ethanol gave 1.2 g. of colorless crystals which melted at 112–113°. The melting point did not change upon recrystallization.

Anal. Calcd. for $C_{22}H_{25}NO_3$: C, 75.18; H, 7.17. Found: C, 75.20; H, 7.39.

Furanization of VIII to II was accomplished by treating a solution of 1 g. of VIII in 5 ml. of acetic anhydride with 0.17 ml. of sulfuric acid (to bring about salt formation) followed by five drops excess. After twenty minutes the mixture was poured into water, where it was neutralized with sodium carbonate and extracted with ether. Evaporation of the ether extract and crystallization of the residue from ethanol gave colorless crystals (melting at 98–100°) which were shown to be II by a mixture melting point with an authentic sample.

Conversion of 1,2-Dibenzoyl-1-methyl-2-(morpholinylmethyl)-ethylene (VII) to 3-(Hydroxymethyl)-4-(morpholinylmethyl)-2,5-diphenylfuran (I).—Five-tenths gram of VII was dissolved in 100 ml. of 6 *N* hydrochloric acid and the solution was extracted with ether. Neutralization of the acid layer with sodium carbonate gave 0.48 g. of material which melted at 168–172° after recrystallization from ethanol; it showed no depression in a mixture melting point with known 3-(hydroxymethyl)-4-(morpholinylmethyl)-2,5-diphenylfuran (I).

1,2-Dibenzoyl-1,2-di-(morpholinylmethyl)-ethane (IX).—A solution of 1 g. of 1,2-dibenzoyl-1-methyl-2-(morpholinylmethyl)-ethylene (VII) in 10 ml. of morpholine was warmed at 75–80° for twenty-four hours. The solution was then poured into water and extracted with ether. Evaporation yielded 0.98 g. of crystals which melted at 135–140°. Several recrystallizations from ethanol raised the melting point to 141–142°. A mixture melting point with 3,4-di-(morpholinylmethyl)-2,5-diphenylfuran (X)[4] (m. p. 143–144°) was depressed to 125–131°.

Anal. Calcd. for $C_{26}H_{32}N_2O_4$: C, 71.53; H, 7.39. Found: C, 71.56; H, 7.55.

Treatment of this material with 6 *N* hydrochloric acid, followed by neutralization with sodium carbonate, produced no change.

Conversion of 1,2-Dibenzoyl-1,2-di-(morpholinylmethyl)-ethane (IX) to 3,4-Di-(morpholinylmethyl)-2,5-diphenylfuran (X).—To a solution of 0.5 g. of IX in 5 ml. of acetyl chloride was added, dropwise, 0.53 ml. of concd. sulfuric acid. After twenty minutes the dark green solution was poured into water and the resulting solution was neutralized with sodium carbonate. Extraction with ether and evaporation of the ether extract gave 0.41 g. of crystals which melted at 115–122°. Several recrystallizations from ethanol raised the melting point to 143–144°. The material showed no depression in a mixture melting point with known 3,4-di-(morpholinylmethyl)-2,5-diphenylfuran (X),[4] but showed a twenty degree depression in a mixture melting point with starting material (IX).

The Dihydrochloride of IX was made by treating an ether solution of IX with excess ethereal hydrogen chloride. It proved to be difficult to purify because of its great hygroscopic properties; for this same reason, a carbon and hydrogen analysis was not made. Several recrystallizations from acetone by the addition of dry ether gave colorless crystals melting at 120–123°.

Anal. Calcd. for $C_{26}H_{34}Cl_2N_2O_4$: Cl^-, 13.92. Found: Cl^-, 13.75.

The dihydrochloride was converted back to IX by neutralizing an aqueous solution of it with sodium carbonate. The yield was 70% and the melting point after one recrystallization from ethanol was 139–141°. There was no depression in a mixture melting point with known 1,2-dibenzoyl-1,2-di-(morpholinylmethyl)-ethane (IX), but a twenty degree depression was observed with known X.

Summary

A rigorous proof of structure for 3-(hydroxymethyl)-4-(morpholinylmethyl)-2,5-diphenylfuran is presented. 1,2-Dibenzoyl-1-methyl-2-(morpholinylmethyl)-ethylene has been made and found to undergo some interesting reactions. Treatment of the latter with hydrochloric acid, followed by neutralization with sodium carbonate, gives 3-(hydroxymethyl)-4-(morpholinylmethyl)-2,5-diphenylfuran, while treatment with morpholine gives 1,2-dibenzoyl-1,2-di-(morpholinylmethyl)-ethane. Mechanisms are discussed.

AUSTIN, TEXAS RECEIVED OCTOBER 15, 1948

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Hydrogenation Products from Furfuralacetofuran

BY KLIEM ALEXANDER AND GEORGE H. SMITH, JR.

The chalcone-like compound, furfuralacetofuran,[2] represents a little known type of furfural condensation product. It is readily obtainable by condensing furfural with 2-acetylfuran. The latter intermediate is conveniently available by the preparative procedure of Hartough and Kosak.[3] Total hydrogenation of furfural and difurfural ketone and aldehyde condensation products, in which all of the ethylenic, carbonyl and furyl groups were saturated, has been reported by several authors.[4,5] Intermediates prepared by selective hydrogenation of the alkene and carbonyl groups have, however, received much less attention. Adkins and associates[4,6] have shown that by suitable choice of catalyst and other reaction conditions, the alkene, carbonyl, and furan ring groups of β-furylacrolein can be selectively hydrogenated in that order. In this instance they also observed a complicating side reaction involving ring closure of an intermediate, probably β-furylpropionaldehyde, and leading to the bicyclic structure 1,9-dioxa-5-spirononane. More drastic conditions of hydrogenation gave various ring cleavage and other hydrogenolysis products.

In this study procedures were developed for the conversion of furfuralacetofuran (I) to 1,3-di-

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(1) One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

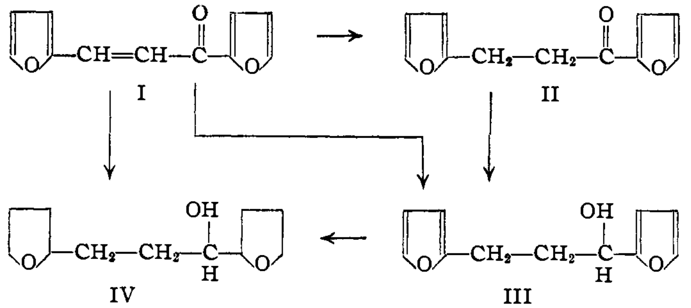
(2) Previously reported by Weygand and Strobelt, *Ber.*, **68**, 1839 (1935).

(3) H. D. Hartough and A. I. Kosak, THIS JOURNAL, **69**, 3093 (1947).

(4) H. Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937.

(5) A. Hinz, G. Meyer and G. Schücking, *Ber.*, **76B**, 676 (1943).

(6) (a) H. E. Burdick and H. Adkins, THIS JOURNAL, **56**, 438 (1934); (b) M. Farlow, H. E. Burdick and H. Adkins, *ibid.*, **56**, 2498 (1934).



furylpropanone-1 (II), 1,3-difurylpropanol-1 (III), and 1,3-ditetrahydrofurylpropanol-1 (IV). With the exception of II → III, which was not attempted, these are stepwise changes as indicated below. A number of trial reactions performed under varying conditions of temperature and catalyst choice served to show that I → IV occurs rapidly and nearly quantitatively with Raney nickel catalyst at temperatures up to 130°. Likewise I → III occurs very rapidly and almost quantitatively at 110–120° with copper–chromium oxide catalyst, the reaction stopping abruptly with the absorption of two moles of hydrogen. Attempts to go from I to III by use of a nickel on kieselguhr catalyst gave confusing results. Of the two moles of hydrogen that would be required for such a change (saturation of the alkene and carbonyl groups), a rapid absorption of about 1.3 moles, apparently, occurred at temperatures in the range 45–65°. At this point absorption became very slow but increased again to a moderate rate in the range 75–100° and continued at a smoothly decreasing rate to nearly complete saturation of the compound. The product, isolated on stopping the reaction when two moles of hydrogen had been absorbed, was a mixture still showing considerable reactivity toward carbonyl reagents.

Conversion of I to II, using nickel on kieselguhr catalyst, was not entirely satisfactory, since, as indicated above, processes other than the simple saturation of an ethylenic bond are evidently taking place during the first rapid absorption of hydrogen.

Consideration has been given to the possibility that cyclization products analogous to those reported by Adkins[6] and others,[5] may have been formed. Careful fractionation of the total reaction mixture resulting from the preparation of IV, however, failed to show any significant amounts of lower boiling components.

Experimental[7]

Catalysts and Apparatus.—The copper–chromium oxide, Raney nickel, and nickel on kieselguhr catalysts employed were prepared according to the procedures of Adkins.[4] All hydrogenations were conducted in a rocker-type, high-pressure hydrogenation bomb assembly.

2-Acetylfuran.—The method of Hartough and Kosak[3] was employed. In agreement with their findings, orthophosphoric acid was the most generally satisfactory catalyst for the acetylation of furan. Yields as high as 77% were obtained from mixtures containing 68 g. (1 mole) of furan and 204 g. (2 moles) of acetic anhydride, to which was added 10 g. of sirupy phosphoric acid (85%). The reaction mixtures were stirred and maintained at 45–60° for one and one-half to two hours.

Furfuralacetofuran (I).—A mixture of water (300 cc.), 95% alcohol (225 cc.), 2-acetylfuran (110 g., 1 mole), and freshly distilled furfural (96 g., 1 mole) was placed in a flask provided with a stirrer and cooled to 5–10° by an ice-bath. To this, with stirring, was added a solution of 50 g. of sodium hydroxide in 150 cc. of water. The temperature rapidly increased to about 25° then gradually fell. When, after six to eight minutes, the temperature had fallen to 10–15°, the ice-bath was removed and stirring continued for three to four hours. The product separated as a crystalline yellow solid. The reaction mixture was cooled in an ice-salt mixture, filtered, and the product washed with water until free of alkali. Crystallization from an alcohol-water mixture, after treatment with activated carbon, gave 168 g. (89% yield) of furfuralacetofuran as pale yellow crystals. The m. p., 89–90°, agrees with that reported by Weygand and Strobelt.[2] *Anal.* Calcd. for $C_{11}H_8O_3$: C, 70.2; H, 4.28. Found: C, 70.3; H, 4.47. The compound is stable, showing no color or other changes on standing for several months.

1,3-Difurylpropanone-1 (II).—Furfuralacetofuran (94 g., 0.5 mole), dissolved in ethanol and the solution made up to a volume of 370 cc., was hydrogenated in the presence of 3 g. of nickel on kieselguhr catalyst at 45–65° (initial hydrogen pressure 1500 p. s. i.) until the pressure drop corresponded to approximately 0.5 mole of hydrogen absorption. This required twenty to thirty minutes. By stopping the reaction at this point 84 g. of a yellow-orange liquid, b. p. 104–110° (0.5 mm.); $n^{27}\text{D}$ 1.5400; d^{27}_{4} 1.1642 was obtained. *Anal.* Calcd. for $C_{11}H_{10}O_3$: C, 69.4; H, 5.29. Found: C, 69.1; H, 5.45. Further distillation indicated a mixture of products but failed to give appreciable separation of them. That the main product is 1,3-difurylpropanone-1 is indicated by the preparation of an oxime and a 2,4-dinitrophenylhydrazone in good yield.

Oxime: colorless needles, m. p. 83–84°. *Anal.* Calcd. for $C_{11}H_{11}O_3N$: N, 6.83. Found: N, 6.82, 6.88.

2,4-Dinitrophenylhydrazone: fine, red needles from ethanol–ethyl acetate mixture, m. p. 157.5–159.5°; yield, 80–85%. *Anal.* Calcd. for $C_{17}H_{14}O_6N_4$: C, 55.2; H, 3.81; N, 15.13. Found: C, 55.15; H, 3.60; N, 15.18.

1,3-Difurylpropanol-1 (III).—Furfuralacetofuran (94 g., 0.5 mole), dissolved in absolute ethanol and the solution, made up to a volume of 370 cc., was hydrogenated in the presence of 4 g. of copper–chromium oxide catalyst. Absorption of hydrogen occurred very rapidly in the temperature range of 90–115° and at pressures of 300–1000 p. s. i. The reaction stopped abruptly when two moles of hydrogen per mole of furfuralacetofuran had been absorbed. Distillation of the product, after removal of catalyst and solvent, gave 87 g. (91% yield) of a nearly colorless liquid, b. p. 99–100° (0.25 mm.); $n^{25}\text{D}$ 1.5133; d^{25}_{4} 1.1388. A sample of this product on further hydrogenation over Raney nickel gave IV in excellent yield. *Anal.* Calcd. for $C_{11}H_{12}O_3$: C, 68.7; H, 6.29. Found: C, 67.4; H, 6.58. This compound formed a 3,5-dinitrobenzoate (colorless, needle crystals from ethanol), m. p. 93.5–94.5°. *Anal.* Calcd. for $C_{18}H_{14}O_8N_2$: C, 56.0; H, 3.65; N, 7.26. Found: C, 55.9; H, 3.48; N, 7.33.

1,3-Ditetrahydrofurylpropanol-1 (IV).—Furfuralacetofuran (62.7 g., 0.333 mole) in 220 cc. of ethanol was hydrogenated in the presence of 5 g. of Raney nickel catalyst at temperatures up to 130°. The initial hydrogen pressure was 1700 p. s. i. Absorption began just above room temperature and was essentially complete (6 moles of hydrogen per mole) in fifty minutes at 130°. Filtration from catalyst, followed by removal of solvent and distillation of the product at reduced pressure, gave 63.2 g. (95% yield)

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(7) All analyses are micro determinations by C. H. Van Etten and Mary B. Wiele of this Laboratory.

of a colorless, somewhat viscous liquid, b. p. 108–112° (0.5 mm.); n^{25}D 1.4727; d^{25}_4 1.0617; *M*D calcd. 52.88; *M*D found, 53.41. It is miscible in all proportions with water and with all the common organic solvents. *Anal.* Calcd. for $C_{11}H_{20}O_3$: C, 66.0; H, 10.05. Found: C, 65.8; H, 10.03.

A 100-g. sample of this product on vacuum fractionation through a Podbielniak semi-micro column was found, except for a 3.3 cc. fore-run, to be homogeneous as regards distillation constants and refractive index.

A liquid benzoate ester was obtained in approximately 70% yield when a 0.25-mole sample was refluxed with excess benzoic acid in dry toluene, with *p*-toluene-sulfonic acid as the catalyst, and the water removed by azeotropic distillation. Its constants were: b. p. 182–183° (0.5 mm.); n^{25}D 1.5158; d^{25}_4 1.1038. A sample of this ester, on alkaline hydrolysis, gave an approximately quantitative recovery of benzoic acid and an oil identical with the above 1,3-ditetrahydrofurylpropanol-1 as shown by density, refractive index, boiling point and solubility behavior. *Anal.* Calcd. for $C_{18}H_{24}O_4$: C, 71.0; H, 7.94; S. E. 304.4. Found: C, 71.0; H, 8.04; S. E., 288, 304, 292.

With 3,5-dinitrobenzoyl chloride in pyridine solution, the alcohol formed a solid derivative, m. p. 93–94° from ethanol. *Anal.* Calcd. for $C_{18}H_{22}O_8N_2$: C, 54.9; H, 5.62; N, 7.10. Found: C, 54.7; H, 5.41; N, 7.18.

This 3,5-dinitrobenzoate ester was different from that of III above, and both of these were different from that of ethanol, as shown by mixed melting point determinations.

Summary

1. Furfuralacetofuran has been obtained in about 90% yield by the alkali-catalyzed condensation of furfural with 2-acetylfuran.

2. Procedures are given for the catalytic hydrogenation of furfuralacetofuran to 1,3-difurylpropanone-1, 1,3-difurylpropanol-1, and 1,3-ditetrahydrofurylpropanol-1. Good yields of these were obtained. These hydrogenation products have been characterized by preparation of several derivatives.

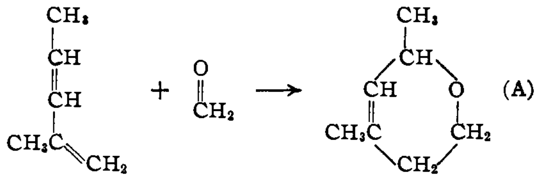
PEORIA, ILLINOIS RECEIVED SEPTEMBER 23, 1948

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

A Diels–Alder Type Reaction with Formaldehyde

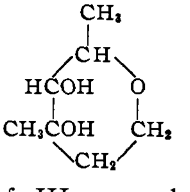
BY THOMAS L. GRESHAM AND THOMAS R. STEADMAN

We wish to report an unusual example of the Diels–Alder reaction,[1] in which formaldehyde (I) participates as a dienophile, reacting (A) with methylpentadiene[2] to yield 2,4-dimethyl-5,6-dihydro-1,2-pyran (III).



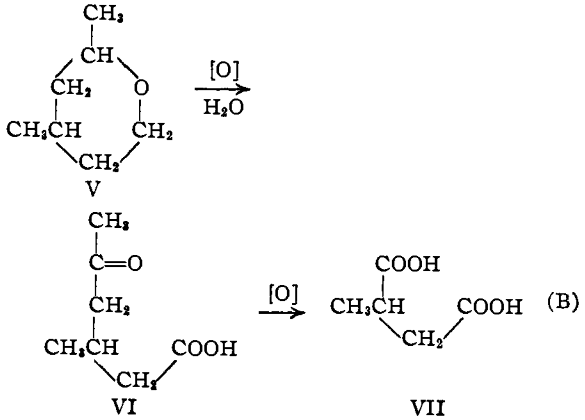
II I III

A solid derivative for III was obtained by hydroxylation of the double bond with either potassium permanganate or *t*-butyl hydroperoxide,[3] yielding *cis*-3,4-dihydroxy-2,4-dimethyl-5,6-dihydro-1,2-pyran (IV).



IV

Hydrogenation of III proceeded readily with either Raney nickel or Adams catalyst, yielding 2,4-dimethyltetrahydropyran (V). Oxidation (B) of V with aqueous chromic acid gave 3-methyl-5-oxohexanoic acid (VI) and methylsuccinic acid (VII) confirming the structure (III) anticipated for the pyran from reaction A on the basis of the respective polarizations of the diene and I. The presence of the isomeric 3,5-dimethyltetrahydropyran should have led to the formation of α,α'-dimethylglutaric acid as well.



VI VII

In a recently issued patent[4] regarding the preparation of II from 2-methyl-2,4-pentanediol, the occurrence of 2,4,6-trimethyl-5,6-dihydro-1,2-pyran among the products was reported. This by-product was considered to have arisen by the reaction of acetaldehyde (formed from the glycol by dehydration and concomitant cleavage) with either an intermediate methylpentenol or II. It seems, therefore, quite probable that in general aldehydes will add to II to yield pyrans. Since we were unable to show that either butadiene or

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(1) Norton, *Chem. Rev.*, **31**, 319 (1942).

(2) The methylpentadiene was a commercially available material obtained from the Shell Development Company, Emeryville, Calif., reported by them to consist of 85% 2-methylpentadiene-1,3 and 15% 4-methylpentadiene-1,3.

(3) Milas and Sussman, THIS JOURNAL, **59**, 2345 (1937); Milas and Harris, *ibid.*, **60**, 2434 (1938).

(4) Schelling and Anderson, U. S. Patent 2,422,802 (1947).