catalyst chamber consisting of a Pyrex glass tube, 1.7 in. diameter, and heated electrically. The metal was activated by oxidation in a stream of air at 500° followed by slow reduction below 300° with hydrogen. The weight of each catalyst and the amount of water produced at the first reduction was as follows, pure nickel (2500 g., 250 cc.), pure cobalt (2300 g., 359 cc.), nickel–copper (50% of each, 2500 g., 607 cc.) and cobalt–copper (50% of each, 2500 g., 425 cc.). Copper chromite (750 g.) prepared by the usual precipitation method was inactive at 225° and 350°. The catalysts were reactivated by oxidation and reduction as above.

Isolation and Analysis of Products.—Dihydropyran was prepared by dehydration of tetrahydrofurfuryl alcohol over aluminum silicate at 350°. After drying over solid sodium hydroxide it had b. p. 86–88°.

The product issuing from the catalytic chamber containing the active metals was passed through a trap at −78° and the condensed portion distilled at atmospheric pressure. Material, b. p. below 20°, consisted of C_4-hydrocarbons. Bromine was added at −78° until addition was complete and the volatile unreacted butane distilled off into a graduated tube where its volume at 0° was measured. The involatile bromide was weighed and the amount of butene to which it corresponded was calculated. The bromide had b. p. 159–160° and would therefore appear to consist essentially of the symmetrical butene dibromide. The boiling point of the 1,2-compound is recorded as 166°.

The fraction of the products collected between 20 and 100° boiled mainly between 70 and 90°. It appeared to contain only di- and tetra-hydropyrans in addition to a little water. The organic substances were estimated in one of three ways depending on the accuracy desired, each method being checked using authentic mixtures. The most accurate was to weigh the precipitated δ-hydroxyvaleraldehyde 2,4-dinitrophenylhydrazone formed by adding a weighed sample to excess of a saturated solution of the hydrazine in hydrochloric acid (2 *N*); the accuracy was 1% with a mixture of equal amounts of the pyrans. A second method, accurate to 6% with the same mixture of pyrans, was to measure the reduction in weight of a sample (5 cc.) after shaking with hydrochloric acid (2 *N*) saturated with sodium chloride. Shaking and separation were carried out in a micro-separatory funnel. This method was only reliable when the pyrans were present in approximately equal amounts. The third method depended on titration of a sample with bromine (about *M*) dissolved in aqueous acetic acid (50%) containing sodium acetate (5%). The last method was the most rapid but least reliable.

Cyclopentanone was estimated in the material, b. p. above 100°, by measuring the reduction in weight after shaking with excess of saturated sodium bisulfite. The method was accurate to within 5% of the ketone which usually amounted to about half the material. A more accurate method for small quantities depended on precipitation with dinitrophenylhydrazine.

In the experiments with nickel, distillation of the material from the last fraction and insoluble in bisulfite gave a small quantity, b. p. 136–142°, which may have been cyclopentanol. It could not be induced to give a solid dinitrobenzoate and was therefore unidentified.

Experiments with cobalt–copper were carried out over a range of temperatures between 200 and 350°. Cyclopentanone was formed in all the experiments above 250° in amounts similar to those with the cobalt catalyst. Reduction and fission were also observed and the catalyst deteriorated in use.

The nickel–copper catalyst was investigated only at one temperature (275°). Dihydropyran (84 g.) was passed over the catalyst with hydrogen (24 l./hr.) during two hours. The product contained *n*-butane, b. p. 0–2° (6 g.), tetrahydropyran, b. p. 87–89° (44 g.), and cyclopentanone, b. p. 129.5–130.5° (7.5 g.), 2,4-dinitrophenylhydrazone, m. p. 142–143°, m. m. p. with an authentic specimen (m. p. 144–145°) was 142–143°. There was no unsaturated material.

Summary

2,3-Dihydropyran has been shown to undergo three simultaneous reactions when passed with hydrogen over catalysts containing nickel or cobalt at a temperature of 200° or above.

The reactions are (1) reduction to tetrahydropyran, (2) fission to butene, butane and carbon monoxide and (3) rearrangement into cyclopentanone.

The mechanism of the reactions is discussed.

NOTRE DAME, INDIANA RECEIVED AUGUST 18, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. X. Catalytic Reduction of Methylfuran to 2-Pentanone

BY CHRISTOPHER L. WILSON

Reference was made some years ago[1] to the formation of small amounts of 2-pentanone (II) and 2-pentanol (III) during the gas phase reduction of methylfuran (I) to tetrahydromethylfuran (IV). Experiment has now shown that either tetrahydromethylfuran or 2-pentanone can be the major product depending on conditions. Results obtained using a nickel catalyst at various temperatures are shown in the diagram. At 100° the chief product (86% yield) was tetrahydromethylfuran but as the temperature was raised the quantity decreased and ketone appeared in increasing amounts attaining a maximum (yield 75%) at about 185°. Along with the ketone a small quantity of its reduction product, 2-pentanol, was also formed. Below 150° conversion of methylfuran was complete but surprisingly enough a proportion escaped reaction above this temperature. This coincided with the formation of quantities of gaseous products, with a slight increase in the amount of tetrahydromethylfuran and with a rapid drop in ketone production. No adequate explanation of these variations has yet been found but the reason is undoubtedly connected with complex surface conditions. Furthermore, nuclear hydrogenation of methylfuran might be reversible.

Other metallic catalysts such as cobalt and mixtures of nickel, cobalt or iron with copper as well as copper chromite also gave some ketone but a

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[1] French Patent 811,695 (1937).

detailed study of their behavior has not been made.

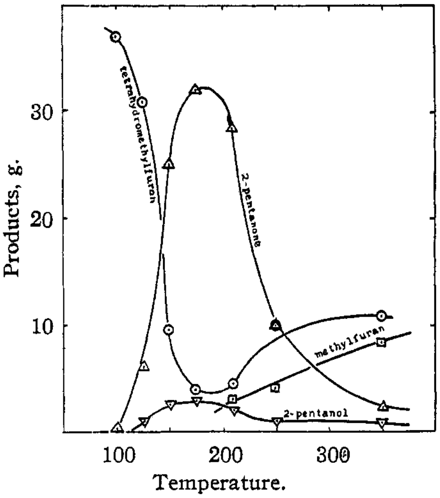
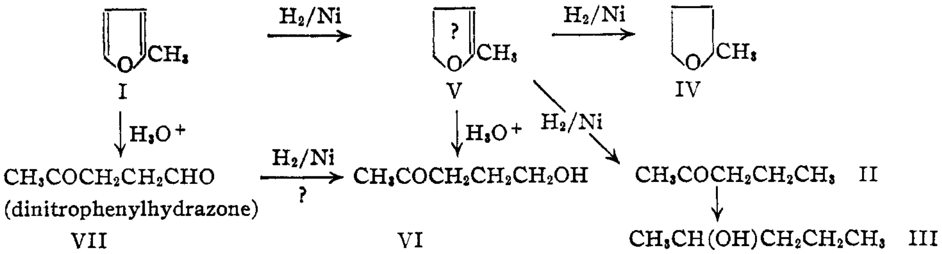


Fig. 1.—Products from methylfuran and hydrogen over a nickel catalyst at various temperatures. Each point corresponds with the passage of 41 g. of methylfuran and 80 liters of hydrogen over the catalyst in two hours.

At present there is little information from which to propose a reaction mechanism. It is particularly uncertain to identify the chemical steps of a catalytic reaction by duplicated experiments with possible intermediates since the conditions on the surface are no longer comparable. Experiment has shown that tetrahydromethylfuran on passage over the catalyst with hydrogen below 200° does not give any ketone. If we ignore the criticism just made of this type of experiment, this fact indicates that ring fission must occur before ring saturation. It may occur therefore either in methylfuran itself or a derived dihydro- compound.



In Part III of this series[2] evidence was presented showing that 2,3-dihydrofuran was much more susceptible to hydrogenative ring fission than either furan or tetrahydrofuran and that the carbon–oxygen bond remote from the carbon double bond was the more readily attacked. Applying these ideas to the reduction of methylfuran would indicate the intermediate formation of an unstable 4,5-dihydromethylfuran (V).

Evidence for the formation of this compound has been presented before[3,4] to account for the formation of some γ-acetopropyl alcohol (VI) during the catalytic reduction of methylfuran in the presence of dilute acid. Presumably dilute acid would hydrolyze 4,5-dihydromethylfuran to acetopropyl alcohol just as it converts 2,3-dihydrofuran into γ-hydroxybutaldehyde.[2]

There still remains the possibility, however, that ring fission occurs in methylfuran itself in the vapor phase by reduction, although the absence of unsaturated products would appear to discount it, and in the experiments in aqueous acid by hydrolysis followed by reduction. In connection with the last point it was shown in the present work during attempts to devise a method for estimating methylfuran that it reacted in the cold with a solution of dinitrophenylhydrazine in dilute hydrochloric acid to give levulinic aldehyde bis-dinitrophenylhydrazone (VII). An analogous reaction is the formation of the dimethylacetal by reaction with methyl alcoholic hydrogen chloride.[5] Levulinic aldehyde might then reduce further to acetopropyl alcohol.

It will be recalled[2] that the reaction of tetrahydrofurfuryl alcohol vapor with a nickel catalyst gave rise to many products including some 2-pentanone. The present work confirms the view then expressed that the ketone arose by fission of methylfuran which was formed from furfuryl alcohol present as an impurity in the commercial tetrahydro-alcohol.

Experimental

Materials.—Methylfuran, b. p. 63–64°, was prepared by reduction of furfuraldehyde using a copper chromite catalyst at 275°. The feed rate was 48 cc. of furfural and 45 liters of hydrogen per hour. The product was distilled, dried over sodium hydroxide and redistilled.

Catalysts.—The description of these excepting iron–copper and pure copper was given in the preceding paper. Iron–copper sintered powder (4% copper, 2200 g., 4–16 mesh) was oxidized at 550° and reduced below 400° giving 64 cc. of water. The pure copper contact material was produced by reducing the granular oxide (1840 g.) below 200°. This metal failed to have any effect on methylfuran either at 280 or 320°. On the other hand, copper chromite gave a 52% yield of 2-pentanone at 340° together with a little pentanol.

Cobalt–copper gave rise to rather more low-boiling materials. The yield of ketone was about 60% at 350°. Iron–copper at 350° gave ketone (4.0 g.), tetrahydro-

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[2] Wilson, *J. Chem. Soc.*, **54** (1945).

[3] Topchiev, *Compt. rend. Acad. Sci., U. R. S. S.*, **19**, 497 (1938); *C. A.*, **32**, 8411 (1938).

[4] Schniepp, Geller and Von Korff, THIS JOURNAL, **69**, 672 (1947).

[5] Harries, *Ber.*, **31**, 41 (1898).

methylfuran (10.8 g.) and unchanged methylfuran (16.1 g.) from an input of 41 g.

Isolation and Analysis of Products.—The products from the reaction chamber were caught in a trap at −78° and freed from water either by filtering with exclusion of atmospheric moisture through a small sintered glass funnel kept very cold or by using anhydrous magnesium sulfate. Distillation was effected at atmospheric pressure with a 12-plate fractionating column. Methylfuran constituted most of the fraction, b. p. 60–70°. The amount was checked by conversion into the maleic anhydride adduct using benzene as solvent. Tetrahydromethylfuran was present in the fraction b. p. 70–90° (most 79–80°); 2-pentanone distilled mainly between 101 and 103°, the fraction being collected between 90 and 110°. This fraction was shaken with saturated aqueous bisulfite and correction applied for the small amount of non-ketonic material. The distillation residue contained 2-pentanol, usually too little for separation by distillation. The material from several experiments was collected, any ketone removed by bisulfite and the material shown by distillation to contain 80% of b. p. 117–120°. The figures for 2-pentanol are perhaps the least accurate of those recorded.

The 2,4-dinitrophenylhydrazone of 2-pentanone after recrystallization from ethyl alcohol had m. p. 146–147°. The 3,5-dinitrobenzoate of 2-pentanol recrystallized from ligroin, b. p. 90–120°, had m. p. 61–62°.

Reduction of 2-Pentanone.—The ketone (15 g.) was passed with hydrogen (15 l./hr.) during thirty minutes over the nickel catalyst at 100°. The product consisted of unchanged pentanone (20 g.) and 2-pentanol (12.3 g.).

Dehydrogenation of 2-Pentanol.—The alcohol (10 g.) was passed over the nickel catalyst at 225° together with hydrogen (30 l./hr.). The product contained 95% ketone. Similar results were obtained at 250°.

Tetrahydromethylfuran.—The cyclic ether, b. p. 80–81° (30 g.), was passed during one hour together with hydrogen (30 l./hr.) over nickel at 250°. No ketone was produced but there was considerable gas formation. At 100° the compound was recovered unchanged.

Reaction of Methylfuran with Dinitrophenylhydrazine.—Methylfuran (1 g.) and 2,4-dinitrophenylhydrazine dissolved in hydrochloric acid (2 *N*) were shaken for several days. The yellow precipitate (1.3 g.) was filtered off, washed with water and hot ethyl alcohol. It was insoluble in all ordinary solvents but was crystallized from dimethylformamide forming dark red prisms, m. p. 231° (dec.).

Anal. Calcd. for $C_{17}H_{16}O_8N_8$: C, 44.3; H, 3.5; N, 24.2. Found: C, 44.4; H, 3.5; N, 24.2.

Acknowledgment.—The author is indebted to M. J. While for help with the experiments and to Revertex, Ltd., in whose laboratories some of the work described in this and the preceding three papers in this series was carried out.

Summary

The variation of products with temperature in the reaction of methylfuran vapor with hydrogen over a nickel catalyst has been studied. At 100° the main product was tetrahydromethylfuran while above this temperature 2-pentanone was formed in large amounts. The yield of ketone was a maximum at 185°. Along with the ketone small amounts of 2-pentanol were also formed and at the higher temperatures quantities of gaseous materials.

Other catalysts containing cobalt, copper and iron also resulted in ketone formation but a detailed study of their behavior was not made.

Notre Dame, Indiana Received August 18, 1947

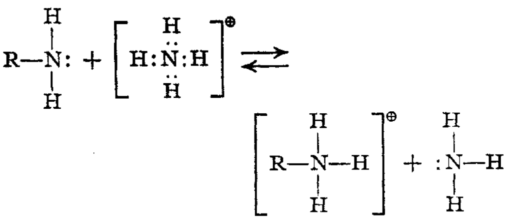
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

A Low Pressure Reductive Alkylation Method for the Conversion of Ketones to Primary Amines[1]

By Elliot R. Alexander and Alice Louise Misegades[2]

It is well known that carbonyl compounds can be hydrogenated in the presence of ammonia to produce mixtures of primary, secondary, and tertiary amines.[3] Originally the reaction was carried out by the hydrogenation of the carbonyl compound in ethanol, saturated with ammonia, at low pressure over a nickel catalyst.[3a] Better yields and more reproducible results, however, have been obtained over Raney nickel with hydrogen pressures of 20 to 150 atmospheres at temperatures ranging from 40 to 150°.[3b,3c] This technique, while readily carried out, requires high pressure apparatus which is not always available. Accordingly, it was the object of this work to improve Mignonac's low pressure reductive alkylation reaction for the preparation of primary amines.

It appeared that this might be done by taking advantage of the fact that a primary amine is more basic than ammonia. If ammonium ions were introduced into the reaction mixture, the following reaction should occur in which the position of equilibrium should favor the products on the right.



$$\mathrm{R{-}\overset{H}{\underset{H}{N}}{:}} + \left[\mathrm{H{:}\overset{H}{\underset{H}{N}}{:}H}\right]^{\oplus} \rightleftarrows \left[\mathrm{R{-}\overset{H}{\underset{H}{N}}{-}H}\right]^{\oplus} + \mathrm{{:}\overset{H}{\underset{H}{N}}{-}H} \qquad (1)$$

Since the alkylammonium ion no longer has an electron pair available for combination with the carbonyl group, the process should tend to stop at the formation of primary amines.

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[1] Taken from a thesis by Alice Louise Misegades submitted to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of bachelor of science.

[2] Present address: Albertus Magnus College, New Haven, Connecticut.

[3] (a) Mignonac, *Compt. rend.*, **172**, 223 (1921); (b) Schwoegler and Adkins, This Journal, **61**, 3499 (1939); (c) Winans, *ibid.*, **61**, 3566 (1939).