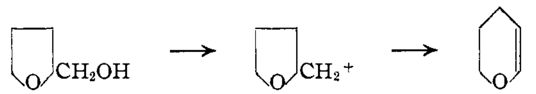
[COMMUNICATION FROM THE UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. XV. Behavior of Tetrahydrofurfuryl Alcohol over Iron–Copper Catalysts[1]

BY HERBERT P. THOMAS AND CHRISTOPHER L. WILSON

It is known that nickel- and cobalt-containing catalysts cause mainly side chain elimination in tetrahydrofurfuryl alcohol but experiments have now shown that iron–copper catalysts give mainly 4-pentenol, 4-pentenal, 2-pentanone, δ-valerolactone and valeric acid without loss of carbon atoms. The first three substances are favored by high iron content of the catalyst and the intermediate formation of methylenetetrahydrofuran is proposed. The lactone and acid are the main products when the catalyst is largely of copper and it is considered likely that tetrahydrofurfural intervenes in their formation.

The behavior of tetrahydrofurfuryl alcohol when the vapor is passed over iron–copper catalysts has not so far been described in this series. This is now remedied. Interest in iron-containing catalysts lies in their effectiveness in hydrogenolizing the alcoholic hydroxyl group as evidenced by the conversion of furfuryl alcohol into methylfuran.[2] Such a reaction is, in part at any rate, akin to a dehydration process and in an alcohol of suitable structure might result in simple loss of water and formation of an olefin. Tetrahydrofurfuryl alcohol (I) is of interest in this respect since dehydration over alumina gives rise to dihydropyran[3] (II), the rearranged olefin. This reaction is most readily explained by intervention of a furfuryl cation (III), rather than a radical since rearrangements are more thoroughly established in such ionic intermediates.



(I) (III) (II)

When passed at 370–390° over a catalyst of 96 iron–copper, tetrahydrofurfuryl alcohol has now been shown to give mainly 4-pentenol, 4-pentenal and 2-pentenone as indicated in the Table I.

TABLE I

COMPOSITION (WT. %) OF DRY PRODUCT FROM IRON–COPPER CATALYST

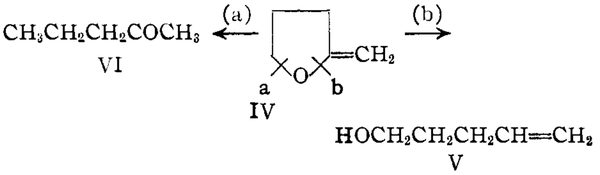
Input rate per hour: 0.5 mole of tetrahydrofurfuryl alcohol, 10 liters of hydrogen

Substance	Catalyst composition (%Fe)		
	96	50	10
Unchanged alcohol	5	36	7.5
4-Pentenol	33	0	0
4-Pentenal	14	19.5	0
2-Pentanone	3	<1	7.7
Cyclopentanone	<1	0.5	0
Pentanoic acid	0	8.0	11.1
5-Hydroxypentanoic acid lactone	2.8	12.7	0
Tetrahydrofurfuryl pentanoate	0	21	48
Recovery of products, %	86	93	97
Reaction temperature, °C.	370–390	300–315	250–290

Although the formation of these substances depends on loss of water, it is clearly different from the reaction occurring when alumina is used[3] unless the dihydropyran reacts further with iron–copper catalysts. Experiment showed that this was not so. Dihydropyran over iron–copper catalysts gives chiefly tetrahydropyran along with a little cyclopentanone. The cyclic ketone is a recognized product of catalytic rearrangement of the pyran.[4] There was no detectable amount of any of the above three open chain C_5 compounds. When the copper content of the catalyst was raised to 50%, more pentenal and less pentenol resulted by reaction of tetrahydrofurfuryl alcohol. This would suggest that the alcohol is the first product and the aldehyde is formed from it by dehydrogenation, a reaction favored by high copper content.

The recovery of material in the catalytic experiments was high and the composition of the product given in the table roughly indicates yield.

Since there is no loss of carbon atoms in the catalytic reactions, the alternatives are simple dehydration or dehydrogenation. The formation of pentenol (V) and 2-pentanone (VI) are most readily accounted for by hydrogenative ring fission of the normal dehydration product, methylenetetrahydrofuran (IV), in the two probable directions (a) and (b).



Methylenetetrahydrofuran, first described by Paul,[5] was prepared by alkaline dehydrohalogenation of tetrahydrofurfuryl bromide, but it is now evident that this material was mainly the isomeric methyldihydrofuran.[6] The methylene compound is stable only when kept free from acidic materials.[6a] At 400°, rearrangement to methyldihydrofuran proceeds.[6a] It is likely, therefore, that under the conditions of the catalytic experiments both isomers were present. Since there is existing evidence to show that methyldihydrofuran splits on hydrogenation wholly to 2-pentanone,[7] the 4-pentenol might arise from the methylene isomer. This could explain why the 96 iron catalyst at 410° instead of 380° gave mainly 2-pentanone instead of 4-pentanol assuming a more complete isomerization before fission at the higher temperature. With reference to the temperature ranges of operation given in the

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(1) Summary given at the A. C. S. Meeting in September, 1950.

(2) Part XI, THIS JOURNAL, **73**, 4790 (1951).

(3) R. Paul, *Bull. soc. chim.*, **53**, 1489 (1933); C. L. Wilson, THIS JOURNAL, **70**, 3004 (1947).

(4) C. L. Wilson, *ibid.*, **70**, 1311 (1948).

(5) R. Paul, *Bull. soc. chim.*, [5] **2**, 745 (1935).

(6) (a) Unpublished work with Dorothy M. Aten. (b) R. Paul has also recently corrected his earlier observations, *Bull. soc. chim.*, [5] **17**, 520 (1950).

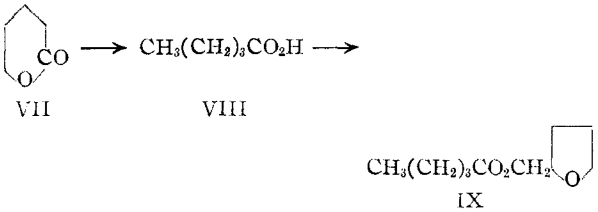
(7) C. L. Wilson, THIS JOURNAL, **70**, 1313 (1948).

table, it should be pointed out that they necessarily differ from catalyst to catalyst because each has an optimum temperature of operation which has to be high enough for appreciable consumption but not too high so that destructive side reactions supervene. It is not possible, therefore, to compare the products from different catalysts operating at the same temperature.

4-Pentenal has been made apparently only once before. Hurd and Pollack[8] obtained it by pyrolysis of allyl vinyl ether. They gave b.p. 103–104°, dinitrophenylhydrazone, m.p. 120°. Our figures were 102–105° and 117–118°, respectively.

As the copper content of the catalyst was raised first to 50 and then to 90%, the formation of carbonyl compounds other than a little 2-pentanone was suppressed. Pentenol also disappeared from the product and instead pentanoic acid and derivatives were formed in major amount. These compounds are not new in this series of papers but have been encountered before, although in small amounts during reaction of tetrahydrofurfuryl alcohol over nickel- and cobalt-containing catalysts.[9]

In this earlier work, it was shown that the lactone (VII) is the parent substance being converted into pentanoic acid (VIII) by further hydrogenation and thence to the ester (IX) by reaction with excess alcohol. There is still no clue to the origin of the lactone itself, but the fact that it is favored by high copper content of the catalyst might indicate a relationship with tetrahydrofurfural with which it is isomeric. Tetrahydrofurfural is the result of a simple dehydrogenation which is facilitated by high copper content.



There were several minor products some of which are indicated in the table. Cyclopentanone is known to result by catalyzed rearrangement of dihydropyran and a little of this substance was isolated from the 50 iron product. The ketone might conceivably also result from vinyl rearrangement of methylenetetrahydrofuran[4] but no evidence for such a change has been found.[6a] A little furan (0.5%), di- and tetrahydrofuran (total 10%) was observed from 10 iron catalyst. These substances are the result of side chain elimination in the familiar manner proceeding through tetrahydrofurfural.

Experimental

I. Apparatus and Procedure.—The following is additional to what is given elsewhere in this series. The figures below record, respectively, the composition of the granulated (4–12 mesh) sintered iron–copper powders (2000 g.) kindly supplied by Metals-Disintegrating Co., Inc., Elizabeth, N.J., the upper limits to the temperatures of oxidation and reduction used in the activation step and the amount of water so produced: 96 iron–copper, 525–550°, 300°, 37 cc.; 50 iron–copper, 450°, 300°, 195 cc.; 500°, 365°, 255 cc.; 10 iron–copper, 450°, 300°, 280 cc.. Hydrogen (10 liters per hour) was added to the input in all experiments and left flowing between runs in order to maintain activity. Tetrahydrofurfuryl alcohol (redistilled) was added at a rate of 0.5 mole per hour.

II. Isolation, Identification and Estimation of Products.—The entire liquid product was distilled through a five-plate column and divided into fractions (1) b.p. below 120°; (2) b.p. 120–150°; (3) b.p. 150–180°; and (4) b.p. above 185°. Fraction (1) contained all the water which was separated and measured after saturation with sodium chloride. Unchanged tetrahydrofurfuryl alcohol was contained in fraction (3) in which it was estimated by acetylation of a sample (0.3–0.5 g.) with acetic anhydride (20% in pyridine) at 100° for 5 min. and back titration with sodium hydroxide solution (0.25 *N*).

2-Pentanone, 4-Pentenal and Cyclopentanone.—Fractions (1) and (2) were shaken separately with sodium bisulfite solution (40%) until no further reduction in volume occurred and the total carbonyl substances determined by precipitation of an aliquot with excess of dinitrophenylhydrazine dissolved in hydrochloric acid (2 *N*). The derivatives were dried at 80°. The carbonyl substances were liberated by neutralization of the bisulfite solution with sodium hydroxide solution (20%) using phenolphthalein, and distilled. The presence of 2-pentanone was shown by separation of an azeotrope with water, b.p. 80–85°; its presence was confirmed by reaction of carbonyl material, b.p. below 110°, with insufficient bisulfite solution which reacted preferentially with the 4-pentenal present. The formation of 2-pentanone was favored by high temperature and high copper content of the catalyst. It was the only detectable carbonyl compound using the 10 iron–copper catalyst. With the 10 iron catalyst, the dinitrophenylhydrazone had m.p. 141–143.5°, mixed m.p. with authentic (m.p. 141–143°) was 141–143°, with 50 iron–copper catalyst the derivative had m.p. 133–135°, mixed m.p. 138–140° and with the 96 iron catalyst m.p. 131–134°, mixed m.p. 137–140°.

Using the 50 iron and the 96 iron catalysts at 375°, the chief carbonyl substance was 4-pentenal, b.p. 102–105°. In the former case, the dinitrophenylhydrazone had m.p. 117–118°, mixed m.p. with authentic 117–118° and in the latter m.p. 111–113°, mixed m.p. 113–114.5°.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.0; H, 4.50; N, 20.01. Found: C, 50.38; H, 4.58; N, 21.21.

The carbonyl substance in fraction (2) was mainly cyclopentanone. The m.ps. of the derivative from 96 iron and 50 iron catalysts were 140–141.5° and 141–143°, respectively. Admixtures with authentic material, m.p. 143–143.5°, showed no depression.

Dihydropyran, Dihydrofuran and Pentenol.—The bisulfite insoluble material from fraction (1) was dried over potassium hydroxide and distilled. The 96 iron catalyst gave very little material of indefinite b.p.; 50 iron–copper yielded a substance, b.p. 80–90°, unsaturated to bromine and shown to be essentially dihydropyran by conversion into 5-hydroxypentanal dinitrophenylhydrazone, m.p. from ethanol 107–108°, mixed m.p. with authentic (m.p. 113–114°), 108–109°. The 10 iron–copper catalyst gave a small amount of a bisulfite-insoluble liquid, b.p. 62–66° containing about 30% of 2,3-dihydrofuran identified by formation of 4-hydroxybutanal dinitrophenylhydrazone, m.p. 118–119°, mixed m.p. with authentic sample (m.p. 116–117°), 116–118°. The remaining 70% was probably tetrahydrofuran judging by the b.p. 64–66°.

The bisulfite insoluble material from fraction (2) was dried over potassium hydroxide and distilled. In the case of the 96 iron catalyst, an appreciable amount of 4-pentenol, b.p. 137–138°, $n^{25}\text{D}$ 1.4290, was obtained.

Anal. Calcd. for $C_5H_{10}O$: C, 69.73; H, 11.70. Found: C, 69.48; H, 11.90.

It was identified by preparation of the 3,5-dinitrobenzoate, m.p. 43.5–45°, mixed m.p. with authentic, 45–46.5°, and by the following reactions.

Oxidation of Catalytic Pentenol to Succinic Acid.—To the alcohol (2 g.), sodium hydroxide (10%, 7 cc.) and water (150 cc.) was added potassium permanganate (18 g.) in small portions with vigorous stirring and cooling to keep the temperature below 60°. After four hours, the precipitated oxide was filtered off and the liquid evaporated at 100° to 30 cc. and cooled. Inorganic salts were separated and the

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[8] Hurd and Pollack, THIS JOURNAL, **60**, 1905 (1938).

[9] Parts XII and XIII, *ibid.*, **73**, 4794, 4798 (1951).

remaining solution acidified and extracted with ether. The extract on evaporation gave succinic acid identified by mixed m.p. both of the acid and its *p*-bromophenacyl ester with authentic specimens.

Reduction of Catalytic Pentenol to Pentanol.—The alcohol (5 g.) was reduced at atmospheric pressure and room temperature using palladium oxide in methanol and hydrogen (1182 cc.). The product, b.p. 136–138°, $n^{27}\text{D}$ 1.4090, gave a 3,5-dinitrobenzoate, m.p. from petroleum ether 45–46°, and an α-naphthylurethan, m.p. 65.5–66.5°. It was identified as 1-pentanol by mixed m.p. of each of the two derivatives with authentic material.

Authentic 4-Pentenol.—Tetrahydrofurfuryl bromide was treated with sodium in ether as described by Paul.[10] The yield of product, b.p. 135–139°, was 70%. The dinitrobenzoate after two crystallizations from petroleum ether had m.p. 46–48°.

Anal. Calcd. for $C_{12}H_{12}N_2O_6$: C, 51.39; H, 4.32; N, 10.00. Found: C, 51.34; H, 3.84; N, 10.32.

Authentic 4-Pentenal.—The alcohol (5 g.) was added slowly to water (60 cc.), potassium dichromate (2 g.) and sulfuric acid (concentrated, 2 cc.) at 50–60°. The distillate gave a dinitrophenylhydrazone which after crystallizing from ethanol had m.p. 116–117.5°.

Pentanoic Acid, 5-Hydroxypentanoic Acid Lactone and Tetrahydrofurfuryl Pentanoate.—These substances were formed in appreciable amounts only with the 50 and 10 iron catalysts. Fractions (3) and (4) contained pentanoic acid, b.p. 180–190°, estimated by titration with standard alkali, extracted from fraction (4) by shaking with excess saturated sodium bicarbonate solution recovered by acidification and identified by preparation of the *p*-bromophenacyl ester. The product from 50 iron catalyst gave a derivative, m.p. 71–72°, mixed m.p. with authentic ester (m.p. 72–73.5°), 72–73.5° and the 10 iron catalyst, m.p. 73–74.5°, mixed m.p. 72.5–73.5°.

In the case of the 96 and 50 iron catalysts, the organic layer left after bicarbonate treatment contained the lactone. It was estimated either by back titration after shaking a sample with excess cold sodium hydroxide (*N*) or by adding liquid ammonia to a sample in toluene solution to precipitate the adduct. This compound served for identification and had m.p. 103.5–105° and 105–106°, respectively, from the two catalysts. The melting point was not depressed by admixture with authentic material (m.p. 108–109°). In the ammonia reaction, it was necessary to use freshly distilled material to ensure the presence of the monomeric lactone. The product, b.p. 220–240°, from the 96 iron catalyst went semi-solid after several months due to formation of the linear polymer. The polymer does not form the characteristic crystalline derivative with ammonia.

With the 50 iron catalyst, the ammonia method gave 12.6% and titration 12.6, 12.7% of the lactone.

After removal of pentanoic acid and the lactone by treatment with cold aqueous alkali the residue from the 50 iron catalyst had b.p. 230–245°. It went slowly into solution on refluxing with 20% sodium hydroxide. Extraction of this solution five times with chloroform gave tetrahydrofurfuryl alcohol, b.p. 175–180°, identified as 3,5-dinitrobenzoate, m.p. 69–72°, mixed m.p. with authentic (m.p. 81–84°), 70–73°. Re-extraction of the acidified aqueous layer with chloroform gave pentanoic acid, b.p. 180–190°, identified as the *p*-bromophenacyl ester. These reactions showed that the high boiling residue was tetrahydrofurfuryl pentanoate. It was quantitatively determined by back-titration after heating a sample (1 g.) with a standard solution of potassium hydroxide in diethylene glycol to boiling for 15 min. After prolonged alkali treatment, the material from the 10 iron catalyst gave a small fraction, b.p. 225–235°. This was probably impure tetrahydrofurfuryl tetrahydrofuryl ether since it gave the dinitrophenylhydrazone of 4-hydroxybutanal, m.p. 118.5–119°, identified by mixed m.p. but the precipitation was not quantitative.

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[10] R. Paul, *Bull. soc. chim.*, [5] **2**, 745 (1935).

[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Studies in the Furan Series. Reactions with Chloral

BY JOE R. WILLARD AND CLIFF S. HAMILTON

Furan and 2-methylfuran have been treated with chloral in the presence of zinc chloride to yield 1-(2-furyl)- and 1-(5-methylfuryl-2)-2,2,2-trichloroethanol, respectively, and the corresponding acetates have been prepared. N,N-Diethyl-2-furamide has been treated with chloral in the presence of concentrated sulfuric acid to give 1-(5-N,N-diethylfuramido-2)-2,2,2-trichloroethanol. Repeated attempts with 2-furanilide with chloral have been unsuccessful. The first furan analog of DDT, 1,1-bis-(5-carbomethoxyfuryl-2)-2,2,2-trichloroethane, has been prepared by condensation of methyl 2-furoate with chloral. The dehydrochlorination and hydrolysis of the latter compound are described. Ultraviolet absorption spectra of representative compounds are presented.

Since the advent of DDT (1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane) as a contact insecticide,[1] many analogous compounds have been prepared and tested; however, little attention has been given, with the exception of the thiophene analogs,[2] to preparation of related compounds containing heterocyclic rings. Therefore, a study of the preparation of some furan analogs was undertaken.

Due to the sensitivity to inorganic acids, which is characteristic of the furan nucleus when stabilizing negative substituents are not present,[3] the usual method of preparation of DDT-type compounds; *viz.*, the condensation of the aromatic hydrocarbon with chloral in the presence of concentrated or fuming sulfuric acid[2,4] would not be applicable to the furan analogs. Studies by Hartough and Kosak[5] indicated that catalytic amounts of anhydrous zinc chloride were effective catalysts in the acylation of furan. While catalytic amounts of zinc chloride were ineffective, furan and 2-methylfuran were found to add to chloral in the presence of molecular quantities of zinc chloride to form the very unstable 1-(2-furyl)-2,2,2-trichloroethanol (I) and 1-(5-methylfuryl-2)-2,2,2-trichloroethanol (III). As was observed by Peters and Fischer[6] in studies on alkyl furylcarbinols, these carbinols could not be esterified by many of the usual acylating agents, such as acetyl chloride, benzoyl chloride and benzoyl chloride in pyridine. Treatment of the carbinols with acetic anhydride in pyridine at room temperature resulted in the

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[1] Muller, U. S. Patent 2,329,074; *C. A.*, **38**, 1056 (1944).

[2] Metcalf and Gunther, THIS JOURNAL, **69**, 2579 (1947); Truitt, Mattison and Richardson, *ibid.*, **70**, 79 (1948); Feeman, Dove and Amstutz, *ibid.*, **70**, 3136 (1948).

[3] Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 142.

[4] Haskelburg and Lavie, THIS JOURNAL, **69**, 2267 (1947); Stephenson and Waters, *J. Chem. Soc.*, 333 (1946).

[5] Hartough and Kosak, THIS JOURNAL, **69**, 1012 (1947).

[6] Peters and Fischer, *ibid.*, **52**, 2079 (1930).