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CATALYTIC SYNTHESIS OF 2-*n*-PROPYL-4-ALKYLTETRAHYDROFURANS

The present article reports on the catalytic synthesis of 2-*n*-propyl-4-alkyltetrahydrofurans from 1-furyl-2-alkylpropan-3-ols. This synthesis further extends the new method we have found for obtaining homologs of tetrahydrofuran on the basis of furfural and aliphatic carbonyl compounds.

In our preceding communication (^{1}) we described the conversion of 1-furylalkan-3-ols into 2-*n*-propyl-5-alkyltetrahydrofurans under hydrogenation conditions over a platinum catalyst in a flow system at ordinary pressure.

$$\text{furyl-CH}_2\text{CH}_2\text{CH(OH)-R} \xrightarrow[220-230^\circ]{\text{H}_2,\ \text{Pt}-\text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{-tetrahydrofuryl-R}$$

The starting compounds—1-furylalkan-3-ols—were obtained by catalytic hydrogenation of furfurylidene ketones, products of the condensation of furfural with aliphatic ketones.

Condensation of furfural with aldehydes, as is evident from the scheme given below, makes it possible to synthesize such dialkyltetrahydrofurans in which one alkyl group is in the β-position:

$$\text{furfural} + \text{H}_2\text{C(R)CHO} \longrightarrow \text{furyl-CH=C(R)-CHO} \xrightarrow{\text{H}_2} \text{furyl-CH}_2\text{-CH(R)-CH}_2\text{OH}$$

$$\xrightarrow[220^\circ]{\text{H}_2,\ \text{Pt}-\text{C}} [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)} - \text{CH(R)} - \text{CH}_2\text{OH}] \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{-4-alkyltetrahydrofuran} + \text{H}_2\text{O}$$

We carried out the condensation of furfural with propionic, butyric, and isovaleric aldehydes. The resulting α-alkyl-β-furylacroleins (I) were reduced to the corresponding 1-furyl-2-alkylpropan-3-ols (II), which were then converted by hydrogenation over platinized charcoal by the flow method into 2-*n*-propyl-4-alkyltetrahydrofurans (III).

Synthesis of α-alkyl-β-furylacroleins (^{2}). To a mixture of 700 ml of water, 300 ml of ethyl alcohol, and 10 g of caustic soda, cooled to 0°, 95 g of furfural was added with stirring, and then, over the course of 4–5 hr, 1.4 gram-moles of aldehyde. After stirring for 1 hr at room temperature, the reaction mixture was neutralized with acetic acid; the dark oil that separated was washed with water and distilled under reduced pressure.

In this way α-methyl-β-furylacrolein (b.p. 92–94° at 8 mm), α-ethyl-β-furylacrolein (b.p. 92–94° at 6 mm), and α-isopropyl-β-furylacrolein (b.p. 89–91° at 5 mm) were obtained in yields of 60–70%.

Hydrogenation of α-alkyl-β-furylacroleins to 1-furyl-2-alkylpropan-3-ols. The α-alkyl-β-furylacroleins were converted, in yields of 75–85%, into the corresponding 1-furyl-2-alkylpropan-3-ols by hydrogenation in the liquid phase at 120–130° over a skeletal Cu—Al catalyst. The catalyst, in the form of small pieces, was prepared by treating a Cu—Al alloy (30% Cu) with a 20% solution of caustic soda, taken in the amount necessary to remove about half of all the alu-

The obtained 1-furyl-2-alkylpropan-3-ols were distilled under reduced pressure and had the following properties:

1-Furyl-2-methylpropan-3-ol, b.p. 72–74° (4); d_4^{20} 1.0243; n_D^{20} 1.4785.
1-Furyl-2-ethylpropan-3-ol, b.p. 81–82° (3); d_4^{20} 1.0059; n_D^{20} 1.4797.
1-Furyl-2-isopropylpropan-3-ol, b.p. 98–99° (4); d_4^{20} 1.0013; n_D^{20} 1.4846.

Conversion of 1-furyl-2-alkylpropan-3-ols into 2-*n*-propyl-4-alkyltetrahydrofurans. 1-Furyl-2-alkylpropan-3-ols were hydrogenated over platinized charcoal in a flow system at ordinary pressure. In this process the indicated alcohols were converted into 2-*n*-propyl-4-alkyltetrahydrofurans. The highest yields of tetrahydrofurans (65–80%) were obtained at temperatures of 215–230°.

The catalyst—platinized charcoal containing 10% platinum—was prepared by impregnating activated charcoal with a solution of chloroplatinic acid and reducing it with hydrogen in the reaction tube at 250–320°. The resulting 2-*n*-propyl-4-alkyltetrahydrofurans were distilled over sodium at ordinary or reduced pressure; they had the following properties:

2-*n*-Propyl-4-methyltetrahydrofuran, b.p. 148–151° (750); n_D^{20} 1.4226; d_4^{20} 0.8463. MR_D found 38.54; for $C_8H_{16}O$, MR_D calculated 38.59.

2-*n*-Propyl-4-ethyltetrahydrofuran, b.p. 63–65° (19); n_D^{20} 1.4280; d_4^{20} 0.8465. MR_D found 43.23; for $C_9H_{18}O$, MR_D calculated 43.21.

2-*n*-Propyl-4-isopropyltetrahydrofuran, b.p. 64–67° (11); n_D^{20} 1.4316; d_4^{20} 0.8478. MR_D found 47.77; for $C_{10}H_{20}O$, MR_D calculated 47.82.

Isomerization of 2-*n*-propyl-4-alkyltetrahydrofurans into aliphatic ketones. Earlier we established (3) that homologs of tetrahydrofuran can isomerize into aliphatic carbonyl compounds in the vapor phase over a platinum catalyst. The obtained 2-*n*-propyl-4-alkyltetrahydrofurans were subjected by us to isomerization over Pt—C in the vapor phase at 300–320°. In agreement with our earlier data (^{3}), it was found that 2-*n*-propyl-4-alkyltetrahydrofurans also isomerize into aliphatic ketones in yields of 80-85%:

$$\text{2-}n\text{-propyl-4-alkyltetrahydrofuran} \xrightarrow[300\text{-}320^\circ]{\text{Pt-C}} CH_3CH_2CH_2-C(=O)-CH_2CH(R)-CH_3, \quad R = CH_3,\ C_2H_5,\ \text{is}$$

The aliphatic ketones formed were isolated from the reaction products by distillation of the catalyzate on a column at normal or reduced pressure. By isomerization of 2-*n*-propyl-4-methyltetrahydrofuran, 2-methylheptan-4-one was obtained, b.p. 154-156°; n_D^{20} 1.4108; d_4^{20} 0.8125. Semicarbazone, m.p. 123-124°. 2-*n*-Propyl-4-ethyltetrahydrofuran as a result of isomerization gave 3-methyloctan-5-one, b.p. 59-60° (10); n_D^{20} 1.4212; d_4^{20} 0.8236. Semicarbazone, m.p. 61-62°. From 2-*n*-propyl-4-isopropyltetrahydrofuran, 2,3-dimethyloctan-5-one was obtained, b.p. 55-56° (4); n_D^{20} 1.4285; d_4^{20} 0.8341.

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Note: Figure translations are in progress. See original paper for figures.

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