sium iodide to the diketone was added to a solution of phenylmagnesium bromide made from 2 g. of magnesium. After the mixture had been boiled for four hours it was decomposed in the usual manner. By fractional crystallization from acetone–petroleum ether the product was separated into two isomeric glycols. The most soluble fraction crystallized in needles melting at 183–184°. It was identified as the glycol described previously (XI). The less soluble fractions were composed of a different glycol which crystallized in cubes and melted at 173°.

*Anal.* Calcd. for $C_{28}H_{26}O_2$: C, 85.3; H, 6.6. Found: C, 85.0; H, 6.7.

**Methyl α-Methyl-β,β-diphenyl Lactate, IX.**—As the first step of an independent synthesis of the glycol represented by X, slightly more than one equivalent of methyl magnesium iodide was added—in the inverse of the usual order—to a solution of the methyl ester of benzhydryl glyoxylic acid. Only the carbonyl group of the ester entered into the reaction, the yield of pure hydroxy ester being 85%. After recrystallization from ether–petroleum ether it melted at 87–88°.

*Anal.* Calcd. for $C_{17}H_{18}O_3$: C, 75.6; H, 6.7. Found: C, 75.7; H, 6.7.

In the second step of the synthesis the hydroxy ester was boiled with excess of phenylmagnesium bromide for four hours. This reaction also went well. The product was identified as the glycol X and the yield was 75%. The structure of the glycol as well as that of the ketol from which it was obtained therefore cannot be doubted.

**Reaction with Phenylmagnesium Bromide, $(C_6H_5)_2$-$CHC(C_6H_5)OHCOC_6H_5$.**—The usual procedure with 10 g. of the diketone and an excess of the reagent gave 9.5 g. of a product which was identified as the hydroxy ketone by comparison with a sample on hand.

**1,3-Diphenyl-1-chloroindanone-2, XIII.**—In an attempt to rearrange benzoyl diphenyl ethylene oxide to the diketone with hydrogen chloride, the dry gas was passed into a suspension of 20 g. of the oxide in 25 cc. of glacial acetic acid at the temperature of a salt–ice freezing mixture. The solid went into solution, the solution became yellow and by the end of an hour began to deposit a colorless solid. The solid was removed and recrystallized from chloroform and petroleum ether. It separated in six-sided prisms and melted, with decomposition, at 174°.

*Anal.* Calcd. for $C_{21}H_{15}OCl$: C, 79.1; H, 4.7. Found: C, 78.5; H, 5.1.

**Oxidation.**—A solution of 2 g. of the indanone and 1.45 g. of sodium chromate in 10 cc. of glacial acetic acid was warmed on a steam-bath for half an hour, then poured into water and manipulated in the usual manner. The product, which melted at 145–146°, was identified as ortho dibenzoyl benzene by comparison with a sample on hand.

**The Corresponding Ethoxyl Compound.**—As was to be expected, the chloro compound reacts very readily with alcohol and forms the ethoxyl compound. This substance crystallized from alcohol in prisms and melted at 133°.

*Anal.* Calcd. for $C_{23}H_{20}O_2$: C, 84.1; H, 6.1; $OC_2H_5$, 13.7. Found: C, 84.3; H, 6.1; $OC_2H_5$, 13.8.

## Summary

This paper describes the preparation of benzhydryl phenyl diketone and gives an account of its most conspicuous chemical properties—its tautomerism, its acylation and alkylation and its behavior toward bases and Grignard reagents.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 25, 1933

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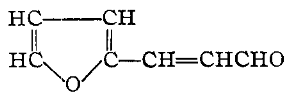
[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

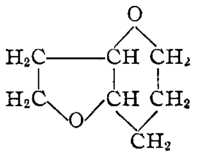
# Hydrogenation and Hydrogenolysis of Furan Derivatives

BY HAROLD E. BURDICK AND HOMER ADKINS

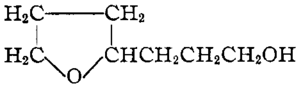
The hydrogenation of β-furylacrolein (I) would presumably result in the formation of 3-tetrahydrofurylpropanol-1 (III). Experiment has shown, however, that there is also produced under certain conditions a hitherto unknown compound to which has been assigned the structure (II), *i. e.*, 1,5-dioxaoctahydroindene. The ratio of the two products varies with a number of factors such as the kind and activity of catalyst, temperature of hydrogenation, etc. However, in nine hydrogenations of from 0.4 to 1.4 moles of β-furylacrolein over Raney nickel at 160° the average yield of the bicyclic compound was about 25% of the theoretical.



I



II



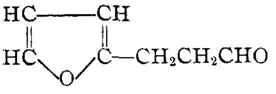
III

The facts on which the conclusion as to the structure of II are based may be summarized as follows: II analyzed to the formula $C_7H_{12}O_2$ and had a molecular refraction corresponding to a compound containing two ether oxygens. II did not react with sodium, acetyl chloride, mild oxidizing agents (Fehling's solution, etc.), or aldehyde and ketone reagents, and was stable in a dilute hydrochloric acid solution. It was not therefore an alcohol, acid, aldehyde, ketone or acetal. II reacted with 48% hydrobromic acid to give a solid whose molecular refraction and analysis showed it to be $C_7H_{12}Br_2O$ and which presumably has the structure

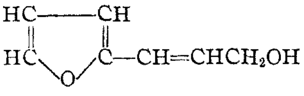
$CH_2CH_2CHBrCHCH_2CH_2CH_2Br$ (O bridging the first and fourth carbons)

The latter in aqueous alcohol was converted into II by the action of a zinc–copper couple. II reacted with hydriodic acid giving a crystalline compound, $C_7H_{12}I_2O$, which upon further treatment with hydriodic acid at 170° in a sealed tube was apparently converted into *n*-heptane although the amount and purity of the hydrocarbon was not such as to make identification certain. II was converted into III by the action of hydrogen over nickel at 200°.

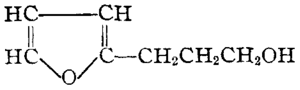
γ-Furylpropionaldehyde (IV), 3-furylallyl alcohol (V), and 3-furylpropanol-1 (VI), might be formed by the hydrogenation of the multiple linkages in the side chain of I and so be intermediates in the formation of II. IV, V and VI have been prepared and submitted to the conditions under which II is formed



IV



V

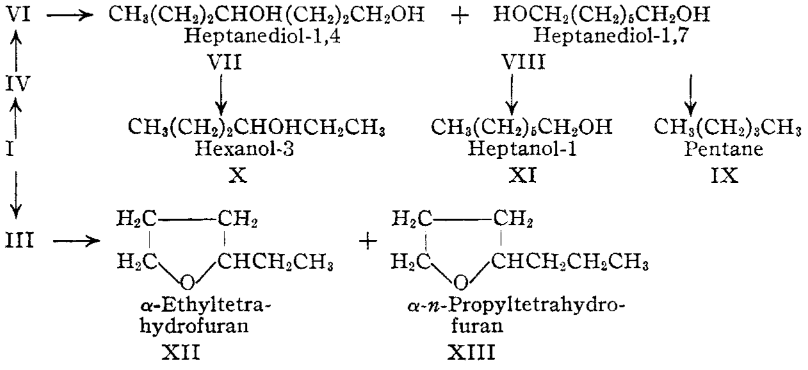


VI

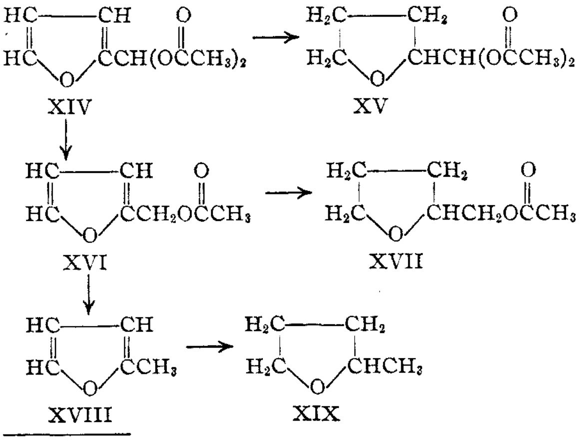
from I. IV gave approximately the same yield of the bicyclic ether (II) as did I, while V gave 4% and VI only a trace of II.

The conclusion seems justified that II is formed primarily from IV. The formation of 4% of II from V is understandable because it is known that catalysts bring about the migration of hydrogen in 2,3-unsaturated alcohols,[1] *i. e.*, $CH_2{=}CHCH_2OH \longrightarrow CH_3CH_2CHO$. (V) could rearrange into IV which then would be converted to II. The formation of II would thus appear to involve an addition between the carbonyl and one of the alkene linkages of the furan ring. A reaction did not take place when β-furylacrolein was heated in the absence of hydrogen or a catalyst but II was formed to a small extent even at room temperature in the presence of hydrogen and nickel or over copper–chromium oxide at 160°.

By suitable control of the time and temperature of reaction and choice of nickel or copper–chromium oxide, I may be hydrogenated satisfactorily not only to II, III, IV or VI but by a combination of hydrogenation and hydrogenolysis may be converted to several other compounds.



I was converted to II in 33% yield over nickel-on-kieselguhr[2] at 160°; to VI in 72% yield over copper–chromium oxide[3] at 120–175°; to IV in 46% yield over Raney nickel[4] at 23°; and to III in 65% yield over Raney nickel at 160°. VI was converted to III in 80% yield over Raney nickel at 160°. I was converted to VII (29%) and VIII (20%) at 200° over copper–chromium oxide. In this latter reduction a small amount of XI accompanied the main reduction products. At 250° over Raney nickel, VII gave a 66% yield of X while VIII under the same conditions gave 21%



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[1] Adkins and Weston, THIS JOURNAL, **50**, 1030 (1928); **51**, 2430 (1929).

[2] Covert, Connor and Adkins, THIS JOURNAL, **54**, 1651 (1932).

[3] Connor, Folkers and Adkins, *ibid.*, **54**, 1139 (1932).

[4] Adkins and Covert, *ibid.*, **54**, 4116 (1932).

IX, and III gave a 60% yield of XII with a little XIII.

Similar reactions were encountered in attempting to convert furfural diacetate (XIV) to tetrahydrofurfuraldehyde. A considerable amount of hydrogenolysis occurred under all conditions studied thus far so that α-methylfuran XVIII and α-methyltetrahydrofuran, XIX, acetic acid, and tetrahydrofurfuryl acetate XVII were produced as well as the desired tetrahydrofurfural diacetate XV.

Under the optimum conditions (160° over nickel-on-kieselguhr) the yield of XV was 24%,[5] while that of XVII was 41%.

TABLE I

CONDITIONS OF HYDROGENATION OR HYDROGENOLYSIS (100–200 ATM.)

| Hydrogen acceptor Name | Moles | Time in hours | Temp., °C. | Catalyst, g. | Products |
|---|---|---|---|---|---|
| β-Furylacrolein | 0.67 | 6.5 | 160 | 4$^{a}$ | α-Ethyl tetrahydrofuran 3%; 1,5-dioxaoctahydroindene 33%; 3-tetrahydrofurylpropanol 38% |
| β-Furylacrolein | .35$^{d}$ | 16.0 | 23 | 4$^{b}$ | β-Furylpropionaldehyde 46%; mixture of 3-furylpropanol and β-furylacrolein 30% |
| β-Furylpropionaldehyde | .33$^{d}$ | 1.0 | 160 | 3$^{a}$ | 1,5-Dioxaoctahydroindene 28%; 3-tetrahydrofurylpropanol 29% |
| β-Furylacrolein | .50$^{d}$ | 5.0 | 160 | 8$^{b}$ | 1,5-Dioxaoctahydroindene 3%; 3-tetrahydrofurylpropanol 65% |
| β-Furylacrolein | .74$^{d}$ | 1.6 | 120–175 | 15$^{c}$ | 1,5-Dioxaoctahydroindene 4%; 3-furylpropanol 72% |
| β-Furylacrolein | 2.00$^{d}$ | 0.25 | 120–175 | 30$^{c}$ | 1,5-Dioxaoctahydroindene 8%; 3-furylpropanol 64% |
| 3-Furylpropanol | 0.21$^{d}$ | 1.5 | 160 | 5$^{b}$ | 3-Tetrahydrofurylpropanol 80% |
| β-Furylacrolein | 2.00$^{d}$ | 9.3 | 200 | 22$^{c}$ | *n*-Heptanol 4%; 3-tetrahydrofurylpropanol 22%; heptanediol-1,4 29%; heptanediol-1,7 20% |
| Heptanediol-1,7 | 0.17 | 6.5 | 250 | 7$^{b}$ | *n*-Pentane 21% |
| Heptanediol-1,4 | .38 | 13.0 | 250 | 10$^{b}$ | Hexanol-3 66% |
| 3-Tetrahydrofurylpropanol | .50 | 5.0 | 250 | 10$^{b}$ | *n*-Pentane 1%; water; α-ethyl tetrahydrofuran 60%; α-*n*-propyltetrahydrofuran 1%; 3-tetrahydrofurylpropanol 9% |
| Furfural diacetate | .49 | 3.5 | 160 | 4$^{a}$ | α-Methyltetrahydrofuran 10%; acetic acid 78%; tetrahydrofurfuryl acetate 41%; tetrahydrofurfural diacetate 24% |
| Furfuryl alcohol | 2.00 | 2.5 | 125 | 3$^{a}$ | Tetrahydrofurfuryl alcohol 85% |
| Furfuroin | .23$^{d}$ | 0.5 | 150 | 5$^{a}$ | 1,2-Dihydroxy-1,2-ditetrahydrofurylethanes 93%; low b. p. isomer 77%; high b. p. isomer 16% |
| Furfuralacetone | .40$^{d}$ | 6.5 | 150 | 4$^{a}$ | 1-Tetrahydrofurylbutanol-3 89% |
| Furfuralacetophenone | .20$^{d}$ | 2.5 | 135 | 2$^{a}$ | 1-Tetrahydrofuryl-3-phenylpropane 31%; 1-tetrahydrofuryl-3-phenylpropanol-3 25% |
| 1-Tetrahydrofuryl-3-phenylpropane | .12 | 0.3 | 200 | 3$^{a}$ | 1-Tetrahydrofuryl-3-cyclohexylpropane 95–100% |
| Ethyl β-furylacrylate | .20$^{d}$ | 2.0 | 120 | 2$^{a}$ | Ethyl β-tetrahydrofurylpropionate 90% |
| 1,5-Dioxaoctahydroindene | .40 | 3.0 | 200 | 3$^{a}$ | 1,5-Dioxaoctahydroindene 32%; 3-tetrahydrofurylpropanol-1 39% |

[a] Nickel on kieselguhr prepared by using ammonium carbonate solution as a precipitant. [b] Raney nickel. [c] Copper–chromium oxide. [d] In ethanol as a solvent.

The reactions described above are, with the exception of the conversion of I to II, in accord with the behavior of compounds with similar structures as previously studied. The cleavage over copper–chromium oxide of the C to O linkages in the furan ring to give glycols (VI to VII and VIII) was observed by Connor.[6] The hydrogenolysis of primary alcohols with the loss of a carbon atom (VIII to IX, VII to X and III to XII) was observed by Wojcik.[7] The readiness of cleavage of C to O linkages in the side chain under the influence of C=C (XIV to XVI, XVI to XVIII) has been known for some time.[8]

In order that the choice of catalysts may not seem arbitrary, it should be pointed out that: Raney nickel is active at low temperatures, especially toward C=C (I to IV) and that either Raney nickel or nickel on kieselguhr are excellent catalysts for the saturation of C=C in the side chain or in an "aromatic" nucleus as in furan, benzene or pyridine (I to III, XIV to XV). Raney nickel is the best catalyst for the cleavage of C to C in primary alcohols (VIII to IX, VII to X, III to XII). Copper–chromium oxide is rather inactive toward the saturation of an "aromatic" nucleus, but is very effective for the cleavage of the ether linkage in furan (VI to VII and VIII), and at lower temperatures for the hydrogenation of multiple linkages in the side

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[5] Scheibler, Sotscheck and Friese [*Ber.*, **57**, 1443 (1924)] reported having obtained XV by hydrogenation of XIV over platinum oxide. They gave a boiling point of 133° (29 mm.), which is much lower than that observed in this Laboratory. They reported having hydrolyzed 10 g. of the diacetate and obtained 6 g. of crude tetrahydrofurfural, a yield which amounts to 120% of the theoretical. We obtained a yield of only 34% in attempting to follow their procedure. Considerable quantities of the aldehyde have been made through the hydrogenation of the ethyl acetal of furfural [Minné and Adkins, THIS JOURNAL, **55**, 299 (1933)].

[6] Adkins and Connor, THIS JOURNAL, **53**, 1093 (1931); **54**, 4688 (1932); Adams and Kaufman [*ibid.*, **45**, 3029 (1923)] observed the cleavage over platinum.

[7] Wojcik and Adkins, *ibid.*, **55**, 1293 (1933).

[8] *Cf.* Covert, Connor and Adkins, *ibid.*, **54**, 1655–1660 (1932).

chain without affecting an "aromatic" nucleus (I to VI).

A number of other derivatives of furfural have been hydrogenated during the course of this investigation but it seems unnecessary to add anything to the data which are given in Table I.

## Experimental

$\beta$-Furylacrolein was prepared by adding acetaldehyde (250 g., 5.7 moles) dropwise to a vigorously agitated solution containing freshly distilled furfural (550 g., 5.7 moles), sodium hydroxide (50 g.), water and crushed ice (5 liters). After standing for one hour without agitation the yellow crystals were filtered, washed with water, sucked dry and distilled. Three hundred and seventy-six grams (53.6%) of product b. p. 94–95° (9 mm.), m. p. 51–52°, was obtained.[9]

Furfural diacetate b. p. 126–129 (12 mm.), m. p. 51–52°, was prepared as by Gilman and Wright.[10]

**Action of Concentrated Hydrobromic and Hydriodic Acids on 1,5-Dioxaoctahydroindene.**—Forty grams (0.312 mole) of 1,5-dioxaoctahydroindene was added to 330 g. of 48% hydrobromic acid. The solution turned dark red and was refluxed for five hours. The heavy oil was drawn off through a separatory funnel, dried with calcium chloride and distilled. The boiling point was 142° (5 mm.) (61.2% yield): $n^{25}_{D}$ 1.5140; $d^{25}_{4}$ 1.6304; $M_D$ calcd. 49.66; found 50.03; m. p. 34°.

*Anal.* Calcd. for $C_7H_{12}OBr_2$: Br, 58.77. Found: Br, 59.24.

Nineteen grams (0.148 mole) of 1,5-dioxaoctahydroindene was added to an excess of constant boiling hydroiodic acid (b. p. 127°; sp. gr. 1.7) and the mixture was heated to boiling. Forty-nine grams (0.134 mole) (87.6% yield) of crystals was obtained which upon recrystallization from ether melted at 45°.

*Anal.* Calcd. for $C_7H_{12}OI_2$: I, 69.37. Found: I, 69.97, 69.64.

The products of reaction (see Table II) were characterized by the formation of solid derivatives where possible and by comparison with the physical properties reported in the literature. In the case of tetrahydrofurfural diacetate and 3-furylallyl alcohol we believe that the boiling points previously reported are incorrect. The analytical data for compounds not hitherto reported are given in Table III.

TABLE II

PHYSICAL CONSTANTS OF PRODUCTS

| Name | B. p., °C. | $n^{25}_{D}$ | $d^{25}_{4}$ | Molecular refraction Calcd. | Found |
|---|---|---|---|---|---|
| $\alpha$-Ethyl tetrahydrofuran[11] | 105–107 (740 mm.) | 1.4145 | 0.8490 | 29.49 | 29.30 |
| 1,5-Dioxaoctahydroindene | 49–50 (10 mm.), 156–157 (740 mm.) | 1.4461 | 1.0314 | 33.49 | 33.12 |
| 3-Tetrahydrofurylpropanol-1[12,13] | 105–106 (10 mm.), 221–224 (741 mm.) | 1.4560 | 1.000 | 35.33 | 35.34 |
| 3-Furylpropanol-1[13] | 93 (10 mm.) | 1.4805 | 1.0548 | 34.64 | 33.98 |
| 3-Furylallyl alcohol[13] | 85–87 (4 mm.) | 1.5518 | 1.1074 | 34.24 | 35.83 |
| Heptanediol-1,4[13] | 127–130 (6 mm.) | 1.4520 | 0.9504 | 37.37 | 37.49 |
| Heptanediol-1,7[14,15] | 148–149 (11 mm.) | 1.4558 | .9570 | 37.37 | 37.46 |
| *n*-Heptanol[16] | 72 (9 mm.), 170–171 (740 mm.) | 1.4237 | .8250 | 35.84 | 35.92 |
| $\beta$-Furylpropionaldehyde[17] | 69–70 (14 mm.), 179–180 (740 mm.) | 1.4470 | 1.0690 | 33.30 | 32.81 |
| $\alpha$-*n*-Propyltetrahydrofuran[18] | 132–133 (739 mm.) | 1.4230 | 0.8533 | 33.91 | 34.06 |
| Hexanol-3[19] | 130–132 (740 mm.) | 1.4180 | | | |
| $\alpha$-Methyltetrahydrofuran[20] | 78–79 (740 mm.) | 1.4034 | | | |
| Tetrahydrofurfuryl acetate[21] | 88–90 (18 mm.), 192–194 (740 mm.) | 1.4350 | 1.0624 | 35.77 | 35.52 |
| Tetrahydrofurfural diacetate[5] | 134–136 (16 mm.) | 1.4398 | 1.1326 | 46.85 | 47.09 |
| Tetrahydrofurfuryl alcohol[22] | 80–82 (20 mm.) | 1.4505 | | | |
| 1,2-Dihydroxy-1,2-ditetrahydrofurylethane[23] | 137–141 (1 mm.), m. p. 75° | | | | |
| 1-Tetrahydrofurylbutanol-3[23] | 95 (6 mm.) | | | | |
| 1-Tetrahydrofuryl-3-phenylpropanol-3[23] | 177–181 (12 mm.) | | | | |
| 1-Tetrahydrofuryl-3-phenylpropane | 160 (28 mm.) | 1.5200 | 0.9795 | 58.24 | 59.01 |
| 1-Tetrahydrofuryl-3-cyclohexylpropane | 121–122 (6 mm.), 150–151 (28 mm.) | 1.4675 | .9135 | 59.42 | 59.63 |
| Ethyl $\beta$-furylacrylate[24] | 132–133 (18 mm.) | | | | |
| Ethyl $\beta$-tetrahydrofurylpropionate[25] | 115–116 (18 mm.) | | | | |

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(9) König and Hey, *Friedlander*, **13**, 110 (1923); *C. A.*, **15**, 2102 (1921).

(10) *Cf.* Gilman and Wright, *Rec. trav. chim.*, **50**, 833 (1931).

(11) Wohlgemuth, *Ann. chim.*, **2**, 430 (1914).

(12) Hamonet, *Ann. chim. phys.*, **10**, 5–30 (1918).

(13) Adams and Bray, THIS JOURNAL, **49**, 2101–2106 (1927).

(14) Müller and Rölz, *Monatsh.*, **48**, 733–736 (1927); m. p. of phenyl urethan, 132°.

(15) Dionneau, *Ann. chim.*, [9] **3**, 248 (1915).

(16) Falk, THIS JOURNAL, **31**, 93 (1909); m. p. of phenyl urethan 59°.

(17) Wienhaus and Leonhardi, *Ber.* Schimmel and Co., 225–232 (1929); m. p. of semicarbazone, 80°.

(18) This compound was also prepared by the reduction of 3-tetrahydrofurylpropylmagnesium chloride.

(19) Oechsner de Coninck, *Bull. soc. chim.*, **25**, 7 (1919).

(20) Bennet and Philip, *J. Chem. Soc.*, 1937 (1928).

(21) Paul, *Compt. rend.*, **193**, 1428 (1931).

(22) Wienhaus, *Ber.*, **53**, 1656 (1920).

(23) Adams and Kaufmann, THIS JOURNAL, **45**, 3029–3044 (1923).

(24) Blumann and Hesse, *Perfumery and Essent. Oil Record*, **22** 382 (1931).

(25) Windaus and Dalmer, *Ber.*, **53**, 2304–2308 (1920).

TABLE III

ANALYSES FOR CARBON AND HYDROGEN

| Name | Molecular formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|
| 1,5-Dioxaoctahydroindene | $C_7H_{12}O_2$ | 65.59 | 65.54 | 9.44 | 9.60 |
| α-*n*-Propyltetrahydrofuran | $C_7H_{14}O$ | 73.63 | 72.70 | 12.36 | 12.41 |
| Tetrahydrofurfural diacetate | $C_9H_{14}O_5$ | 53.46 | 53.28 | 6.98 | 6.92 |
| 1-Tetrahydrofuryl-3-phenylpropane | $C_{13}H_{18}O$ | 82.15 | 82.15 | 9.48 | 9.37 |
| 1-Tetrahydrofuryl-3-cyclohexylpropane | $C_{13}H_{24}O$ | 79.63 | 79.45 | 12.26 | 12.28 |

## Summary

The conversion of various furan derivatives by hydrogen over nickel or copper chromium oxide to a variety of products has been described. Especially noteworthy was the cyclization of β-furylacrolein or β-furylpropionaldehyde to 1,5-dioxaoctahydroindene.

MADISON, WIS. RECEIVED SEPTEMBER 25, 1933

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

# Structure of Reactants and Extent of Acetal Formation. II[1]

BY RALPH E. DUNBAR AND HOMER ADKINS

Originally it was planned to study the effect of modifications in the structure of aldehydes and alcohols upon acetal formation by determining the concentration of an aldehyde at equilibrium with "representative" alcohols, or of alcohols with "representative" aldehydes. The necessity for such a limitation upon the number of reaction mixtures to be studied is obvious when it is noted that 680 acetals might be prepared from the 34 alcohols and 20 aldehydes that so far have been investigated for acetal formation in this Laboratory. Actually 108 of these reactions have been followed and it is not yet certain which are the "representative" aldehydes and alcohols that will best serve as standards for comparison. However, it appears that for present purposes the extent of reaction of the straight chain unsubstituted aldehydes and alcohols with each other may be regarded as the standard; *e. g.*, the average percentage conversion in eight cases of 5 moles of ethyl, propyl, butyl, pentyl or heptyl alcohol with 1 mole of acetaldehyde, propionaldehyde, butyraldehyde or heptaldehyde was 80%. Similarly, for 8 acetals formed from the secondary alcohols propanol-2, butanol-2, pentanol-2 and octanol-2 the percentage conversion at equilibrium was 46%.

The experimental results summarized in Table I are concerned primarily with the behavior of hexahydrobenzaldehyde, cyclopentylaldehyde and trimethylacetaldehyde. Attention was directed

TABLE I

EXTENT OF REACTION OF VARIOUS ALCOHOLS AND ALDEHYDES

| Alcohol | (11 alc. to 1 ald.) % conv. | (11 alc. to 1 ald.) $K$ | (5 alc. to 1 ald.) % conv. | (5 alc. to 1 ald.) $K$ |
|---|---|---|---|---|
| Hexahydrobenzaldehyde | | | | |
| Methanol | 98 | 6.48 | 93 | 6.35 |
| Tetrahydrofurfuryl | .. | ... | 92 | 5.38 |
| 3-Tetrahydrofuryl-propanol-1 | .. | ... | 91 | 4.63 |
| Isoamyl | .. | ... | 88 | 3.15 |
| Cyclohexylcarbinol | .. | ... | 87 | 2.75 |
| Butanol-1 | .. | ... | 80[a] | 1.44 |
| Ethanol | 91 | 1.21 | 78[a] | 1.22 |
| Cyclohexanol | 88 | 0.84 | 75 | 0.96 |
| Octanol-2 | .. | ... | 74 | .88 |
| Cyclopentanol | 60 | .107 | 44 | .101 |
| Propanol-2 | 43 | .037 | 29 | .035 |
| Benzaldehyde | | | | |
| Cyclohexylcarbinol | .. | ... | 35 | .059 |
| Cyclohexanol | 35 | .021 | 23 | .019 |
| Trimethylacetaldehyde | | | | |
| Ethanol | 73 | .25 | 56[b] | ... |
| Cyclohexylcarbinol | 58 | .095 | 42[b] | ... |
| Octanol-2 | 38 | .026 | 26[b] | ... |
| Cyclohexanol | 24 | .007 | 16[b] | ... |
| Propanol-2 | 21 | .006 | 11[b] | ... |
| Cyclopentylaldehyde | | | | |
| Octanol-2 | .. | ... | 50 | .168 |
| Ethanol | 61 | .114 | 45 | .122 |
| Cyclohexylcarbinol | .. | ... | 41 | .092 |
| Cyclohexanol | .. | ... | 35 | .056 |
| Propanol-2 | 19 | .005 | 13[b] | ... |

[a] This value was duplicated by the hydrolysis of the acetal. [b] This value was calculated from the value of $K$ obtained from the percentage conversion at the 11 to 1 ratio of reactants.

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[1] The previous paper of the same title [Minné and Adkins, THIS JOURNAL, **55**, 299 (1933)] gives leading references to earlier papers.