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.

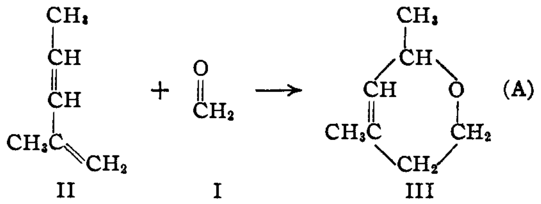
Peoria, Illinois Received September 23, 1948

[Contribution from the B. F. Goodrich Research Center]

A Diels–Alder Type Reaction with Formaldehyde

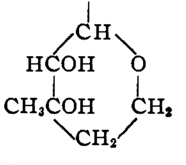
By Thomas L. Gresham and Thomas R. Steadman

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).



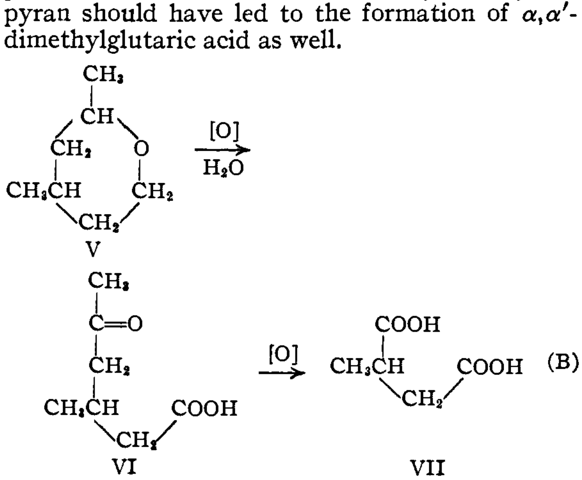
II I III (A)

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.



V VI VII (B)

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).

piperylene would react with I under conditions leading to pyran formation from I and II, we conclude that II is a very active diene in the Diels–Alder synthesis by reason of the favorable polarizing influence of the methyl groups.

Experimental

Formaldehyde and Methylpentadiene—A mixture of 125 g. (1.5 moles) of methylpentadiene and 22.5 g. (0.75 mole) of α-polyoxymethylene was heated in a sealed, stainless steel pressure vessel at 185° for 6.5 hours with agitation. The cooled reaction mixture was dried over anhydrous magnesium sulfate and distilled from a Claisen flask. There was recovered 28 g. (22.5%) of methylpentadiene. A 51.6 g. yield (61.2% yield based on I) of the pyran was obtained: b. p. 125–130° (734 mm.). The properties of a purified sample were: b. p. 126–127° (740 mm.); $n^{30}\text{D}$ 1.4401, d^{30}_4 0.877; *MR*D, calcd. for III, 33.5, obs., 32.9. An examination of the infrared absorption spectrum[5] led to the conclusion that no impurity containing an hydroxyl group was present. From the reaction mixture there was also obtained 27 g. of methylpentadiene dimer, b. p. 110–114° (30 mm.), which accounted for a further 22% of the starting material.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.47, 74.60; H, 10.75, 10.65. Equivalent weight: calcd. for III, 56. Found[6]: 56.0, 57.5 (bromination with pyridine sulfate bromide); 58.3 (hydrogenation over Adams catalyst).

Hydroxylation of III.—To a well-stirred, cooled (15–20°) mixture of 600 ml. of water and 82.5 g. of III was added a solution of 233 g. of potassium permanganate in 3 l. of warm water over a period of three hours. After standing two days at room temperature the reaction mixture was filtered free of the precipitated manganese dioxide and the filtrate evaporated on a steam-bath to a volume of 250 ml. This concentrate was extracted continuously with ether overnight. The ether was distilled from the extract and the residual ether and water removed by distillation with carbon tetrachloride. On cooling, the carbon tetrachloride solution yielded 27.5 g. of crude glycol (IV) (25.6% yield). Recrystallization of crude IV from carbon tetrachloride yielded white crystals, m. p. 74.0–74.5°. On standing for a few days in a vial, the material was found to have changed in melting point: m. p. 90.0–90.5°. By heating this higher melting form for a few minutes above its melting point and allowing crystallization to take place spontaneously, it proved possible to secure the lower melting form.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.55; H, 9.58; mol. wt., 146.2. Found: C, 57.55, 57.40; H, 9.59, 9.62; mol. wt., 144, 141; equivalent weight (neutral sodium periodate), 148, 148.[7]

The same glycol (IV) was obtained by mixing 56 g. (0.5 mole) of III and 90 g. of *t*-butyl hydroperoxide dissolved in 270 g. of anhydrous *t*-butyl alcohol, with 5 ml. of 0.5% osmium tetroxide solution (in *t*-butyl alcohol) as catalyst. After standing six days at room temperature, the reaction mixture was distilled at atmospheric pressure to remove most of the *t*-butyl alcohol. At a pressure of 21 mm., IV distilled as a yellow oil, b. p. 120–130°, which partially solidified on seeding. A recrystallization from carbon tetrachloride gave 5.2 g. of slightly yellow crystals, which after two more recrystallizations melted at 89–91°. The melting point of a mixture with IV obtained by permanganate oxidation showed no depression.

2,4-Dimethyltetrahydropyran (IV).—In the reaction vessel of a Burgess–Parr hydrogenation apparatus was placed 56 g. of III and 13 g. of Raney nickel (moist with ethanol). The theoretically expected amount of hydrogen was absorbed during a period of three hours. Distillation of the filtered reaction mixture gave 47 g. of V, b. p. 116–121° (740 mm.). The infrared absorption curve[5] of the material showed the presence of a small amount of an hydroxyl containing material, arising presumably by hydrogenolysis. This impurity was removed by refluxing the product for two hours with 2 g. of sodium. A sample, distilled from sodium, b. p. 118–119°, had the following physical properties: d^{25}_4 0.8422; $n^{25}\text{D}$ 1.4188; *MR*D, calcd. for IV, 34.0, obs., 34.2.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.78, 73.80; H, 12.20, 12.25.

Oxidation of 2,4-Dimethyltetrahydropyran.—To a mixture of 149 g. of anhydrous sodium dichromate, 750 ml. of water and 224 g. of concentrated sulfuric acid was added 65 g. of V dropwise with good stirring, keeping the temperature of the reaction mixture between 30 and 40° with the aid of a cold-water-bath. When all the V had been added, the reaction mixture was warmed to 50° for one hour and then heated to the reflux temperature for thirty minutes. The unoxidized V was steam-distilled from the reaction mixture (23 g. recovered) and the residue continuously extracted with ether for sixteen hours. The dried extract was boiled down on a steam-bath, yielding a mixture of VI and VII. A portion of this mixture when treated with semicarbazide yielded a semicarbazone, m. p. 169.5–170.5°. This derivative of VI has been previously reported[8] as melting sharply at a temperature between 170° and 174°, depending on the rate of heating.

Anal. Calcd. for $C_8H_{15}N_3O_3$: C, 47.75; H, 7.51; N, 20.88; neutral equivalent, 201.2. Found: C, 47.74, 47.80; H, 7.53, 7.45; N, 20.93, 20.85; neutral equivalent, 196, 198.

Distillation of the crude mixture of acids gave 9.5 g. of an oil, b. p. 137–142° (9 mm.), neutral equivalent 114.6, 114.1. Calcd. for VII, neutral equivalent 66; calcd. for VI, neutral equivalent 144. Therefore, the mixture was 62% VI and 38% VII. On standing for two weeks a crystalline deposit of VII was observed in the distilled mixture of acids, m. p. 109–110° after one recrystallization from chloroform. A mixed melting point with a specimen of methylsuccinic acid obtained by hydrogenation of itaconic acid showed no depression.

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10; neutral equivalent, 66.0; mol. wt., 132.1. Found: C, 45.54, 45.40; H, 6.22, 6.16; neutral equivalent, 67, mol. wt. (ebullioscopic, acetic acid), 130, 134.

Summary

Formaldehyde reacts with 2-methylpentadiene-1,3 to yield 2,4-dimethyl-5,6-dihydro-1,2-pyran.

BRECKSVILLE, OHIO RECEIVED SEPTEMBER 13, 1948

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(5) Data J. J. Shipman.

(6) Analysis by A. K. Kuder.

(7) Analysis by W. P. Tyler.

(8) Auwers and Peters, *Ber.*, **43**, 3091 (1910).