**16.** *Reactions of Furan Compounds. Part III. Formation of Tetrahydrofuran, 2 : 3-Dihydrofuran, and Other Substances by Passage of Tetrahydrofurfuryl Alcohol Vapour over a Nickel Catalyst.*

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The side chain of tetrahydrofurfuryl alcohol is eliminated as carbon monoxide and hydrogen to give tetrahydrofuran and 2 : 3-*dihydrofuran* when the vapour is passed over a nickel or nickel-containing catalyst above 200°.

By-products include propylene, furan, butyl alcohol, methyl *n*-propyl ketone, and *tetrahydrofurfuryl tetrahydrofurfuryl ether*. Their formation is discussed.

The new reaction now described was the outcome of attempts to open the tetrahydrofuran ring by catalytic reduction. In the belief that the most drastic conditions which could be applied were those of Sabatier and Senderens's method, the vapour of tetrahydrofurfuryl alcohol, together with hydrogen, was passed over reduced nickel. This alcohol was chosen as the most readily available tetrahydrofuran compound. There was no reaction at 200°, but at 265° a vigorous decomposition ensued, marked by the evolution of gases not condensed at − 78°. The liquid product was shown to consist mainly of tetrahydrofuran. Omission of the added hydrogen did not inhibit the reaction, and in this case the gaseous products consisted of carbon monoxide and hydrogen in approximately equimolecular proportion. The reaction is represented by the equation $C_4H_7O \cdot CH_2 \cdot OH \longrightarrow C_4H_8O + CO + H_2$.

The rest of this paper is concerned with some of the more important features of the reaction, such as the nature of the catalyst and the products.

*Activity of Different Materials as Catalysts.*—It was soon evident that only catalysts containing nickel were effective. Finely divided iron, cobalt, and copper were useless. Chromium oxide deposited on activated alumina, a catalyst usually associated with dehydrogenation processes, also failed to give any tetrahydrofuran.

Many different types of catalyst containing nickel were made. The most effective was prepared by packing the catalyst tube with rolls of nickel gauze which was active after the surface had been converted into finely divided metal. Since nickel is not readily oxidised even at a red heat, the gauze was treated with chlorine at 500°, and the surface layer of chlorides reduced with hydrogen. Another satisfactory catalyst was prepared by reducing nickel oxide deposited on granulated pumice : the substitution of silica gel for pumice gave an inferior catalyst. Nickel chromite was rather poor.

Catalysts containing other metals in addition to nickel were also investigated. One of these, prepared by reducing a mixture of nickel, copper, and manganese oxides on pumice, behaved like pure nickel except that its activity decreased rather more rapidly in use.

The most useful catalytic materials were prepared from nickel alloys. Those investigated had the following compositions : Monel metal (Ni, 66·5 ; Cu, 30·0%), " Ferry " alloy (Ni, 43·9 ; Cu, 54·3%), cupronickel (Ni, 19·7 ; Cu, 80·3%), Raney alloy (Ni : Al about 50 : 50), " Permalloy " (Ni, 78·3 ; Fe, 21·4%), " Brightray " (Ni, 78·0 ; Cr, 20·0%). Like pure nickel gauze, each alloy had to be activated before it showed any catalytic effect. Raney alloy and Brightray were resistant to high-temperature oxidation, but the former was converted into an extremely active nickel by treatment with hydrogen chloride at 450°, which removed aluminium without, apparently, disrupting the granular form of the alloy. Attempts to activate Brightray wire by chlorination failed ; a vigorous reaction ensued to give a mixture of powdered metal chlorides with complete disintegration of the structure. The alloys containing iron and copper were all readily activated by oxidation at 550°, followed by reduction at a lower temperature.

*Deterioration and Reactivation of Catalysts.*—During the passage of tetrahydrofurfuryl alcohol over each catalyst, activity as measured by consumption * of alcohol slowly fell off. It was simple, however, to reactivate a deteriorated catalyst by oxidation at 550°, followed by reduction at 330°. With some of the alloy catalysts successive reactivations gave not only gradually increasing amounts of water at the reduction stage, but also gradually increasing consumptions of alcohol. A deteriorated catalyst could also be reactivated by a stream of hydrogen at a high temperature, but the catalyst so produced did not have as long an active life as one regenerated by oxidation and reduction.

*Products of the Reaction.*—In addition to carbon monoxide and hydrogen, the exit gases from the catalyst tube contained some propylene and a little propane. There were no indications, however, of the formation of $C_4$ hydrocarbons. The liquid product was distilled, and many of its constituents identified and estimated by methods described in the experimental section. Tetrahydrofuran was the major constituent of the fraction of b. p. < 160°. A cut was made at this temperature because it divided material containing all the tetrahydrofuran from a residue consisting mainly of unchanged alcohol. Some of the constituents of the low-boiling fraction from a nickel-on-pumice catalyst are indicated in Table I. In Table II a comparison of different catalysts is made.

The origin of some of the more interesting by-products is discussed below.

*2 : 3-Dihydrofuran.*—This compound is new. It was detected in the tetrahydrofuran by formation of

* In this paper " consumption " refers to the proportion of alcohol used up in a single passage over the catalyst. In the tables it is given as a percentage. " Yield " is estimated as a percentage of the theoretical yield based on consumption and not on input.

TABLE I.

*Composition of crude tetrahydrofuran (b. p. <160°) from a nickel-on-pumice catalyst.*

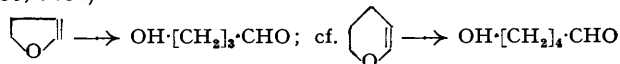| Substance. | % by wt. | Substance. | % by wt. |
|---|---|---|---|
| Furan | 3·4 | n-Butyl alcohol | 1·5 |
| Tetrahydrofuran | 61·8 | Crotyl (?) alcohol | 0·5 |
| 2 : 3-Dihydrofuran | 5·0 | cycloPentanone | 0·4 |
| n-Butaldehyde | 9·9 | Water | 6·3 |
| Methyl n-propyl ketone | 0·6 | Tetrahydrofurfuryl alcohol | 2·8 |

TABLE II.

*Chief constituents (wt.-%) of crude tetrahydrofuran (b. p. <160°) from a nickel gauze and various alloy catalysts.*

| Substance. | Ni gauze. | Monel metal. | " Ferry " alloy. | Raney alloy. | " Perm-alloy." * |
|---|---|---|---|---|---|
| Furan | 3·0 | — | 3·0 | 3·5 | — |
| Tetrahydrofuran | 63·0 | 52 | 47 | 58·5 | 41 |
| 2 : 3-Dihydrofuran | 3·5 | 12 | 20 | 6·5 | 12 |
| n-Butaldehyde | 9 | 3 | 5 | 5 | 4 |
| Water | 6 | 5 | 6 | 6 | 4 |

\* This catalyst consisted of nickel and iron oxide.

*γ-hydroxybutaldehyde-2 : 4-dinitrophenylhydrazone.* The hydrolysis of 2 : 3-dihydrofuran to γ-hydroxy-butaldehyde under the conditions employed is analogous to that of dihydropyran to δ-hydroxyvaleraldehyde (Paul, *Compt. rend.*, 1933, **197**, 1652) :

$$\text{(structure)} \longrightarrow \text{OH·[CH}_2]_3\text{·CHO}; \quad cf. \quad \text{(structure)} \longrightarrow \text{OH·[CH}_2]_4\text{·CHO}$$

Absence of s-dihydrofuran was indicated by the equivalence of catalytic hydrogen absorption with the amount of precipitate given by Brady's reagent.

Reference to Table II indicates that, although the amount of dihydrofuran varies widely with different catalysts operating under optimum conditions, the yield of hydrogenated furans, *i.e.*, a mixture of only di- and tetra-hydrofuran, remains fairly constant (43±4%). This could mean that dihydrofuran is formed largely at the expense of tetrahydrofuran. Subsidiary experiments, however, showed that tetrahydrofuran is not dehydrogenated to dihydrofuran by passage over active nickel or " Ferry " alloy, and the dihydrofuran must, therefore, arise in some other way. The situation regarding the dehydrogenation-decarbonylation of simple aliphatic alcohols to hydrocarbons is somewhat similar. Experiment here, too, has shown that the olefin which is frequently observed is not produced by dehydrogenation of the saturated hydrocarbon (Badin, *J. Amer. Chem. Soc.*, 1943, **65**, 1809; Suen and Fan, *ibid.*, p. 1243). Böeseken and van Senden (*Rec. Trav. chim.*, 1913, **32**, 23) suggested that olefin arose by elimination of formaldehyde from the alcohol, but in our experiments there is certainly no support for this hypothesis.

Some interesting variations in the amount of dihydrofuran, $C_4H_6O$, formed by different catalysts are indicated in Tables II and III, the latter relating to the composition of the hydrogenated furan mixture containing only 2 : 3-di- and tetra-hydrofuran.

TABLE III.

*Dihydrofuran content of hydrogenated furan mixture from various catalysts.*

| Catalyst. | $C_4H_6O$, %. | Catalyst. | $C_4H_6O$, %. |
|---|---|---|---|
| Raney nickel | 1·0 | " Permalloy " (Ni, Fe oxide) | 23·1 |
| Ni gauze (atm. press.) | 4·0 | ,, (Ni, Fe) | 28·6 |
| Ni on pumice | 4·1 | " Ferry " alloy | 30·4 |
| Ni on silica gel | 11·2 | Cupronickel | 37·7 |
| Monel metal | 18·3 | | |

Too much attention should not be paid to the absolute value of the dihydrofuran data, since with any one catalyst its formation varied with activity. Progressive fall in activity, as measured by consumption of alcohol, was accompanied by a steady rise in dihydrofuran content of the hydrogenated furan mixtures; *e.g.*, when the activity of nickel had fallen to half its initially high value the dihydrofuran yield was about doubled. The data in Table III refer to freshly reactivated catalysts before deterioration became appreciable. Similar effects were noticeable amongst the nickel–copper alloys : as the copper content increased, the active life decreased and, as Table III shows, the dihydrofuran yield also increased. The effect of pressure on dihydrofuran formation with nickel is referred to later.

The variations in the amount of dihydrofuran formed under different conditions could, perhaps, be explained by assuming that this substance was intermediate in the formation of tetrahydrofuran, the catalyst having to fulfil the rôle of facilitating both the formation and the reduction of dihydrofuran. This leaves unexplained why dihydrofuran should be the primary product of side-chain elimination.

*Tetrahydrofuryl Tetrahydrofurfuryl Ether.*—The formation of this *compound* might be connected with that of dihydrofuran. It was isolated as a liquid, b. p. 101—102°/11 mm., from the high-boiling fractions of the

reaction product, and the important clue to its structure was the identification of its hydrolysis products with dilute acid as $\gamma$-hydroxybutaldehyde (dinitrophenylhydrazone identical with that from dihydrofuran) and tetrahydrofurfuryl alcohol : $C_4H_7O \cdot CH_2 \cdot O \cdot C_4H_7O \longrightarrow C_4H_7O \cdot CH_2 \cdot OH + OH \cdot [CH_2]_3 \cdot CHO.$

*Furan and Methyl* n-*Propyl Ketone.*—Experiment showed that tetrahydrofuran was not dehydrogenated by a nickel catalyst to furan. The most plausible explanation for the presence of a small amount of furan in the reaction product is that it was formed from a trace of furfuryl alcohol present as impurity in the tetra-hydrofurfuryl alcohol used. The presence of such an impurity has not been definitely proved by isolation, but it would explain this and three other observations : (i) the darkening of the alcohol by addition of a little concentrated hydrochloric acid, a reaction indicative of a furan compound (furfuraldehyde was shown to be absent) ; (ii) the presence of a small amount of furfuraldehyde, which might arise by dehydrogenation of furfuryl alcohol, in the reaction product from the nickel–copper alloys; (iii) the formation of a little methyl n-propyl ketone, the presence of which would be hard to explain if it were not for Padoa and Ponti's demon-stration (*Gazzetta,* 1907, **37**, 105) that it is formed by Sabatier–Senderens reduction of furfuryl alcohol.

Both furan and methyl n-propyl ketone are assumed, therefore, to have arisen from furfuryl alcohol, which is a likely impurity, since tetrahydrofurfuryl alcohol is manufactured by catalytic reduction of furfuraldehyde.

*Butyl Alcohol and* n-*Butaldehyde.*—The original tetrahydrofurfuryl alcohol was shown to contain up to 1% of butyl alcohol (see p. 57), which is scarcely sufficient to account for that present in the reaction product, and still less for the butaldehyde. This conclusion was confirmed by the demonstration that butyl alcohol was readily decomposed to gaseous products (propane, propylene) by an active nickel catalyst and would not, therefore, withstand passage over the nickel without considerable loss.

The butyl alcohol fraction of the reaction product also contained an unsaturated alcohol. Its structure is uncertain but it is provisionally assumed to be crotyl alcohol (b. p. 117—120°) from the distillation range, 115—120°, of the fraction containing butyl alcohol. The presence of allylcarbinol is not excluded.

These alcohols probably arise by reductive fission of the hydrogenated furans, but confirmation is lacking.

cyclo*Pentanone and Tetrahydrofurfuraldehyde.*—Since the loss of the side chain of tetrahydrofurfuryl alcohol probably proceeds *via* the aldehyde (cf. Wojcik and Adkins, *J. Amer. Chem. Soc.,* 1933, **55**, 1293), it was remarkable that no trace of tetrahydrofurfuraldehyde could be found in the product from a nickel catalyst, although a special search was made for it. Later, however, it was shown, by formation of the dinitro-phenylhydrazone, to be present to a very small extent in the product from a nickel catalyst operating under reduced pressure or from the alloys " Ferry ", cupronickel and " Permalloy " employed at ordinary pressure. Surprisingly enough, with Monel metal, as with nickel at ordinary pressure, the fractions which might have contained the aldehyde gave instead only the dinitrophenylhydrazone of cyclopentanone. No adequate explanation for the presence of cyclopentanone can be given. A careful search was made for cyclopentanol, a possible precursor of the ketone, in the original alcohol, but without success. The only hydroxy-compound which was isolated boiling between 100° and 150° was butyl alcohol.

*Effect of Temperature.*—With each of the catalysts studied, increase of temperature caused a rise in con-sumption of alcohol. Between 200° and 300° this usually rose from a very low figure to 100%. On the other hand, the yield of hydrogenated furans, calculated after allowance for recovered alcohol, was at a maximum between 245° and 280°.

Data for a nickel gauze catalyst are in Table IV. This catalyst was, perhaps, the most satisfactory for semi-quantitative studies, since its hold-up was very small and its deterioration in use not too rapid. The whole series of experiments, each of which corresponds with an input of 0·25 g.-mol. of alcohol, was carried out without reactivation. " Consumption " and " yield " have the significance given to them on p. 52 (footnote).

TABLE IV.

*Effect of temperature on the formation of hydrogenated furans from tetrahydrofurfuryl alcohol :*
*nickel gauze catalyst.*

(Input : 0·5 g.-mol./hr. Each expt. used 0·25 g.-mol. Activation of catalyst before the series by oxidation and reduction gave 8·5 c.c. of water.)

| Expt. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Temp. ($\pm$ 5°) | 300° | 300° | 260° | 280° | 240° | 300° |
| Alcohol consumed (%) | 99 | 98 | 73 | 93 | 33 | 97 |
| Hydrogenated furans,* yield (%) | 17 | 20 | 45 | 39 | 43 | 28 |

\* About 96% tetrahydrofuran.

It is noticeable that, whereas consumption rose progressively with temperature, yield attained a maximum at about 260°. Deterioration of the catalyst is just perceptible from a comparison of expts. nos. 1, 2 and 6 ; the gradual fall in activity is not sufficient, however, to obscure the effect of temperature.

Reactivation of the nickel gauze catalyst by hydrogen has already been mentioned. The effect of varying temperature with this catalyst was to produce a maximum yield of 50% at 280°.

The other catalysts all deteriorated more rapidly than nickel gauze, and the effect of temperature with each was not followed in detail. However, with activated Raney alloy the maximum yield (39%) was obtained at 245° with a consumption of 52%, and with the nickel–copper alloys, Monel and Ferry, the highest yield (45%) was obtained at about 290°.

Consumption and active life with cupronickel and Permalloy were too small to permit temperature variation to be followed.

*Effect of Rate of Alcohol Input.*—The nickel gauze catalyst being used, it was shown that increase in rate of alcohol input reduced consumption, and to a lesser extent, yield (see Table V).

TABLE V.

*Effect of input on formation of hydrogenated furans from tetrahydrofurfuryl alcohol : nickel gauze catalyst.*

(Temperature, 260° ± 5°. Each expt., 0·25 g.-mol. Catalyst gave 8·5 c.c. of water by oxidation and reduction.)

| Input (g.-mol./hr.) | 0·25 | 0·35 | 1·1 | 2·5 |
|---|---|---|---|---|
| Alcohol consumed (%) | 84 | 65 | 49 | 38 |
| Hydrogenated furans,* yield (%) | 43 | 45 | 43 | 35 |

\* About 96% tetrahydrofuran.

*Influence of Carrier Gases.*—Large volumes of carbon monoxide and hydrogen are produced during the reaction; it is not surprising, therefore, that with nickel gauze the addition of further hydrogen only had the effect of lowering consumption, due, presumably, to reduced time of contact between alcohol and catalyst. Carbon dioxide behaved similarly. In the present work carrier gas was not usually introduced during the reaction but only to sweep out the catalyst chamber after an experiment.

*Effect of Pressure.*—A few experiments were carried out under reduced pressure. The apparatus used did not permit a detailed study of the effect of pressure on the reaction but the results obtained (Table VI) showed that the optimum working temperature, about 225°, was somewhat lower than that, about 260°, obtaining at atmospheric pressure. The catalyst deteriorated more rapidly, however.

TABLE VI.

*Effect of pressure on formation of hydrogenated furans : nickel catalyst.*

(Input 0·5 g.-mol./hr. Each expt., 0·5 g.-mol. Water from activation, 8·6 c.c.)

| Temp. (± 5°) | 250° | 270° | 225° |
|---|---|---|---|
| Pressure (mm. Hg) | 250 ± 100 | 300 ± 30 | 120 ± 40 |
| Alcohol consumed (%) | 63 | 94 | 52 |
| Hydrogenated furans, yield (%) | 38 | 26 | 43 |

Perhaps the most interesting feature of these experiments was the large amount—in the experiment at 225° it was 25·5%—of 2 : 3-dihydrofuran present in the hydrogenated furan mixture produced. There was also evidence that the amount of butaldehyde produced was lower than in the experiments at ordinary pressure. This suggests that some at any rate of the aldehyde probably arises by reductive fission of dihydrofuran.

EXPERIMENTAL

I. *Preparation of Catalysts.*—(a) *Nickel on silica gel.* Silica gel (150 g.), freed from sulphur compounds by boiling with concentrated nitric acid, followed by thorough washing with water, was stirred into a hot mixture of nickel nitrate (hexahydrate, 100 g.), nickel carbonate (50 g.), and water (50 c.c.). The mass was kept hot on a steam-bath and frequently stirred until it became crumbly. It was then packed into the catalyst tube, heated slowly to 400°, and when water and nitrogen oxides ceased to be evolved, reduced with hydrogen.

(b) *Nickel–copper–manganese oxides on pumice.* Copper nitrate (22 g.), manganese nitrate (142 g.), and nickel nitrate (126 g.), all as hexahydrates, were dissolved in hot water (100 c.c.), and pumice (8—16 mesh, 100 g.) added. The mixture was stirred at 100° until it was sufficiently dry to be packed into the catalyst tube, and then reduced at 400°.

(c) *Nickel on pumice.* Nickel nitrate (hexahydrate, 290 g.) was melted at 100°, granulated pumice (8—16 mesh, 150 g.) added, and stirring continued at 100° until the mass was granular. The temperature was very gradually raised at first. Reduction was carried out at 350°. This catalyst gave tetrahydrofuran between the temperature limits 200—400°. At 200° the consumption was only 18% and at 400° activity was rapidly lost. Catalysts (a), (b), and (c) were much improved by air oxidation at 550°, followed by reduction at 350°.

(d) *Nickel gauze.* Nickel gauze (28 mesh, 6 sq. ft., 620 g.) was fashioned into two compact rolls and fitted into a Pyrex tube of 26 mm. internal diameter. The length of the filling was 58 cm. A Pyrex thermometer pocket was fitted down the centre of the first roll of gauze. The nickel was quite inactive towards tetrahydrofurfuryl alcohol at 300°. Successive air oxidations at 550° followed by reduction produced the following amounts of water (c.c.) : 0·2, 0·2, 0·4, 0·8. Even then only very slight conversion of alcohol into tetrahydrofuran was observed. The nickel was therefore treated with chlorine at 550°, reduced, and then oxidised by air and reduced till no more hydrogen chloride was formed. Reduction gave 5 c.c. of water. A further chlorination raised this figure to 8·0 c.c. During use this figure varied by a few tenths of a c.c. and tended to rise slowly.

(e) *Nickel chromite on pumice.* Nickel chromite (63 g.; Adkins, Richards, and Davis, *J. Amer. Chem. Soc.*, 1941, **63**, 1320) was well mixed with moistened pumice (100 g.), and the mixture packed in the catalyst tube, heated, and reduced at 400°. Only about 0·8 c.c. of water was produced by oxidation and reduction.

(f) *Copper.* Three types were used. One was made by reduction of the oxide (B.D.H., *ex* wire) at 250° by hydrogen, another by reduction of copper nitrate on pumice; neither showed any activity. A third, copper chromite in pellet form, was reduced at 300°; in use at 365°, 95% of the alcohol input was consumed and a 41% yield of dihydropyran resulted.

(g) *Cobalt.* Cobalt nitrate (hexahydrate, 150 g., containing 0·11% of nickel) was heated with water (50 c.c.) and granulated pumice (150 g., 8—16 mesh) with stirring until granular. Reduction was carried out at 350—400°. The catalyst was inactive at 300°.

(h) *Iron.* Prepared in the usual way from granulated pumice and ferric nitrate (hexahydrate, 250 g.), the deposited oxide was difficult to reduce. After 12 hrs. at 550° in a stream of hydrogen, 13·5 c.c. of water were collected. The theoretical quantity for the reaction $Fe_2O_3 \longrightarrow 2Fe$ is 19 c.c., and for $Fe_2O_3 \longrightarrow Fe_3O_4$, 2 c.c. The catalyst was inactive at 400°.

(j) *Platinum.* Granulated pumice (60 g.) was treated with platinic chloride solution (19·5%, 55 c.c.) and reduced at 400°. The catalyst was rather ineffective at 300°.

(k) *Chromic oxide on alumina.* Active alumina (Grade A, British Aluminium Co., 4—6 mesh) was treated with a hot 25% solution of chromic oxide in water. After being heated and cooled twice, the alumina was dried. Its weight showed that about 7% of $CrO_3$ was present. The catalyst was finally heated in hydrogen at 400—450°. Passage of tetrahydrofurfuryl alcohol over this catalyst at 300° gave dihydropyran.

(l) *Raney alloy.* Granulated and sieved alloy (8—16 mesh, 460 g.) was packed into the Pyrex catalyst tube and treated at 450° with hydrogen chloride (15 l./hr.) for 5 hours. Aluminium chloride sublimed. The material was then removed from the tube, well mixed, and replaced. Oxidation of the catalyst with air at 550°, followed by reduction at 330°, gave 6·4 c.c. of water. The catalyst so prepared was very active, causing much decomposition to gaseous products at 270°. Active Raney catalyst suffered from the disadvantage of possessing considerable hold-up due to its porous nature.

(m) *Monel metal.* The alloy in the form of gauze (354 g., 60 mesh) was shown by analysis to contain : Cu, 30·0; Ni, 66·5; Fe, 1·2; Mn, 1·0%. It was clipped into pieces about 3 mm. square and packed into the catalyst tube around a central Pyrex thermometer pocket. Oxidation by air at 550°, followed by reduction, gave successively the following amounts of water : 1·5, 2·5, 3·1, 3·2, 3·3, 4·3 c.c. It was then used in the catalytic reaction.

(n) " *Ferry* " *alloy.* Alloy in the form of wire process scrap (241 g., about 30—36 S.W.G.) was shown to contain : Cu, 54·3; Ni, 43·9; Fe, 0·4; Mn, 1·1%. It was cut into small tufts and packed in the tube. Successive activations by oxidation and reduction gave 3·1, 3·9, 5·1, 5·6, 6·6, 8·4 c.c. of water. It is evident, therefore, by comparing these figures with those given above for Monel metal, that Ferry is the more easily oxidised alloy.

(o) *Cupronickel.* Bullet envelope cut-offs had the composition : Cu, 80·3; Ni, 19·7; Fe, 0·05%. The pieces (585 g.) were treated as before by oxidation and reduction and gave 1·3, 1·3, 3·1, and 4·0 c.c. of water. This catalyst was not very active, giving low consumption. It also deteriorated very rapidly.

(p) " *Permalloy.* " The alloy contained Ni, 78·3; Fe, 21·4% and was in the form of thin strip. This (212 g.) was cut into small pieces and packed into the catalyst tube. Successive air oxidations, followed by reduction, at 500—530°, gave the following volumes of water : 0·5, 1·6, 2·2, 3·1, 3·8 c.c.; this depended on the temperature of reduction—*e.g.*, after the above series of activations a prolonged period of air oxidation at 580° gave only 1·2 c.c. of water by reduction at 330°, but much more water was then produced at 400—430° (3·1 c.c.), and no further reduction occurred until the temperature rose to 500—530°, whereat a further 1·5 c.c. were formed. It was concluded that reduction below 430° produced a mixture of nickel and iron oxide (probably $Fe_3O_4$), whereas only at the highest temperature was metallic iron formed. The high- and the low-temperature catalyst behaved differently in the reaction, as indicated in Table III; the latter was the more active, although less water had been evolved during its formation.

The crude tetrahydrofuran fraction (b. p. <160°) obtained from the low-temperature reduced catalyst contained 54% of di- and tetra-hydrofurans. The corresponding figure for the catalyst prepared by high-temperature reduction was 49%.

II. *Apparatus.*—The catalyst (100—150 c.c.) was contained in a Pyrex tube of 1 in. external diameter, resting inside an electric furnace inclined at 15° to the horizontal. The heated portion of the catalyst tube measured 24 ins., of which the middle 12 ins. were at a temperature constant to $\pm$ 5°. A series resistance enabled the temperature to be varied between 150° and 650°. Temperature was measured by a thermometer or thermocouple as described under catalyst (d).

Tetrahydrofurfuryl alcohol was dripped on a strip of asbestos paper, along which it soaked gradually into the hotter part of the furnace. The exit end of the catalyst tube was connected to a suitable series of traps. The progress of a particular experiment, particularly in regard to catalyst activity, could be fairly well assessed by the size and luminosity of the flame obtained by igniting the issuing gases at a jet.

Reactivation was usually carried out by air oxidation at 550—580°, followed by reduction at 300—350°. It was also possible to reduce the nickel catalysts (c) and (d) after air oxidation by methanol at 370—380° or ethanol at 380—390°.

III. *Analysis of Products.*—The pyrolysate was divided into three fractions : (1) b. p. 50—160°, containing all the tetrahydrofuran ; (2) b. p. 160—185°, consisting largely of unchanged alcohol ; (3) residue. Fractionation through a 12" column packed with stainless steel rings was not sufficient to separate butaldehyde from tetrahydrofuran ; about 2% remained. According to circumstances various methods were used to analyse the crude low-boiling fraction. Water was determined by either drying over a known weight of calcium chloride or freezing and filtering at — 78° through a pad of 90-mesh nickel gauze. *n*-Butaldehyde and 2 : 3-dihydrofuran were determined together by precipitation with aqueous dinitrophenylhydrazine. After potash treatment and distillation, which removed carbonyl compounds, dihydrofuran was determined alone as γ-*hydroxybutaldehyde*-2 : 4-*dinitrophenylhydrazone*. This formed golden laminæ, m. p. 116—117° (Found : C, 44·6; H, 4·7; N, 20·5. $C_{10}H_{12}O_5N_4$ requires C, 44·7; H, 4·5; N, 20·9%), from aqueous ethyl alcohol. Its solubility in water was 0·04% at 20°.

The higher-boiling material present in fraction (1) from a pure nickel catalyst contained methyl *n*-propyl ketone, b. p. 101—102°, identified and estimated as 2 : 4-dinitrophenylhydrazone. The only other substances present in any quantity were a liquid, b. p. 115—120°, which contained much butyl alcohol (identified as 3 : 5-dinitrobenzoate), and an unsaturated substance. The liquid (92 g.) was treated with excess of acetic anhydride at the b. p., a few drops of sulphuric acid being used as catalyst, and then saturated with bromine. The product was distilled, giving butyl acetate (93 g.), b. p. 124—127°, and a liquid (62 g.), probably a dibromobutyl acetate, b. p. 132—138°/16 mm.

Passage of the gaseous products not completely caught in Drikold traps through bromine gave a liquid, b. p. 142—144°/763 mm. (Found : .C, 18·2; H, 3·0; Br, 77·75. Calc. for $C_3H_6Br_2$ : C, 17·8; H, 3·0; Br, 79·2%), obviously propylene dibromide. After addition of bromine to the liquid, b. p. < 0°, from the pyrolysate, a substance, b. p. — 40° to — 30°, distilled off which was considered to be propane, since it was saturated and inflammable.

Fraction (3), the residue, b. p. > 185°, collected from many experiments, was washed with aqueous alkali and distilled. It contained 20% of tetrahydrofurfuryl alcohol and a substance, b. p. 100—101°/10 mm. (67% by wt.), believed to be *tetrahydrofuryl tetrahydrofurfuryl ether* (Found : C, 62·4; H, 9·0. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%). It was only very slightly soluble in water or aqueous alkali, but in the presence of 0·01N-mineral acid it rapidly dissolved without evolution of appreciable heat. The solution then gave the 2 : 4-dinitrophenylhydrazone of γ-hydroxybutaldehyde. A quantitative experiment, however, showed that the derivative was formed only to the extent of 79% of that expected from its proposed structure. Attempts at further purification by fractionation were of no avail, successive fractionations giving figures of 60 and 50%. A solution of the octahydro-ether (26 g.) in hydrochloric acid was treated with solid potassium carbonate, which caused the separation of an upper layer. This, which was completely miscible with water, was dried over potassium carbonate and distilled ; two-thirds of it had b. p. 68—80°/14 mm., the remainder (7 g.) being mainly unchanged ether. The larger fraction was warmed to 80° with potassium hydroxide and distilled at 75°/12 mm. This product still gave a precipitate with dinitrophenylhydrazine, but treatment with 3 : 5-dinitrobenzoyl chloride in pyridine at 100° gave tetrahydrofurfuryl dinitrobenzoate which, after recrystallisation from petrol (b. p. 80—100°), had m. p. 83—84; it was identified by mixed m. p.

Fraction (3), from each vapour-phase experiment recorded in the tables, was treated with 4 vols. of 10% sodium hydroxide solution, which separated unchanged alcohol (soluble) from the octahydro-ether (insoluble). The amount of alcohol thus indicated was taken into account, along with that in fraction (2), when calculating consumption.

Fraction (2), bulked from many related experiments with a given catalyst, was distilled in a vacuum, and the proportion of tetrahydrofurfuryl alcohol in it ascertained. With the nickel catalysts (c) and (d) it contained 85—87% of pure unchanged alcohol, b. p. 66°/12 mm., together with 6% of the above octahydro-ether and 6% of b. p. < 66°/12 mm. The lowest-boiling fraction on redistillation had b. p. 120—150°/756 mm. and contained about 5% [*i.e.*, 0·3% on original fraction (2)] of *cyclo*pentanone, identified and estimated as dinitrophenylhydrazone.

IV. *Detection of Tetrahydrofurfuraldehyde.*—This aldehyde was first found in the recovered alcohol, fraction (2), from experiments with nickel under reduced pressure (see Table VI). The alcohol fraction, 15·2 c.c., was treated with aqueous 2 : 4-dinitrophenylhydrazine, and the precipitate recrystallised from ethyl acetate–ethyl alcohol (1 : 1). The hydrazone formed orange-yellow, prismatic needles, m. p. 130—131° (Found : C, 47·35; H, 4·55; N, 20·0. Calc. for $C_{11}H_{12}O_5N_4$ : C, 47·2; H, 4·3; N, 20·0%). It did not depress the m. p. of an authentic specimen (see below).

The "Ferry" and "Permalloy" catalysts also produced small amounts of tetrahydrofurfuraldehyde. The recovered alcohol from experiments with Monel metal gave the dinitrophenylhydrazone of *cyclo*pentanone, which after one crystallisation from ethyl alcohol had m. p. 140—141°.

V. *Preparation of Tetrahydrofurfuraldehyde-2 : 4-dinitrophenylhydrazone.*—Repetition of the methods described in the literature for the preparation of the aldehyde did not give satisfactory results. Two other reactions, pyrolysis of the mixed barium salts of tetrahydrofuroic and formic acids, and Stephen's stannous chloride reduction of the nitrile, gave unexpected products. The former produced only tetrahydrofurfuryl alcohol (identified as 3 : 5-dinitrobenzoate) and the latter gave a small amount of δ-hydroxyvaleraldehyde. Finally, samples were successfully prepared in two ways, (i) lead tetra-acetate oxidation of the pinacol produced by catalytic reduction of furoin, and (ii) dehydrogenation of tetrahydrofurfuryl alcohol by means of a copper–chromium oxide catalyst.

(i) *Catalytic reduction of furoin.* Furoin was prepared as described by Buck and Ides (*J. Amer. Chem. Soc.*, 1932, **54**, 3302), although it was found better to distil the product (b. p. 158—162°/9 mm.) instead of recrystallising it. The ketol (125 g.) was reduced in methyl alcohol (375 g.) by means of Raney nickel (30 g.) and hydrogen (139 atm./18°). Rapid absorption occurred at 160—165° and ceased after 2·25 hrs. The pressure when cold was 84 atm. The product was separated into three fractions by distillation : (1) b. p. 122—146°/0·5 mm., 68 g.; (2) b. p. 160—180°/0·5 mm., 5 g.; (3) residue, 30 g. On treatment with cold water, fraction (1) largely dissolved, leaving an insoluble white substance (9·0 g.). This was non-ketonic and crystallised from hot water in prisms, m. p. 168—169°, which agrees with published data for the octahydroglycol (Kaufmann and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 3029) (Found : C, 59·5; H, 8·75. Calc. for $C_{10}H_{18}O_4$ : C, 59·4; H, 8·9%). Fraction (2) was mixed with the water-soluble part of fraction (1) and redistilled, giving 54 g. of b. p. 125—130°/0·5 mm. On standing, this solidified, and a sample, after removal of contaminating oil by pressure, was recrystallised twice from petrol (b. p. 60—80°); it formed rosettes of needles, m. p. 80—81°, and was very soluble in all solvents. Analysis showed that it, too, was an octahydroglycol (Found : C, 58·85; H, 8·8%). It is probably identical with the second substance, m. p. 75°, isolated but not identified by Kaufmann and Adams.

Precipitation with aqueous dinitrophenylhydrazine showed that the low-melting glycol and the oil removed from it by pressure contained a carbonyl compound. The original crude, unpressed material, b. p. 125—130°/5 mm. (54 g.), was estimated to contain about 10% (5·5 g.) of carbonyl compound, possibly octahydrofuroin.

*Oxidative fission of the tetrahydrofurfuraldehyde pinacols by lead tetra-acetate.* The liquid glycol (13 g.), pressed from the low-melting solid (above), was treated in glacial acetic acid (25 c.c.) with lead tetra-acetate (24 g.; *Inorg. Syntheses*, 1939, **1**, 47). Excess of sulphuric acid was then added, and the mixture filtered. The resulting clear solution gave a positive test for furfuraldehyde (aniline acetate), and a scarlet dinitrophenylhydrazone. It would appear,· therefore, that the crude glycol contained some furfuryl pinacol.

The low-melting glycol (not recrystallised, 2·02 g.) was dissolved in water (25 c.c.), and a solution of lead tetra-acetate (4·43 g.) in warm glacial acetic acid (30 c.c.) added with stirring. After 15 minutes, 5N-sulphuric acid (5 c.c.) was added, and the solution filtered. The clear filtrate gave a 2 : 4-dinitrophenylhydrazone which contained a small amount of the less soluble scarlet furfuryl compound. This was removed by crystallisation from ethyl acetate, and the remainder formed prisms, m. p. 128—130°, identical (mixed m. p.) with the hydrazone described in the next paragraph.

The recrystallised high-melting glycol (1·0 g.) and lead tetra-acetate (2·21 g.) in 15 g. of acetic acid gave a pure, homogeneous dinitrophenylhydrazone, which formed pale yellowish-brown prisms, m. p. 130—131°, from ethyl acetate, of the tetrahydrofurfuraldehyde derivative (Found : C, 47·4; H, 4·5; N, 20·0. Calc. for $C_{11}H_{12}O_5N_4$ : C, 47·2; H, 4·3; N, 20·0%). Admixture with *cyclo*pentanonedinitrophenylhydrazone caused m. p. depression.

(ii) *Catalytic dehydrogenation of tetrahydrofurfuryl alcohol.* A catalyst similar to that described in B.P., 540,133, was prepared by mixing chromium nitrate (hydrate, 9 g.), copper nitrate (hexahydrate, 300 g.), copper oxide (25 g.), water glass (40 g.), copper carbonate (2Q0 g.), and silica gel (60 g.) to a thick paste by warming; this was dried at 80° and fused in small portions before an air–gas blowpipe on an ordinary brick. The resulting material was broken up, packed in a furnace tube, and reduced at 300° in a stream of hydrogen. Tetrahydrofurfuryl alcohol was then passed over the catalyst at 300—350°. The product was distilled, giving about 12% of b. p. 60—170°. This fraction was accumulated from many experiments and redistilled after drying over sodium sulphate. There was no definite aldehyde fraction but the liquid of b. p. 140—160° gave tetrahydrofurfuraldehyde-2 : 4-dinitrophenylhydrazone which, after recrystallisation, had m. p. 130—131°.

In addition to the above, the 2 : 4-dinitrophenylhydrazones of the following carbonyl compounds were also prepared for reference purposes : γ-hydroxybutaldehyde, m. p. 116—117°; δ-hydroxyvaleraldehyde, m. p. 112—113° (Found : C, 47·1; H, 5·05; N, 19·75. $C_{11}H_{14}O_5N_4$ requires C, 46·8; H, 5·0; N, 19·9%); *n*-butaldehyde, m. p. 121—122°; methyl *n*-propyl ketone, m. p. 140—142°; *cyclo*pentanone, m. p. 140—141° (Found : C, 49·85; H, 4·55; N, 21·35. Calc. for $C_{11}H_{12}O_4N_4$ : C, 49·9; H, 4·5; N, 21·2%).

VI. *Composition of Commercial Tetrahydrofurfuryl Alcohol.*—A large amount (2470 g.) of the alcohol was fractionated. More than 94·7% had b. p. 80—80·5°/19 mm. The higher-boiling residue amounted to 2·4%, and the fraction of b. p. 35—80°/19 mm to 2·5%. After drying, about a third of the latter had b. p. 118—121°. This gave *n*-butyl 3 : 5-dinitrobenzoate.

No trace of *cyclo*pentanol (b. p. 139—140°) could be found in the fractions from the commercial alcohol, nor was there any indication of furfuryl alcohol.

VII. *Behaviour of Tetrahydrofuran over the Gauze Catalyst* (d).—Tetrahydrofuran (41·5 c.c., 36 g., 0·5 g.-mol.) was passed over the reactivated catalyst during 1 hr. at 300—310°. The product (33 c.c.) consisted of 28 c.c., b. p. 57—67°, mostly tetrahydrofuran and free from *n*-butaldehyde or 2 : 3-dihydrofuran (dinitrophenylhydrazine), and 1·5 c.c. of b. p. < 0°. The latter was partly unsaturated towards bromine and gave 1 c.c. of water-insoluble dibromide, probably propylene dibromide. The rest was probably propane. The exit gases contained about one-third of their volume of carbon monoxide. Similar results were obtained at 280°, but less propylene was formed. Furan, b. p. 32—33°, could not be detected.

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