring in 2-alkylfurans is hydrogenolysed mainly in two ways, at the 1,5 C–O bond (60–75%) and at the 1,5 and 4,5 bonds (20–40%). At 235° the conjugate hydrogenolysis of these compounds takes place in these two ways (33–37% and 14–16% respectively) and also in a third way, at the 1,5 and 3,4 bonds (41–45%).

A comparative examination of the hydrogenolysis of sylvan and of tetrahydrosylvan, as well as of 2-propylfuran and tetrahydro-2-propylfuran on a foraminate Ni–Al catalyst, leads to the conclusion that the fission of C–O and

C–C bonds takes place in an adsorption complex formed by the furan ring and the catalyst surface. As a result, the alkylfuran molecule is converted on the surface either into an alkyltetrahydrofuran or into open-chain compounds, which are then desorbed from the catalyst surface.

The foraminate Ni–Al is so far the only catalyst on which conjugate hydrogenolysis of the furan ring is known to occur. Neither foraminate Ni–Zn nor other nickel catalysts are able to effect conjugate hydrogenolysis.

Conjugate hydrogenolysis of the furan ring opens up new synthetic possibilities, since the products are ketones and alcohols containing the carbonyl or hydroxyl group in positions 2, 3, or 4. On other catalysts, on which hydrogenolysis occurs only at the C–O bond, compounds are in general obtained containing the functional group in position 4.

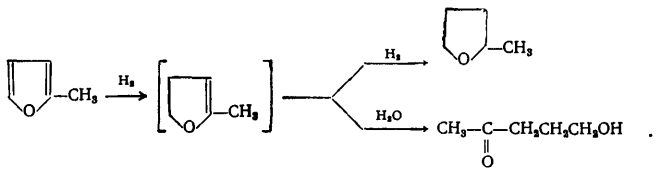
The foraminate Ni–Al catalyst has been investigated also for the hydrogenation of sylvan at a high pressure (50 atm) in a flow system. In this case, too, raising the hydrogen pressure has a very substantial effect in changing the direction of hydrogenation towards affecting mainly the cyclic multiple bonds. At 270° sylvan forms ~50% of tetrahydrosylvan, 45% of aliphatic ketones and alcohols (butan-2-ol, ethyl methyl ketone, and methyl propyl ketone), and 5% of pentane[34].

Mechanism of Hydrogenolysis of the Furan Ring

Since the hydrogenation of furan compounds yields on the one hand the corresponding tetrahydrofurans and on the other hydrogenolysis products of the furan ring, the question arises as to whether the tetrahydrofurans do not constitute an intermediate stage, from which the hydrogenolysis products are formed. The problem of the mechanism of hydrogenolysis includes the further question of whether hydrogenolysis of the C–O bond does not take place after only one C=C bond in the furan ring has been hydrogenated, *i.e.* in the dihydrofuran ring. The method used to prove the validity of one mechanism or the other consisted in a comparative study of the hydrogenation of corresponding furans, dihydrofurans, and tetrahydrofurans under identical conditions.

The behaviour of furan and tetrahydrofuran[37] and of furfuryl and tetrahydrofurfuryl alcohols[3] has been examined under the conditions of liquid-phase hydrogenation on a platinum catalyst, and that of sylvan and tetrahydrosylvan, as well as of the above alcohols[38], on copper chromite. These investigations proved that, under the conditions of liquid-phase hydrogenation, the tetrahydrofuran ring is completely devoid of that capacity for hydrogenolysis which is so highly characteristic of the furan ring. This difference in behaviour between furan and tetrahydrofuran rings under conditions of catalytic hydrogenation is exhibited also when the reaction is carried out in the vapour phase over nickel catalysts.

Shuikin and Bel'skii[39] showed that, on Pt–carbon at 250°–300°, the homologues of tetrahydrofuran isomerise into aliphatic ketones. However, this reaction occurs far more slowly than direct hydrogenolysis of the alkylfurans themselves under the same conditions, and therefore tetrahydrofurans cannot be regarded as intermediates in the hydrogenolysis of furan compounds. Thus all these investigations lead to the conclusion that hydrogenolysis of the C–O bond can take place either in the furan ring itself or in the dihydrofuran ring. Formation of the latter as an intermediate is proved by the conversion of sylvan into 5-hydroxypentan-2-one on hydrogenation over Pd in the presence of water[40]

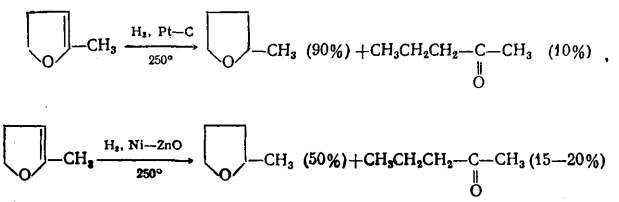


Another indirect proof of stepwise hydrogenation of the bonds in the furan ring is provided by the formation of spirans in the hydrogenation of 3-furylalkanols on nickel and copper–chromium catalysts.

On the basis of these experimental results several investigators[26] consider the formation of dihydrofurans to be an intermediate stage in hydrogenolysis of the furan ring. On the other hand, by measuring the rate of hydrogenation of furan on a platinum catalyst, Bradley[41] found that the addition of three moles of hydrogen does not take place in stages, since all the hydrogenation curves were smooth. This fact, in conjunction with what has been said above, can be interpreted on the basis that hydrogenation in the presence of water produces conditions which favour a different reaction path, and hence that the question of the mechanism of hydrogenolysis cannot be settled from a consideration of the results for hydrogenation of the furan ring in the presence of water.

A direct proof that dihydrofurans are not formed as intermediates in the hydrogenolysis of the furan ring was provided by an investigation of the hydrogenation of 4,5-dihydro-2-methylfuran in the gas phase over platinised carbon and nickel on zinc oxide at 250°–260°.[42] As has been shown above, under these conditions sylvan is completely split at the 1,5 C–O bond with the formation of methyl propyl ketone.

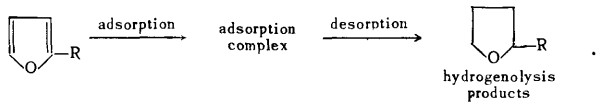
Dihydrosylvan, if it is formed as an intermediate in the hydrogenolysis of sylvan, should be converted into methyl propyl ketone just as easily and just as completely as sylvan, but experiments show[42] that the main reaction in the hydrogenation of dihydrosylvan on Pt–C and Ni–ZnO at 250°–260° is not hydrogenolysis of the C–O bond but hydrogenation of the cyclic C=C double bond:



These results confirm the conclusions of the multiplet theory, according to which hydrogenation of the first double bond in the furan ring occurs with considerably greater difficulty than that of an olefinic bond and approximately similarly to hydrogenolysis of a C–O bond in the furan ring. Hence it follows that rupture of C–O bond should be considerably more probable for furan itself.

On the basis of the above investigations it can be stated that the formation of dihydrofurans and tetrahydrofurans is not an intermediate stage in the hydrogenolysis of the furan ring, *i.e.* after a series of elementary acts in the process

of hydrogenation, either tetrahydrofurans or products of the hydrogenolysis of the furan ring are desorbed from the catalyst surface:



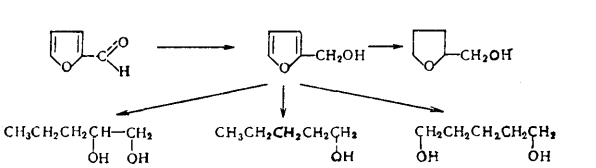
2. HYDROGENATION OF FURAN COMPOUNDS CONTAINING A CARBONYL GROUP IN THE SIDE CHAIN

The first work on the catalytic reduction of furfuraldehyde was published in 1906 by Padoa and Ponti [1], who passed its vapour mixed with hydrogen over a nickel catalyst at 190°. They found that the primary product of hydrogenation was furfuryl alcohol. However, further hydrogenation always took place, and sylvan, tetrahydrosylvan, pentan-2-one, and pentan-2-ol were isolated from the mixture of products. This shows that ring cleavage took place in the hydrogenation of furfuraldehyde. These workers also established that raising the temperature of hydrogenation to 270° results in the formation of furan and carbon monoxide.

Wienhaus [43] reduced furfuraldehyde in the presence of activated carbon impregnated with palladium chloride solution, at ordinary temperatures and a hydrogen pressure of 1 atm. The main product of hydrogenation was tetrahydrofurfuryl alcohol.

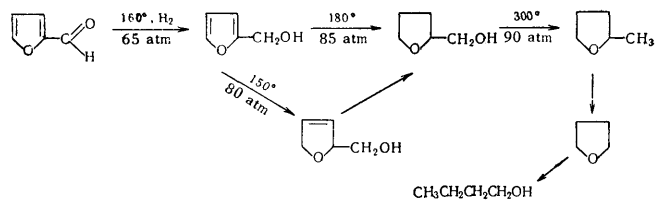
Pringsheim and Noth [44] passed a mixture of furfuraldehyde vapour and hydrogen over an iron catalyst at 200°, and observed the formation of the same products as in Padoa and Ponti's experiments together with furan and dihydrofuran. They point out that furfuraldehyde can undergo conversion in three ways: (1) the aldehyde group may be reduced to a methyl group; (2) the carbonyl may be eliminated to yield furan; and finally (3) the furan ring may be broken.

The above work was not systematic in character. A more extensive study of a wider range of problems was undertaken by Kaufmann and Adams [3], who investigated the reduction of furfuraldehyde and several of its derivatives in alcoholic solution in the presence of platinum oxide at ordinary temperatures and a hydrogen pressure of 1–2 atm. Absorption of an equivalent amount of hydrogen converts furfuraldehyde quantitatively into furfuryl alcohol. Further reduction led to the formation of a mixture of four products: tetrahydrofurfuryl alcohol (the main product), pentane-1,2-diol, pentane-1,5-diol, and n-pentyl alcohol. These workers concluded that the formation of glycols and pentan-1-ol cannot involve tetrahydrofurfuryl alcohol as an intermediate stage, since under these conditions the latter does not undergo hydrogenolysis to any appreciable extent. They represent the scheme of successive reactions in the hydrogenation of furfuraldehyde as follows:



They postulate that the C–O bond can undergo fission directly in the furan ring, with the intermediate formation of unsaturated glycols and subsequent hydrogenation of the latter to alkanediols.

A great amount of research has been devoted to finding conditions for the hydrogenation of furfuraldehyde to sylvan and to furfuryl and tetrahydrofurfuryl alcohols. We shall deal only with a few of the chief papers. Komatsu and Masumoto [45] showed that, depending on the temperature, the hydrogenation of furfuraldehyde on reduced nickel may yield various products, as can be seen from the following scheme

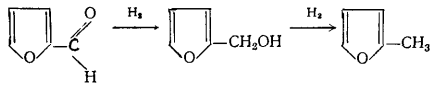


Schoeller and Jordan [46] discovered the conditions under which furfuraldehyde can either be smoothly converted into tetrahydrofurfuryl alcohol or give glycols as a result of fission of the ring. If the aldehyde is hydrogenated in the presence of reduced nickel on a carrier at 100°–150° and 40 atm hydrogen pressure, a catalysate is obtained containing 95% of tetrahydrofurfuryl alcohol and 5% of glycols. If, however, the hydrogenation is carried out at 200°–220°, the reaction products comprise only a mixture of pentane-1,2- and -1,5-diols with a small admixture of n-pentanol.

In 1931 Adkins and Connor [6] used copper chromite as catalyst for the hydrogenation of various classes of organic compounds. In their first research they investigated the liquid-phase hydrogenation of furfuraldehyde, among many other organic compounds. At 150° and a hydrogen pressure of 100–150 atm over copper chromite a quantitative yield of furfuryl alcohol was obtained. However, in the vapour-phase hydrogenation of furfuraldehyde over copper chromite, the main product will be sylvan. Schniepp *et al.* [47] obtained sylvan by hydrogenating furfuraldehyde in the vapour phase at 250° over copper chromite deposited on activated carbon. Besides sylvan (yield 92%) the products included furfuryl alcohol and unchanged aldehyde. Natta *et al.* [48] investigated the hydrogenation of furfuraldehyde and other furan derivatives on various catalysts. The aldehyde was hydrogenated in the presence of nickel, copper, cobalt, iron, silver, and mixtures thereof at various temperatures. Nickel catalysts proved to be more active for the hydrogenation of the aldehyde group and of the ring, which resulted in the formation of furfuryl and tetrahydrofurfuryl alcohols. Catalysts containing nickel and cobalt, and also nickel and iron, favoured complete reduction of the side group, and were thus most effective in the conversion of furfuraldehyde into sylvan and tetrahydrosylvan.

Copper and especially copper chromite were most active in opening the furan ring, so that glycols were obtained. When furfuryl alcohol was hydrogenated in the presence of these catalysts, pentane-1,2- and -1,4-diols were obtained; however, hydrogenation of tetrahydrofurfuryl alcohol under the same conditions gave only pentane-1,5-diol, whereas furfuraldehyde gave a mixture of all three isomers. Vigorous hydrogenation of furfuraldehyde, furfuryl and tetrahydrofurfuryl alcohols, and also tetrahydrosylvan on a copper catalyst yields pentan-1-ol, and on other catalysts pentan-2-ol.

The most detailed investigation of the conditions for the hydrogenation of furfuraldehyde to sylvan and furfuryl alcohol was made by Bremner and Keeys[49]. They established that the course of the reaction is affected by the nature of the catalyst, the temperature, and the flow velocity of the substance. Vapour-phase hydrogenation at normal pressure over copper catalysts forms mainly furfuryl alcohol and sylvan, together with a small quantity of furan and traces of n-pentanol. Hydrogenation of furfuraldehyde on a foraminate Cu–Al catalyst yields furfuryl alcohol at temperatures below 200° and sylvan at 250°. At 300° and above, however, the main product of hydrogenation becomes furfuryl alcohol, although the catalyst then loses its activity rapidly. Copper chromite possesses similar properties to a Cu–Al catalyst, but gives sylvan both at 250° and at 300°. These workers studied the effect of alkali on the selectivity of the catalysts, and found that addition of increasing quantities of alkali to the catalyst results in the formation predominantly of furfuryl alcohol. Thus a Cu–Al catalyst, after treatment of the alloy with alkali and incomplete washing with water, gave 2% of furfuryl alcohol and 88% of sylvan at 253°, whereas a Cu–Al catalyst which had been treated with 5% sodium carbonate solution with heating yielded 70% of the alcohol and 12% of sylvan. Bremner and Keeys concluded that the alcohol is an intermediate in the formation of sylvan from furfuraldehyde:



Actually, it was shown that the formation of the alcohol is favoured by carrying out the reaction with insufficient hydrogen and by a high rate of supply of the substance.

Bremner *et al.*[50] obtained sylvan from furfuraldehyde in the vapour phase at atmospheric pressure in the presence of a copper catalyst, which had been prepared from alloys of copper with metals which dissolve in acids or alkalis more readily than does copper. Satisfactory catalysts were obtained from alloys of copper with aluminium and with silicon. These workers point out that it is important to keep the temperature of the catalyst below some maximum value during the hydrogenation. On a copper–aluminium catalyst at 190°–250° furfuraldehyde was converted into sylvan with an 85% yield.

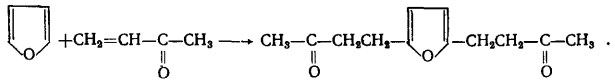
Starkey and Bremner[51] described the continuous hydrogenation of furfuraldehyde, over cobalt–aluminium and copper–aluminium catalysts, to furfuryl and tetrahydrofurfuryl alcohols, pentane-1,2- and -1,5-diols, and pentanols. Passage of the aldehyde over a Co–Al catalyst at 15° and 250 atm gave a mixture containing 40% of furfuryl alcohol and 60% of unchanged furfuraldehyde. Over a Cu–Al catalyst under the same conditions, but at 80°, the aldehyde was completely converted into furfuryl alcohol, whereas at 120° the ring was opened, the reaction products including 30% of a mixture of pentane-1,2- and -1,5-diols, and at 150° ~30% of pentanols. On a Co–Al catalyst at 50° and 250 atm furfuraldehyde was hydrogenated to tetrahydrofurfuryl alcohol, and under the above conditions a mixture of 50% of the aldehyde and 50% of tetrahydrofurfuryl alcohol was obtained.

Mizuguchi and Iwase[52] examined the relative activities of reduced copper, Raney copper, copper chromite, and reduced nickel in the hydrogenation of furfuraldehye to furfuryl alcohol. In the presence of the copper catalysts the aldehyde was quantitatively reduced to the alcohol at 140° and 100 atm; the greatest activity was shown by copper chromite, and this was attributed to the presence of chromic oxide in the catalyst. The nickel catalyst was comparatively inactive, after prolonged reaction it gave only 56% of furfuryl alcohol together with other products. Stewart[53] described the preparation of a Cu_2O catalyst which was active towards the hydrogenation of organic compounds. It could be activated by the oxides of aluminium, calcium, chromium, or vanadium. With a catalyst containing Cu_2O, CaO, and Al_2O_3 furfuraldehyde was almost quantitatively hydrogenated to furfuryl alcohol at 155°.

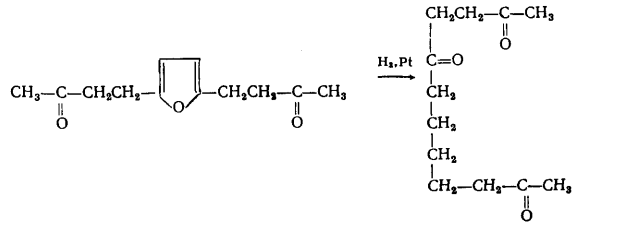
Howk[54] proposed a ruthenium catalyst for the hydrogenation of furfuraldehyde to tetrahydrofurfuryl alcohol. A 78% yield of the latter was obtained at 110° and 150 atm in the presence of RuO_2.MgO. We can confine ourselves to these papers, since they give the principal experimental results establishing the conditions for the selective hydrogenation of furfuraldehyde to furfuryl and tetrahydrofurfuryl alcohols and sylvan. Selective hydrogenation of the oxo- to a hydroxyl group without affecting the furan ring is best accomplished by hydrogenating furfuraldehyde in the liquid or the vapour phase over copper catalysts (copper chromite, foraminate copper, activated cuprous oxide) at both normal and elevated hydrogen pressures. Under the same conditions, but at higher temperatures, copper catalysts are highly effective in opening the furan ring, as a result of which furfuryl alcohol is converted into pentane-1,2- and -1,5-diols. The primary reduction product of furfuraldehyde on nickel and platinum catalysts is also furfuryl alcohol, which is obtained in quantitative yield after an equivalent amount of hydrogen has been absorbed. The complete hydrogenation of furfuraldehyde in the liquid phase over nickel, platinum, and ruthenium catalysts gives high yields of tetrahydrofurfuryl alcohol. Conversion of the aldehyde into sylvan necessitates carrying out the hydrogenation in the vapour phase, the best results being obtained on copper catalysts (copper chromite, foraminate copper).

The next most simple furan system containing a carbonyl group is formed by the furan ketones. Those containing the carbonyl group in positions 1 or 3 relative to the furan nucleus are available in practice.

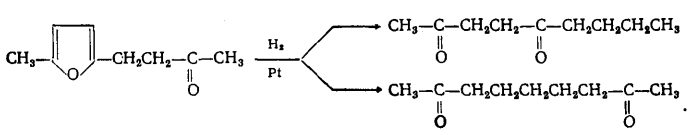
Continuing the investigations of Scherlin *et al.*, Alder and Schmidt[55] showed that the interaction of furan and sylvan with unsaturated aldehydes and ketones does not follow the pattern of diene synthesis but that of substitutive addition. Thus furan and methyl vinyl ketone yielded 2,5-bis-3′-oxobutylfuran:



In a similar manner, with methyl vinyl ketone and with phenyl vinyl ketone, sylvan gave 4-5′-methylfur-2′-ylbutan-2-one and 2-5′-methylfur-2′-ylethyl phenyl ketone respectively. These ketones were hydrogenated in ethyl acetate solution at ordinary temperatures in the presence of PtO_2. Hydrogenation of 2,5-bis-3′-oxobutylfuran yielded dodecane-2,5,11-trione:



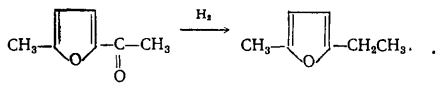
The hydrogenation products of the methylfurylbutanone were two acyclic diketones, nonane-2,5- and -2,8-diones:



These results show that, when ketones of the furan series are hydrogenated in the liquid phase over PtO_2, the primary reaction is hydrogenolysis of the ring with formation of aliphatic diketones and triketones, the carbonyl group remaining unreduced. In contrast to the above ketones, the methylfurfurylacetophenone does not undergo hydrogenolysis under analogous conditions, probably owing to the stabilising influence of the phenyl group on the furan ring.

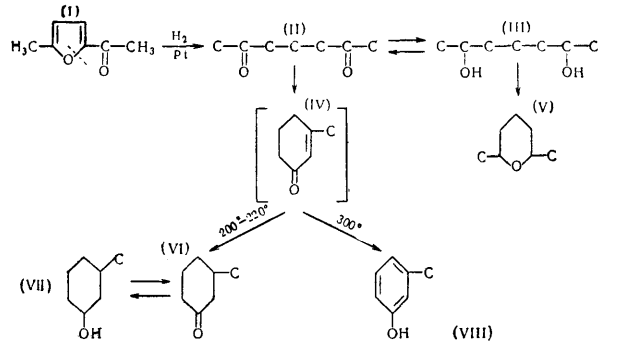
Interesting results were obtained in the vapour-phase hydrogenation of furan ketones containing the carbonyl group adjacent to the furan ring, *i.e.* 2-acyl-5-alkylfurans. Depending on the nature of the catalyst, the primary reaction was found to be either reduction of the carbonyl to a methylene group with preservation or subsequent hydrogenolysis of the furan ring[56] or else hydrogenolysis of the furan ring at the ether bond adjacent to the carbonyl group with formation of δ-diketones and the corresponding diols[57]. A more detailed investigation was made of the hydrogenation of methyl 5-methylfur-2-yl ketone on various catalysts: Pt–C, Pd–C, Ni–ZnO, Ni–CdO, and foraminate Cu–Al.

1. On Ni–ZnO, Ni–CdO, and foraminate Cu–Al catalysts the methyl methylfuryl ketone is reduced, in the vapour phase at 250°, to 2-ethyl-5-methylfuran in yields of ~60% on nickel catalysts and 90–95% on the foraminate Cu–Al catalyst:

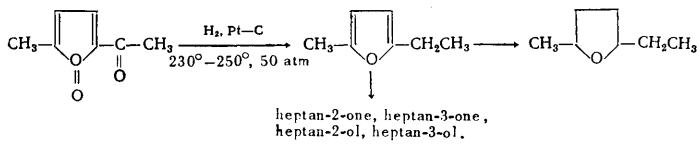


A side reaction is hydrogenolysis of the ring to form heptan-2-one, which is especially noticeable on Ni–ZnO.

2. Extremely interesting changes occur in the hydrogenation of the methyl methylfuryl ketone (I) on a platinum catalyst: among the principal products are heptane-2,6-dione, 3-methylcyclohexanone, 3-methylcyclohexanol, *m*-cresol, and tetrahydro-2,6-dimethylpyran. The formation of carbocyclic and heterocyclic compounds in the hydrogenation of the acetylsylvan is possible only if fundamental structural changes take place in the molecule of this heterocyclic ketone, and is undoubtedly the result of a series of consecutive reactions. A probable mechanism for these changes may be that hydrogenolysis of the furan ring at the 1,5 C–O bond gives heptane-2,6-dione (II), which undergoes either hydrogenation to heptane-2,6-diol (III) or cyclisation to 3-methylcyclohex-2-enone (IV), as in the treatment of δ-diketones with acids or alkalis. The heptane-2,6-diol then cyclises into tetrahydro-2,6-dimethylpyran (V), while the methylcyclohexenone is converted into either 3-methylcyclohexanone (VI) or *m*-cresol (VIII):



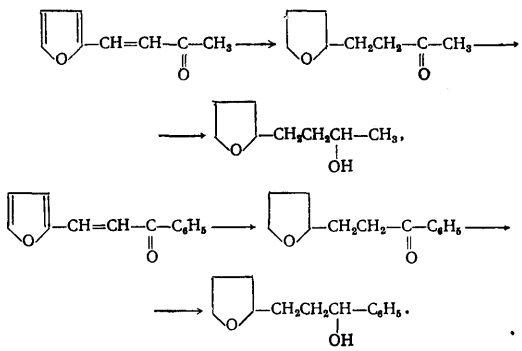
The transformation of 2-acyl-5-alkylfurans into δ-diketones, 2,6-dialkyltetrahydropyrans, alkylcyclohexanones, and alkylphenols is a general phenomenon, since it has been established that various homologues of 2-acylfurans can be transformed according to the above scheme. Variation of the reaction conditions, especially temperature, enables the course of the reaction to be controlled. δ-Diketones as the primary products of hydrogenation can be isolated in greatest quantity (~35%) from the catalysates obtained in the hydrogenation of 2-acyl-5-alkylfurans on platinised asbestos at 200°.[58] The yield of 2,6-dialkyltetrahydropyrans is especially dependent on temperature, since the hydrogenation of diketones to diols is favoured by a low temperature. On platinised carbon at 200°–220° the 2,6-dialkyltetrahydropyrans are formed in yields of 20–40%.[59] At 270°–300° the catalysate from 2-acetyl-5-methylfuran (methyl 5-methylfur-2-yl ketone) contains 50% of *m*-cresol, while 3-methylcyclohexanone is absent, but at 215°–220° some 25% of the latter compound is formed mixed with 3-methylcyclohexanol, and *m*-cresol is practically absent. Roughly similar relations are observed in the hydrogenation of other 2-acyl-5-alkylfurans[60]. The conversion of these compounds into δ-diketones, tetrahydropyrans, cyclohexanones, and phenols may prove a convenient method for the catalytic synthesis of compounds of these classes, in view of the fact that not only 2-acyl-5-alkylfurans, obtained from furfuraldehyde, but also 2-acyl-3,5-dialkylfurans, which are synthesised from alkenes and aliphatic acid chlorides *via* pyrylium salts[61], are readily available. The hydrogenation of methyl 5-methylfur-2-yl ketone on platinised carbon was further investigated at high pressures of hydrogen under flow conditions. As in the other cases considered earlier, the pressure of hydrogen has a substantial effect on the character of the hydrogenation of the 2-acetyl-5-methylfuran. The only primary reaction at 230°–250° and 50 atm of hydrogen is reduction of the carbonyl group, resulting in the formation of 2-ethyl-5-methylfuran, which is further hydrogenated to 2-ethyltetrahydro-5-methylfuran (55%) and undergoes hydrogenolysis with the formation of heptan-2- and -3-ones and the corresponding alcohols[34]:



3. HYDROGENATION OF FURAN COMPOUNDS CONTAINING AN OLEFINIC BOND AND A CARBONYL GROUP IN THE SIDE CHAIN

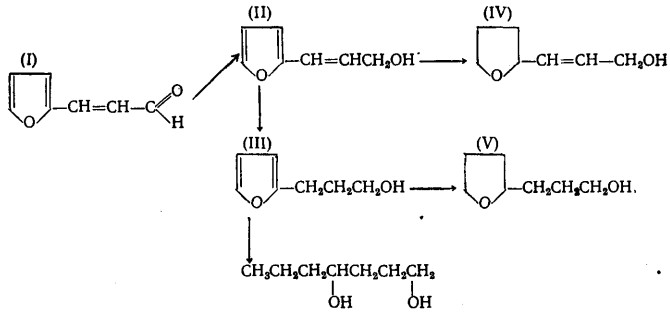
Ketones and aldehydes of the furan series, obtained by the condensation of furfuraldehyde with ketones and aldehydes, constitute the most convenient compounds for studying the possibilities of selective hydrogenation, since they contain three types of unsaturated bonds: olefinic and carbonyl in the side chain, and double bonds in the furan ring. Ketones and aldehydes of this structure have been subjected to hydrogenation in the liquid phase in the presence of various catalysts: Pt, Pd, Ni, Cu, etc.

Kaufmann and Adams[3] investigated the hydrogenation of furfurylideneacetone and furfurylideneacetophenone on a platinum catalyst at room temperature and a hydrogen pressure of 1–2 atm. These compounds were converted first into the corresponding tetrahydrofuran ketones, and then into the corresponding alcohols:



These workers studied several properties of the platinum catalyst. They showed that pure platinum oxide is not an effective hydrogenation catalyst. However, the addition of small quantities of ferric chloride exerts a promoter action, and the platinum oxide acquires excellent hydrogenating properties. With increasing content of ferric chloride in the catalyst, the rate of reduction increases to a maximum and then decreases. In the latter stage the increased content of ferric chloride in the catalyst has a greater effect in suppressing the ability to hydrogenate the ring than to reduce the aldehyde group.

Bray and Adams[62] examined the possibility of the selective hydrogenation of furylacraldehyde at ordinary temperatures and 2–3 atm pressure over a platinum catalyst. Addition to the platinum of iron salts and zinc acetate not only increased its activity but also favoured selective hydrogenation of the furylacraldehyde. By interrupting hydrogenation after the absorption of a definite quantity of hydrogen these workers obtained products of different degrees of saturation. They established that the hydrogenation of furylacraldehyde involves the following reactions: first of all the aldehyde group is reduced, and the furylacraldehyde (I) is converted into furylallyl alcohol (II), the latter undergoing change in two ways: the side-chain olefinic bond is hydrogenated to form furylpropyl alcohol (III) and the double bonds in the furan ring are hydrogenated, tetrahydrofurylallyl alcohol (IV) then being formed, but in considerably smaller amount than furylpropyl alcohol; this shows that the side-chain olefinic bond is more reducible than the cyclic double bonds. Furylpropyl alcohol on further reduction is converted mainly into tetrahydrofurylpropyl alcohol (V), and to a slight extent undergoes hydrogenolysis to heptane-1,4-diol (VI)



Thus the reactions involved in hydrogenation of the various bonds in furylacraldehyde on a platinum catalyst promoted with iron and zinc salts can be arranged in the following sequence according to their ease of occurrence: (1) hydrogenation of the C=O bond in the side chain; (2) hydrogenation of the C=C bond in the side chain; (3) hydrogenation of the C=C bonds in the furan ring; (4) rupture of a C–O bond in the furan ring.

We are now able to draw some general conclusions on the basis of the experimental results obtained for the hydrogenation of furan ketones and aldehydes on platinum catalysts.

Kaufmann and Adams showed that, in the hydrogenation of furfuraldehyde in the presence of a platinum catalyst promoted with ferric chloride, furfuryl alcohol is formed at first, and this on further hydrogenation gives a mixture of tetrahydrofurfuryl alcohol and pentane-1,2- and -1,5-diols. Since a quantitative yield of furfuryl alcohol is obtained after the absorption of one mole of hydrogen, it is obvious that the hydrogenation of furfuraldehyde first involves reduction of the carbonyl group, and then hydrogenation of the double bonds and hydrogenolysis of the cyclic C–O bonds. In the hydrogenation of furfurylideneacetone and furfurylideneacetophenone on the same catalyst, however, these workers obtained tetrahydrofuran ketones, *i.e.* compounds containing a tetrahydrofuran ring and an unchanged carbonyl group. The sequence of reactions was obviously different in this case from that observed in the hydrogenation of furfuraldehyde, since tetrahydrofuran ketones can be formed as a result of hydrogenation of the furan ring before reduction of the carbonyl group. On the other hand, Alder and Schmidt showed that, in the hydrogenation of furan ketones, for example, 5-methylfurfurylacetone, on an Adams catalyst, hydrogenolysis of the furan ring takes place before reduction of the carbonyl group. These facts show that the relative ease of hydrogenation of the carbonyl group and of the furan ring depends on the chemical structure of the compounds undergoing hydrogenation.

The role of the catalyst as the main factor governing the selectivity of hydrogenation is seen especially clearly from a comparison of the results for the hydrogenation of furfurylideneacetone and of furylacraldehyde, since these two compounds contain the same system of an olefinic and a carbonyl bond in the side chain.

Under conditions of vapour-phase hydrogenation, platinum catalysts effect hydrogenolysis of the furan ring also before reduction of the carbonyl group. For example, as

already mentioned above, 2-acetyl-5-methylfuran on vapour-phase hydrogenation over platinised carbon or asbestos gives first of all heptane-2,6-dione by hydrogenolysis of the furan ring. Since, however, the carbonyl group in the acetyl derivative is adjacent to the furan ring, another primary reaction, reduction of the C=O to a CH_2 group, takes place at the same time. A condition for the selective reduction of a carbonyl group adjacent to a furan ring is vapour-phase hydrogenation over copper catalysts (foraminate copper, copper chromite). Under these conditions furfuraldehyde is smoothly converted into sylvan[47], and 2-acetyl-5-methylfuran into 2-ethyl-5-methylfuran[56]. Selective hydrogenation of the olefinic bond in unsaturated furan ketones and aldehydes is possible on various catalysts. Thus Alder and Schmidt found that, in the 5-methylfurfurylideneacetophenone molecule in the presence of Pd at 25°, only the olefinic bond is hydrogenated, while the carbonyl group and the furan ring remain unaffected[55]. A similar effect is shown by a foraminate Cu–Al catalyst, on which various furfurylidene ketones are hydrogenated at 30°–40° to the corresponding saturated ketones with yields of 70–85%.[63] At higher temperatures (120°–140°) furylacraldehydes and furfurylidene ketones are hydrogenated on foraminate Cu–Al to the corresponding furan alcohols in yields of 75–85% and 90–95% respectively[56].

Much research has been done† on the hydrogenation of unsaturated ketone and aldehyde derivatives of furan on nickel catalysts. We shall deal only with the most important work.

Burdick and Adkins[64] made a detailed investigation of the hydrogenation of furylacraldehyde and several products of its partial reduction, on copper–chromium and nickel catalysts (nickel on kieselguhr and Raney nickel), in the liquid phase at hydrogen pressures of 100–200 atm.

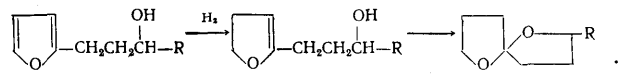
Raney nickel proved to be an active catalyst at moderate temperatures for the hydrogenation of a side-chain olefinic bond. In the presence of this catalyst at 23° furylacraldehyde was converted into furylpropionaldehyde in 46% yield. Raising the temperature of hydrogenation ot 160° resulted in the formation of tetrahydrofurylpropyl alcohol in 65% yield. Hence at elevated temperatures Raney nickel is an effective catalyst for hydrogenation of the C=C bonds in the furan ring. A copper–chromium catalyst is relatively inactive towards the hydrogenation of the furan ring, but proves extremely effective for opening the cyclic ether bond. At moderate temperatures a copper–chromium catalyst is active in hydrogenating side-chain olefinic and carbonyl bonds without affecting the ring. In the presence of copper chromite at 120°–175° furylacraldehyde gave a 72% yield of furylpropyl alcohol. Thus at this temperature the olefinic bond and the aldehyde group were hydrogenated, but the ring remained untouched. At 200° the ring was split at the C–O bonds with the formation of heptane-1,4-diol (yield 29%) and heptane-1,7-diol (20%).

Raney nickel was extremely active also in the fission of C–C bonds in primary alcohols. Tetrahydrofurylpropyl alcohol on this catalyst at 250° suffered cleavage of a side-chain C–C bond, with the formation of 2-ethyltetrahydrofuran (yield 60%) and tetrahydro-2-propylfuran (yield 1%). Under the same conditions heptane-1,4-diol was converted into hexan-3-ol (yield 66%), and heptane-1,7-diol into n-pentane (yield 21%).

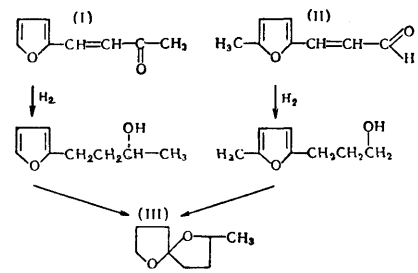
† See monograph by A.P.Dunlop and F.N.Peters, "The Furans", New York, 1953.

Nickel on kieselguhr, like Raney nickel, was a good catalyst for hydrogenation of the furan ring. It was also the most effective in converting furylacraldehyde into 2,2′-spirobitetrahydrofuran, a 33% yield of which was obtained at 160°.

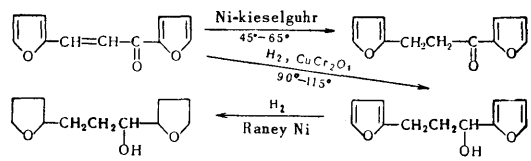
Burdick and Adkins considered that only 3-furylpropionaldehyde can be converted into a spiran, whereas 3-furylpropan-1-ol merely gives traces of this compound. However, this was not confirmed subsequently. Alexander *et al.*[65] established that 2,2′-spirobitetrahydrofuran and its 5-methyl derivative are formed by the hydrogenation of 3-furylpropan-1-ol and 3-furylbutan-1-ol respectively in the presence of nickel on kieselguhr at 70°–125°. Spiro-compounds were obtained also by the hydrogenation of furfurylideneacetone and difurfurylideneacetone [1-fur-2′-ylbut-1-en-3-one and 1,5-difur-2′-ylpenta-1,4-dien-3-one (Ed. of Translation)] on a copper–chromium catalyst[66]. From these facts Alexander *et al.* concluded that the formation of spirans is a general reaction in the hydrogenation of γ-furylalkanols on copper chromite or nickel deposited on kieselguhr. They suggested the following mechanism of spiran formation:



The structure of the spirans obtained by the hydrogenation of γ-furylalkanols was demonstrated by the work of Farlow *et al.*[67] and also of Ponomarev *et al.*[68] The latter showed that the hydrogenation of furfurylideneacetone (I) and of 5′-methylfurylacraldehyde (II) yields the same 5-methyl-2,2′-spirobitetrahydrofuran (III), as can be seen from the following scheme:



Alexander and Smith[69] investigated the hydrogenation of 1,3-difur-2′-ylprop-2-enone in the presence of Raney nickel, nickel on kieselguhr, and copper chromite. Their results support the conclusions reached earlier by Burdick and Adkins[64] from the hydrogenation of furylacraldehyde:



At moderate temperatures (20°–60°) only the side-chain olefinic bond is hydrogenated on Raney nickel and nickel deposited on kieselguhr; at temperatures above 100° (130°–160°) these catalysts effect complete reduction of the C=C and C=O bonds in the side chain and hydrogenation of the double bonds in the ring. A copper–chromium catalyst, in contrast to Raney nickel and nickel on kieselguhr, does not exhibit any appreciable activity towards hydrogenation of the cyclic double bonds.

A large number of derivatives containing one or two furan rings in the molecule together with olefinic and carbonyl bonds in the side chain have been obtained by condensing furfuraldehyde, furylacraldehyde, and acetylfuran with various aldehydes, ketones, and esters. Hydrogenation of these compounds on Raney nickel at 170°–180° and 125–250 atm gives up to 90% yields of tetrahydrofuran derivatives (esters or alcohols)[70], but in the presence of copper chromite at 110°–135° only hydrogenation of the side-chain olefinic bond and carbonyl group takes place, with formation of the corresponding furan alcohols[71]. Hydrogenation on nickel deposited on kieselguhr converts these into tetrahydrofuran alcohols (yields up to 75%) and spirans, which are homologues of 2,2′-spirobitetrahydrofuran[71].

Balandin and Ponomarev[72] employed the multiplet theory to determine the sequence of reactions in the hydrogenation of furan compounds on a nickel catalyst. They calculated the energies of formation E' of the intermediate multiplet complexes from the starting materials and the catalyst, using a doublet reaction scheme:

1.	Hydrogenation of olefinic bond	-2.9
2.	Hydrogenation of carbonyl bond	-10.1
3.	Hydrogenation of first double bond in furan ring	-10.9
4.	Hydrogenolysis of ether bond in furan ring	-11.8
5.	Formation of spiran from furan alcohol	-15.8
6.	Hydrogenolysis of carbon–oxygen bond	-16.8
7.	Hydrogenolysis of carbon–carbon bond	-48.4

Since the activation energy $E = -\frac{3}{4}E'$, the above reaction sequence obviously indicates the relative ease of occurrence of the reactions on a nickel catalyst. Those reactions for which E' has the highest numerical value will occur more readily, *i.e.* at a lower temperature; hence in the hydrogenation of furan compounds on a nickel catalyst, the reactions should take place in the order of decreasing values of E'. However, owing to the closeness of the values of E' for reactions 2–4, some of them can be expected to occur simultaneously or even in the reverse order. In fact, experiment shows[73,74] that in some cases hydrogenation of C=C bonds in the furan ring can precede, on a nickel catalyst, reduction of the side-chain carbonyl group. On the other hand, hydrogenolysis of C–O bonds in the furan ring takes place earlier, on a nickel catalyst, than hydrogenation of the cyclic double bonds. No catalyst has yet been found which would hydrogenate the furan ring before the aldehyde group is reduced, and would, for example, convert furfuraldehyde into tetrahydrofurfuraldehyde. In the case of ketones, however, hydrogenation of the ring double bonds can take place before reduction of the carbonyl group on some nickel catalysts, resulting in the formation of ketones of the tetrahydrofuran series. Thus the statement[72] that substituents have no decisive effect in the hydrogenation of furan compounds cannot be accepted unreservedly. It was shown[72] that, in the hydrogenation of furan compounds, the sequence of reactions depends on the nature of the catalyst. Thus theory explains why, over copper, hydrogenolysis of a C–O bond in the furan ring takes place more readily than hydrogenation of the cyclic C=C bonds. In general, the agreement between theoretical calculations based on the multiplet theory and experiment can be regarded as quite satisfactory (especially for the conditions of liquid-phase hydrogenation), if it is borne in mind that the conclusions of the theory relate to a nickel catalyst of average properties.

4. HYDROGENATION OF FURAN COMPOUNDS CONTAINING A HYDROXYL OR AN AMINO-GROUP IN THE SIDE CHAIN

As was shown above, the simplest representative of the furan alcohols, furfuryl alcohol, is readily obtained by hydrogenating furfuraldehyde on various catalysts. The synthesis of other furan alcohols containing the hydroxyl group adjacent to the furan ring is accomplished by hydrogenating 2-acylfurans or by the Grignard reaction from furfuraldehyde and alkyl halides. Another readily available group of furan alcohols are those containing the hydroxyl group in position 3 with respect to the furan nucleus. Furan alcohols of this type are obtained by hydrogenating furylacraldehydes and furfurylidene ketones in the liquid phase on copper catalysts (see above).

In the case of the furan alcohols the problem of hydrogenation reduces in the first instance to finding conditions under which they would be converted into tetrahydrofuran alcohols. Those catalysts which are used for the hydrogenation of homologues of furan prove suitable for this purpose. Douris[75] hydrogenated 1-furylpropanol on a nickel catalyst at 175°, and obtained the tetrahydrofuryl derivative as the main product.

Pierce and Adams[76] reduced 1-furylpropanol and 1-furylpentanol in the presence of platinum black (prepared from PtO_2) at ordinary temperature and a hydrogen pressure of 1–2 atm. The hydrogenation products of the former compound were heptan-3-ol, 1-tetrahydrofurylpropanol, and heptane-3,4-diol; from the products of the hydrogenation of the furylpentanol they isolated nonan-5-ol, 1-tetrahydrofurylpentanol, and nonane-4,5- and -1,5-diols. Thus the 1-furylalkanols investigated by Pierce and Adams gave open-chain products on hydrogenation as well as their tetrahydro-derivatives.

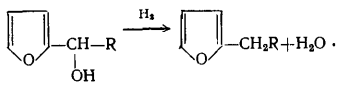
Paul[77] investigated the hydrogenation of furfuryl alcohol, 1-furylethanol, 1-furylpropanol, 1-furylbutanol, and α-furylbenzene alcohol, and found that, depending on the nature of the catalyst and the temperature, hydrogenation of these compounds yielded 1-tetrahydrofurylalkanols, 1,5- and 4,5-diols, and also other products (furans, carbinols, hydrocarbons). He examined platinum catalysts, colloidal palladium, copper chromite, reduced nickel, nickel on kieselguhr, and Raney nickel. The best catalyst for hydrogenation of the ring was Raney nickel, which is already active at moderate temperatures (50°–80°). Yields of 90–100% of tetrahydrofuran derivatives were obtained on it.

In 1932 Connor and Adkins[38] published results obtained by hydrogenating furfuryl and tetrahydrofurfuryl alcohols on copper–chromium and nickel catalysts. On copper chromite at 200°–250° the former alcohol is hydrogenated to a slight extent to the latter, but the main reaction under these conditions is hydrogenolysis of the ring at the C–O bonds, yield pentane-1,2-diol (14%) and pentane-1,5-diol (15%), as well as sylvan (20%) and pentan-1-ol (10%). On a nickel catalyst, in contrast, furfuryl alcohol was hydrogenated to tetrahydrofurfuryl alcohol in high yields. They established that, in contrast to furfuryl alcohol, tetrahydrofurfuryl alcohol is considerably more resistant to hydrogenolysis of the ring. On copper chromite the latter alcohol gave, after hydrogenation for 11 h, tetrahydrosylvan and water (5%) as well as pentane-1,5-diol, about 77% of the alcohol remaining unchanged. Undergoing hydrogenolysis to a slight extent, tetrahydrofurfuryl alcohol gave pentane-1,5-diol almost exclusively, whereas furfuryl alcohol

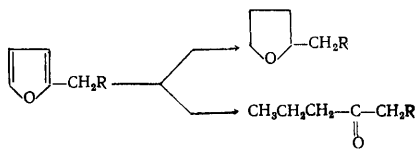
under the same conditions was converted into a mixture of almost equal quantities of pentane-1,2-diol and pentane-1,5--diol. Hence it follows that the furan ring undergoes hydrogenolysis considerably more readily than, and in a different way from, the tetrahydrofuran ring.

Let us draw some conclusions. Nickel catalysts, and especially Raney nickel, have proved extremely effective for the hydrogenation of furan alcohols to tetrahydrofuran alcohols. On a platinum catalyst promoted with iron salts, the hydrogenation of furfuryl alcohol[3] and of 1-furylalkan--1-ols[21] also results mainly in formation of the corresponding tetrahydro-derivatives. However, even at low temperatures this catalyst tends to cause hydrogenolysis of the furan ring at one or both ether bonds, with the production of alkanediols and alkanols. This last reaction takes place especially readily on copper catalysts, in particular on copper chromite. Extremely interesting peculiarities are exhibited in the hydrogenation of furan alcohols in the vapour phase. Under these conditions alcohols containing the hydroxyl group in positions 1 or 3 with respect to the furan nucleus undergo completely different changes.

1. 1-Furylalkan-1-ols on vapour-phase hydrogenation at 200°–250° over Pd–C, Ni–ZnO, and foraminate Pd–Al, Cu–Al, and Ni–Zn catalysts are reduced to 2-alkylfurans in yields of 60–95%:[56,78-80]



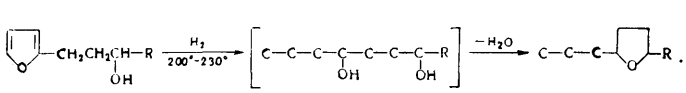
Small quantities of the corresponding 2-alkyltetrahydrofurans and aliphatic ketones are also formed. These compounds, the yields of which are increased by passing the furylalkanols more slowly through the catalyst, are obtained as secondary products of hydrogenolysis and hydrogenation of the alkylfurans which are formed:



The ready fission of the bond between the carbon atom and the hydroxyl group in 1-furylalkan-1-ols under the action of hydrogen in the presence of a catalyst is a specific property of this type of compound, depending on the presence of a furan ring adjacent to a hydroxyl group. The corresponding tetrahydrofurylalkanols are not reduced at all under the same conditions. 1-Tetrahydrofurylethanol remained unchanged[78] over palladised carbon under conditions under which the hydroxyl group in 1-furylethanol was reduced.

Thus the aromatic system formed by the furan ring has the same effect on the stability of the bond between a carbon atom and a hydroxyl group adjacent to the ring as has the benzene nucleus[81].

2. Furan alcohols containing the hydroxyl group in position 3 relative to the furan nucleus are converted into homologues of tetrahydrofuran on vapour-phase hydrogenation over a platinum catalyst at 200°–230°:[82,83]



The reaction consists of two consecutive stages: hydrogenolysis of the furan ring to form alkane-1,4-diols, and intramolecular cyclisation of the latter, with elimination of water, to yield homologues of tetrahydrofuran. The formation of alkane-1,4-diols as intermediate compounds is favoured by a low temperature. The highest yields of tetrahydrofurans are obtained at 200°–230°. The catalyst must be active in effecting hydrogenolysis of the furan ring at moderate temperatures. Therefore catalysts other than platinum can be used, for example, foraminate Cu–Al and Ni–Zn. The structure of the tetrahydrofuran homologues which are formed is ultimately determined by that of the aliphatic oxo-compounds with which furfuraldehyde condenses. With aliphatic aldehydes furfuraldehyde yields successively 2-alkyl-3-furylacraldehydes, 2-alkyl-3-furylpropanols, and finally 3-alkyltetrahydro-5-propylfurans. 2-Alkyltetrahydro-5-propylfurans are obtained by the hydrogenation of 3-furylalkanols, which are reduction products of furfurylidene ketones. The catalytic method of synthesising tetrahydrofuran homologues also enables trialkyltetrahydrofurans to be obtained if ketones of the type RCH_2COCH_2R' are condensed with furfuraldehyde. The limits of applicability of this method may be further extended by replacing furfuraldehyde by other carbonyl derivatives of furan, for example, 2 acylfurans.

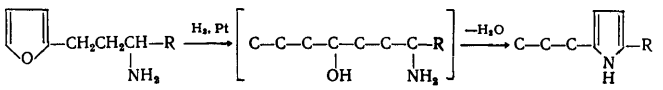
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Amines of the furan series are obtained from furan ketones either by reductive amination or by conversion of the ketones into oximes with subsequent reduction of the latter to amines. Consequently those furan amines which are accessible in practice contain the amino-group in positions 1 or 3 of the side chain with respect to the furan nucleus (corresponding in structure to the furan ketones). Among derivatives having the amino-group in position 1, the hydrogenation of furfurylamine has been investigated in some detail. Early work established[84] that platinum oxide is an effective catalyst both for hydrogenation of the furan ring in furfurylamine and for hydrogenolysis of the resulting tetrahydrofurfuran nucleus. In the presence of PtO_2 furfurylamine in the liquid phase at room temperature and a hydrogen pressure of 1.5–2 atm is smoothly hydrogenated to tetrahydrofurfurylamine. Further hydrogenation results in the tetrahydrofurfuran ring being opened mainly at the C–O bond adjacent to the substituent, with the formation of 5-aminopentanol. Under analogous conditions furylpropylamine gives an 88–89% yield of tetrahydrofurylpropylamine, and on further hydrogenation is converted into 7-aminoheptanol, a product of the hydrogenolysis of tetrahydrofurylpropylamine at the ether bond adjacent to the substituent[85,86].

Palladium deposited on carbon has proved to be a satisfactory catalyst for hydrogenation of the ring in furfurylamine, a yield of ~75% of tetrahydrofurfurylamine being obtained in glacial acetic acid solution in its presence[87]. Vil'yams found that the rate and the course of hydrogenation in nitrogen-containing furan compounds are affected by the nature of the solvent[88] as well as the catalyst. Furan amines of more complicated structure, 2,5-bis-(3-aminopropyl)furan and 2,5-bis-(3-aminobutyl)furan, were hydrogenated, in dioxan solution over Ru–C at 120°–160°, to 80–87% yields of the corresponding tetrahydrofuran amines[89]. It was pointed out in this work that the yields are lower on Raney nickel than on Ru–C, since hydrogenolysis of the furan ring occurs to a greater extent on the former catalyst. These

not entirely satisfactory properties of a nickel catalyst were noted also by Ponomarev *et al.*, who succeeded in hydrogenating quite smoothly on Raney nickel, not the furan amines themselves, but their *N*-acetyl derivatives[90].

The vapour-phase hydrogenation of furan amines has been little studied to date, but the results already obtained open up possibilities for the synthesis from these amines of heterocyclic compounds containing nitrogen. The hydrogenation of 3-furyl-1-alkylpropylamines, investigated over Pt–C in a flow system at 200°–210°, gave 70–80% yields of 2-alkyl-5-propylpyrrolidines[91]



It must be stressed that the conversion of 3-furyl-1-alkylpropylamines into homologues of pyrrolidine, and that of 3-furylalkanols into homologues of tetrahydrofuran (see above), constitute reactions of the same type, which can be represented as follows: if the side chain of a furan compound contains functional groups capable of interaction with the hydroxyl or carbonyl produced by hydrogenolysis of the furan nucleus, and if the bifunctional aliphatic compounds resulting from hydrogenolysis of the ring are of the γ-series, the vapour-phase hydrogenation of such furan compounds results in the formation of new five-membered heterocyclic rings. It is not difficult to see that the conversion of 2-acyl-5-alkylfurans into 2,6-dialkyltetrahydropyrans, discussed above, also belongs to this type of reaction. In this case the bifunctional aliphatic compounds formed as intermediates are of the δ-series, and give six-membered heterocycles by intramolecular cyclisation.

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In conclusion, let us consider the kinetics of the hydrogenation of furan compounds.

Pierce and Parks[92] examined the effect of temperature on the rate of reduction of furfuraldehyde in the presence of platinum black, and found that the rate increases with rise in temperature from 0° to 40°, passes through a maximum, and falls with further rise in temperature to 60°. The reason for this is a more rapid loss in activity by the catalyst at 60°. The only product of the hydrogenation of furfuraldehyde was furfuryl alcohol.

Smith and Fuzek[37] studied the kinetics of the hydrogenation of furan, sylvan, 2,5-dimethylfuran, furfuraldehyde, furfuryl alcohol, pyromucic acid, and dibenzofuran in acetic-acid solution over an Adams platinum catalyst. They found that: (1) the hydrogenation of furan compounds is of the first order with respect to hydrogen and of zero order with respect to the compounds undergoing hydrogenation; (2) the reaction velocity is directly proportional to the quantity of catalyst taken for the reaction; (3) the rate constants and the activation energies for the hydrogenation of furan compounds are greater than the corresponding values for hydrogenation of analogous benzene derivatives. These workers established that hydrogenolysis of the ring at the carbon–oxygen bonds was the principal reaction in the hydrogenation of furan compounds, either the 1,2 or the 1,5 C–O bond undergoing cleavage, depending on the nature of the side chain. Thus hydrogenolysis of pyromucic acid occurred at the 1,2 C–O bond with the formation of 5-hydroxyvaleric acid, while sylvan and furfuryl alcohol underwent hydrogenolysis at the 1,5 C–O bond to give respectively pentan-2-ol (yield 80–90%) and an almost quantitative yield of pentane-1,2-diol. Small quantities of tetrahydrosylvan and tetrahydropyromucic acid from the products of the hydrogenation of sylvan and pyromucic acid were isolated also.

Furan and 2,5-dimethylfuran gave only butan-1-ol and hexan-2-ol on hydrogenation. In contrast to all these compounds, the furan ring in dibenzofuran did not undergo hydrogenolysis, for the only product of its hydrogenation was perhydrodibenzofuran. An experimental proof was obtained that tetrahydrofuran derivatives are not intermediates in the formation of hydrogenolysis products. Tetrahydrofuran remained unchanged on subjection to hydrogenation under conditions under which furan was converted quantitatively into butan-1-ol. From this and also some other facts it was concluded that hydrogenation of furan compounds on a platinum catalyst involves two simultaneous reactions, hydrogenation of the ring with the formation of tetrahydro-derivatives, and hydrogenolysis of the ring with the formation of open-chain compounds.

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U.D.C. 541.15:547.024

THE RADIOLYSIS OF FROZEN AQUEOUS SOLUTIONS

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