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Reactions of Furan Compounds. XIV. Catalytic Preparation of Tetrahydrofuran from Tetrahydrofurfuryl Alcohol

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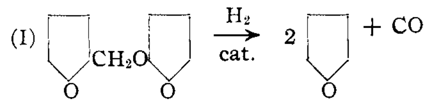
Previous work in this series has shown that the best catalyst for eliminating the side chain of tetrahydrofurfuryl alcohol to give tetrahydrofuran is 44 nickel–copper. A large scale preparation of tetrahydrofuran has now been carried out with this catalyst. Activity was well maintained in four continuous runs, involving in all 186 kg. of tetrahydrofurfuryl alcohol. The yield gradually increased during use and finally attained 85%, the same as that obtained earlier in small scale experiments. Recovered high-boiling material was recycled over the catalyst until no unchanged alcohol remained in it. This increased the amount of pentanoic acid, butyric acid and their esters at the expense of ethers and hydroxypentanoic acid lactone.

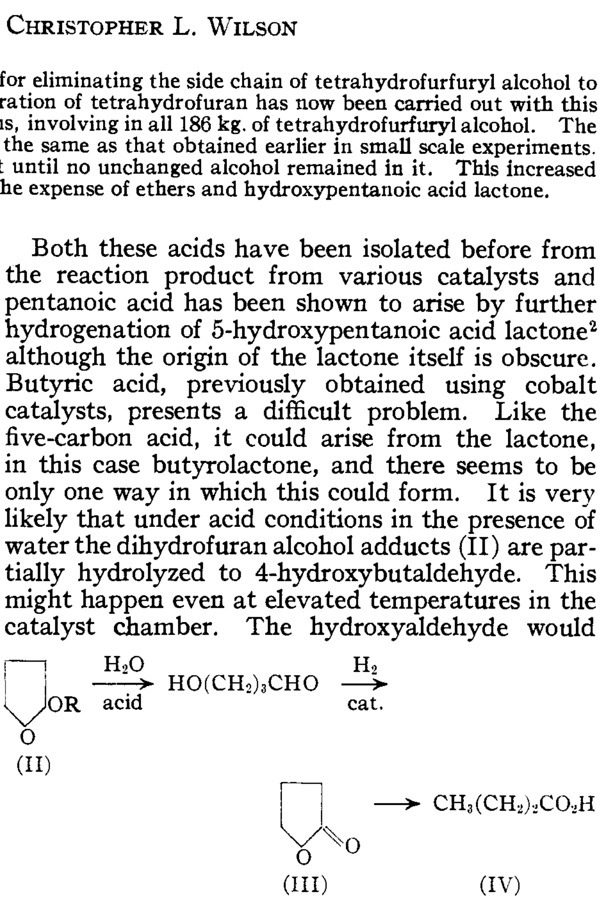
Amongst catalysts containing nickel or cobalt with or without added copper that containing 44 nickel–56 copper was by far the best for converting tetrahydrofurfuryl alcohol into tetrahydrofuran.[1,2] A special apparatus consisting of a tubular iron catalyst chamber has now been constructed and tetrahydrofurfuryl alcohol and hydrogen passed over the sintered 44 nickel catalyst at 240°. The experiments in all consumed 1826 moles of alcohol in four separate runs interspersed with catalyst reactivations. In the first two rate of input was that (alcohol 0.5 mole, hydrogen 22.5 liters per hour) used earlier[2] and in the second and third runs alcohol input was doubled and that of hydrogen halved. This did not seem adversely to affect the yield of tetrahydrofuran, neither did it appreciably enhance the rate of deactivation. Increase of the alcohol input still further, to 2.0 moles per hour, resulted in appreciable catalyst-deterioration over 24 hours so that consumption fell from 85 to 60%.

The yield of tetrahydrofuran in the four runs was 73, 76.3, 77.3 and 80.8%, respectively. The yield was calculated on consumed alcohol but surprisingly enough when the high-boiling residue was recycled over the catalyst until no more alcohol remained the last two figures rose to 82.6 and 85.3%, respectively. The high-boiling material must, therefore, have contained compound or compounds which although reacting negatively toward the acetylation procedure for determination of alcohol did, nevertheless, give rise to tetrahydrofuran when passed over the catalyst. Experiment showed that these compounds were alcohol adducts of 2,3-dihydrofuran. Tetrahydrofuryl tetrahydrofurfuryl ether (I) on passage with hydrogen over the catalyst gave tetrahydrofuran (82.5%) as required by the equation indicated.



When the high boiling residue no longer contained alcohol, it was found to consist solely of butyric and pentanoic acids and their butyl and tetrahydrofurfuryl esters. After complete hydrolysis, the pentanoic acid amounted to about 0.8% yield (pentanoic acid is isomeric with tetrahydrofurfuryl alcohol) and butyric acid about a third of this.

Both these acids have been isolated before from the reaction product from various catalysts and pentanoic acid has been shown to arise by further hydrogenation of 5-hydroxypentanoic acid lactone[2] although the origin of the lactone itself is obscure. Butyric acid, previously obtained using cobalt catalysts, presents a difficult problem. Like the five-carbon acid, it could arise from the lactone, in this case butyrolactone, and there seems to be only one way in which this could form. It is very likely that under acid conditions in the presence of water the dihydrofuran alcohol adducts (II) are partially hydrolyzed to 4-hydroxybutaldehyde. This might happen even at elevated temperatures in the catalyst chamber. The hydroxyaldehyde would then cyclize by dehydrogenation over the catalyst to the lactone (III) and thence to the acid (IV). The analogy for the catalytic cyclization is the known reaction of butanediol over copper catalysts[3] to give butyrolactone. A similar sequence of reactions from dihydropyran might explain the formation of pentanoic acid were it not for the fact that the pyran and its ethers are, unlike dihydrofuran, scarcely detectable and are known to be much less easily hydrolyzed, two facts quite contradictory to the preponderance of the five-carbon acid in the present experiments.



Experimental

I. **Apparatus.**—The iron furnace tube, 60 × 2 in. diameter, constituted the catalyst chamber. Into this was placed 4.5 kg. of granular (4–20 mesh) sintered 44 nickel–copper powders of about 30% porosity. A central axial tube 0.25 in. in diameter served as thermocouple and thermoregulator pocket. The tube was electrically heated in four 12-in. sections, the top one serving as preheater.

The catalyst was activated by oxidation at 500–550° in a stream of air and reduced by hydrogen at a temperature sufficiently low to avoid overheating. Reduction began at 180° and was completed at 320°. The four runs were preceded by activations which gave 828, 860, 680 and 890 cc. of water, respectively.

II. **Operation.**—Technical grade (95.7%) tetrahydrofurfuryl alcohol was added from a large (1.25 liters) con-

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[1] C. L. Wilson, *J. Chem. Soc.*, 52 (1945).

[2] W. H. Bagnall, E. P. Goodings and C. L. Wilson, THIS JOURNAL, **73**, 4794 (1951); E. P. Goodings and C. L. Wilson, *ibid.*, **73**, 4798 (1951).

[3] W. Reppe, H. Kröper and W. Schmidt (to I. G. Farben), German Patent 699,945 (1940); *C. A.*, **35**, 6977 (1941).

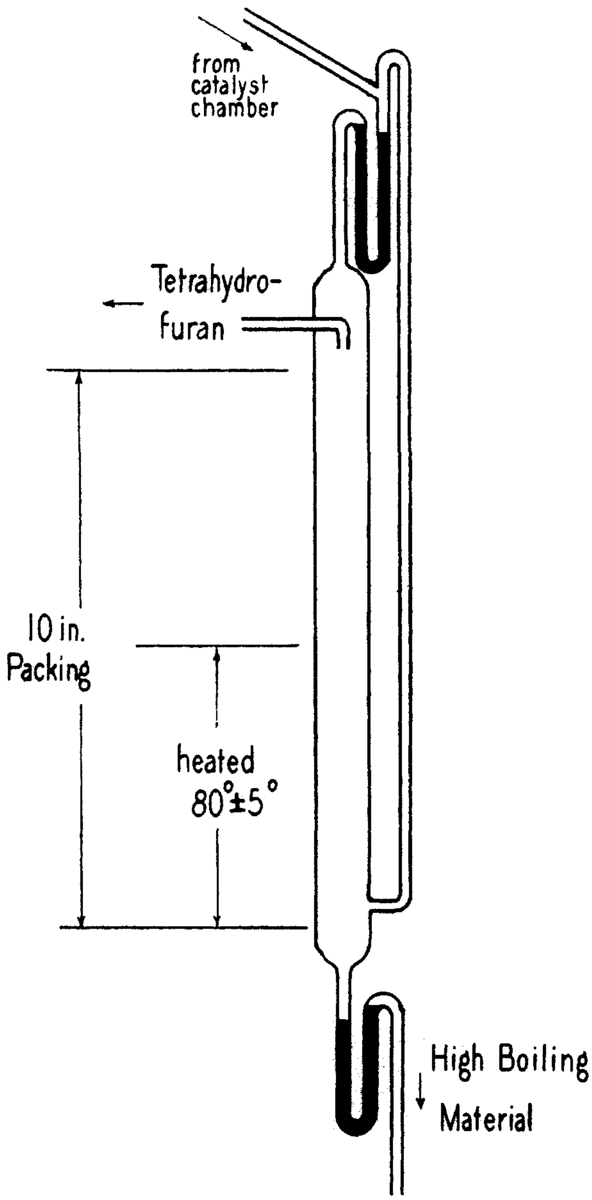

Fig. 1.—Stripper.

stant-head dropping funnel along with hydrogen. The exit (lower) end of the catalyst chamber was connected to a scrubber shown in the diagram. By adjusting the temperature of the lower half, the low-boiling material could be stripped from the high-boiling substances by the gases from the catalyst chamber. At an input rate per hour of 0.5 mole of alcohol and 22.5 liters of hydrogen, the temperature was maintained between 65 and 70°. With rates of 1.0 mole of alcohol and 11.3 liters of hydrogen, the temperature was set at 74–86°. Under these circumstances, the high-boiling material collecting beneath the scrubber contained less than 1.5% tetrahydrofuran. The gases and vapors were passed through first a water condenser, then a Dry Ice-cooled trap to separate tetrahydrofuran. The issuing gases containing mainly hydrogen, carbon monoxide and a little propane were burned.

The four runs involved 642, 284, 210 and 690 moles of alcohol corresponding with 52, 22, 8 and 28 days continuous operation, respectively. The first two runs were carried out at low input and the last two at high input. The first and fourth runs failed owing to catalyst deterioration. In the first, the tube was actually blocked by accumulated high-boiling material on the catalyst. The second and third runs came to a premature end because electrical defects in the relay system allowed an undue rise in catalyst temperature and consequent failure.

During the runs, consumption was kept above 75%. This necessitated a gradual increase in operating temperature which at the outset was 235°. When it had risen to 285°, the yield usually began to fall off slightly and the catalyst was considered expended.

III. **Products.**—The low-boiling fraction contained 91, 88, 92.7 and 91.7% tetrahydrofuran in each of the four runs before further distillation. The impurities were principally water, butanal, 1-butanol and a little furan. 2,3-Dihydrofuran was present only when the catalyst was becoming inactive. It never rose above 2.5%.

Applying a correction for the purity of the input alcohol, the yield of tetrahydrofuran in the four runs was 73, 76.3, 77.3 and 80.0%. In the last two runs the high-boiling material was recycled with hydrogen over the catalyst until no further reaction occurred. This raised the yield in these two runs to 82.6 and 85.3%, respectively.

IV. **Composition of Final Residue.**—The material left (720 g.), after recycling the high-boiling material from passage of 210 moles of alcohol a further three times over the catalyst with 10 l. per hour hydrogen, was refluxed for four hours with 33% sodium hydroxide (1500 cc.). Steam distillation gave some water-insoluble liquid which was separated and dried. It proved to be essentially 1-butanol (47 g.) identified as 3,5-dinitrobenzoate, m.p. 62–64°. The alkaline solution was extracted five times with chloroform which gave tetrahydrofurfuryl alcohol, b.p. 175–178°, (112 g.) and then strongly acidified (Congo red) with hydrochloric acid. The separated upper layer (430 g.) was washed with saturated brine and distilled. The material, b.p. 160–167.5 (54 g.), gave an anilide, m.p. 92.5–94°, identified as that of butyric acid. Redistillation gave a major fraction, b.p. 161.5–162°, which had an equivalent weight by titration of 92 (theory 88) and gave a *p*-bromophenacyl butyrate, m.p. 61.5–63° after recrystallization from methanol. The main fraction had b.p. 175–183° (175 g.) and gave a pentananilide, m.p. 63–64°.

V. **Behavior of Tetrahydrofuryl Tetrahydrofurfuryl Ether over the Catalyst (a) with Hydrogen.**—The ether (86 g.) and carrier (22.5 liters) were passed during one hour over the nickel–copper catalyst at 230°. The product (68 g.) consisted of tetrahydrofuran (54 g.) containing 1.4% dihydrofuran, tetrahydrofurfuryl alcohol (7.5 g.) identified as α-naphthylurethan, m.p. 91.5–92°, and unchanged ether (2.5 g.).

(b) **With Nitrogen.**—The same amounts of input as in (a) gave 60.7 g. of product consisting of tetrahydrofuran (49.6 g.) containing 7.7% dihydrofuran, tetrahydrofurfuryl alcohol (2.2 g.) identified as α-naphthylurethan, m.p. 92.5–93.5, and unchanged ether (0.5 g.).

The derivatives mentioned above were all identified by non-depression of m.p. on admixture with authentic specimens.

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