Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN, I. F. BELSKII,

and G. K. VASILEVSKAYA

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN,
I. F. BELSKII,
and G. K. VASILEVSKAYA

CATALYTIC CONVERSION OF 2-ALKYL-5-ACYLFURANS INTO ALKYLPHENOLS

The direction of hydrogenolysis of the furan ring in the presence of substituents in the α-position depends on the chemical nature of these substituents. Thus, on one and the same catalyst—Adams platinum—the hydrogenolysis of sylvan and furfuryl alcohol proceeds at the C—O bond not adjacent to the substituent, whereas hydrogenolysis of pyroslijic acid under the same conditions proceeds with cleavage of the C—O bond adjacent to the carboxyl group (1). Hydrogenolysis of 2-alkylfurans on Pt—C in the vapor phase proceeds exclusively at the C —O bond 1,5, with formation of aliphatic ketones (2). Of fundamental interest are the results obtained by us in the hydrogenation of 2-methyl-5-acetylfuran and of the methyl ester of pyroslijic acid on a platinum catalyst (3). In both cases the carbonyl-containing groups exert such an influence that cleavage of the furan ring occurs at the C—O bond adjacent to the carbonyl-containing substituent. In this case methyl butyrate is formed from the methyl ester of pyroslijic acid, while from 2-methyl-5-acetylfuran, depending on the temperature, 3-methylcyclohexanone or *m*-cresol is formed:

$$CH_3-(\text{furan ring})-C(=O)CH_3 \xrightarrow{H_2,\ Pt-C} \text{3-methylcyclohexanone} \quad \text{or} \quad \text{m-cresol}$$

This interesting reaction, as a result of which ketones of the furan series are converted directly into six-membered carbocyclic oxygen-containing compounds, deserves further study. In the present work we investigated the catalytic hydrogenation on Pt—C in a flow system at ordinary pressure of the following alkylacylfurans: 2-acetylfuran, 2-ethyl-5-acetylfuran, 2-methyl-5-propionylfuran, and 2-*n*-propyl-5-acetylfuran. Hydrogenation was carried out at 300–310°.

In all cases, hydrogenolysis of the furan ring proceeded at the C—O bond adjacent to the carbonyl group. The 1,5-diketones formed as intermediates as a result of this underwent cyclization under the conditions of vapor-phase hydrogenation, with formation of homologs of cyclohexanone, which then dehydrogenated into the corresponding homologs of phenol.

Carbocyclization of unsymmetrical 1,5-diketones can, in the general case, lead to the formation of two isomeric phenols, as shown below for the example of the conversion of octane-2,6-dione:

$$\begin{array}{l}\text{2-ethyl-5-acetylfuran}\\ \text{2-methyl-5-propionylfuran}\end{array} \longrightarrow CH_3CH_2COCH_2CH_2CH_2COCH_3 \longrightarrow \left\{\begin{array}{l}\text{ethylphenol}\\ \text{dimethylphenol}\end{array}\right.$$

Hydrogenolysis of 2-ethyl-5-acetylfuran and 2-methyl-5-propionylfuran gives, as the primary product, one and the same diketone, octanedione-2,6, which, upon cyclization with formation of a bond between carbon atoms 1 and 6, gives 3-ethylphenol, and upon formation of a bond between carbon atoms 2 and 7 gives 2,3-dimethylphenol. In an analogous way, 3-*n*-propylphenol and 2-ethyl-3-methylphenol should be formed from 2-*n*-propyl-5-acetylfuran:

$$CH_3CH_2CH_2\text{-furyl-}COCH_3 \longrightarrow CH_3CH_2CH_2COCH_2CH_2CH_2COCH_3 \longrightarrow \left\{\begin{array}{l}\text{3-}C_3H_7\text{-phenol,}\\ \text{2-}C_2H_5\text{-3-}CH_3\text{-phenol.}\end{array}\right.$$

Indeed, as a result of reduction of the phenols formed from 2-methyl-5-propionylfuran and 2-*n*-propyl-5-acetylfuran, the corresponding aromatic hydrocarbons were obtained: in the first case ethylbenzene and *o*-xylene, and in the second *n*-propylbenzene and 1-methyl-2-ethylbenzene. Thus, cyclization of unsymmetrical diketones, formed as intermediates under the conditions of vapor-phase hydrogenation of 2-alkyl-5-acylfurans, proceeds in both possible directions, with final formation in each case of mono- and dialkylphenols.

At the same time, alongside this principal direction of the reaction, to a lesser extent there occurs primary reduction of the carbonyl group with subsequent hydrogenolysis of the furan ring at one of the C—O bonds and formation of the corresponding aliphatic ketones:

$$\text{R-furyl-COR}_1 \xrightarrow{H_2,\ \text{Pt–C}} \text{R-furyl-CH}_2\text{R}_1 \xrightarrow[\text{bond cleavage 1–5}]{\text{bond cleavage 1–2}} \left\{\begin{array}{l}RCH_2CH_2CH_2COCH_2R_1,\\ RCOCH_2CH_2CH_2CH_2R_1.\end{array}\right.$$

Among the compounds investigated, 2-acetylfuran occupies a special place. Its hydrogenolysis at the C—O bond adjacent to the carbonyl group gives a ketoaldehyde, which does not cyclize as a diketone but is completely decarbonylated to pentanone-2:

$$\text{2-acetylfuran} \longrightarrow [\,OHCCH_2CH_2CH_2COCH_3\,] \longrightarrow CH_3CH_2CH_2COCH_3 + CO$$

Experimental Part

The 10% Pt–C catalyst was prepared by impregnating birch activated carbon with a solution of chloroplatinic acid, followed by reduction in a catalytic tube at 300-350°.

The 2-alkyl-5-acylfurans were obtained by acylation of the corresponding alkylfurans with acetic or propionic anhydride in the presence of phosphoric acid (4). They had the following properties:

1. 2-Acetylfuran: b.p. 64-66° (13 mm), m.p. 31-32°.
2. 2-Ethyl-5-acetylfuran: b.p. 93-95° (12 mm), n_D^{20} 1.5067; d_4^{20} 1.0372; semicarbazone: m.p. 167-168°.
3. 2-Methyl-5-propionylfuran: b.p. 100-101° (21 mm), n_D^{20} 1.5063; d_4^{20} 1.0432; semicarbazone: m.p. 155-156°.
4. 2-*n*-Propyl-5-acetylfuran: b.p. 110-112° (20 mm), n_D^{20} 1.5011; d_4^{20} 1.0102; semicarbazone: m.p. 71°.

Hydrogenation of 2-alkyl-5-acylfurans was carried out in a flow system at atmospheric pressure and 300-310°, with a space velocity of 0.1 h^{-1}. The catalyzates were fractionated on an efficient column, first at atmospheric pressure and then under reduced pressure.

From the catalyzates of 2-ethyl-5-acetylfuran and 2-methyl-5-propionylfuran, a fraction was isolated (yield ~ 60%) with b.p. 102-105° (22 mm), 65-67° (3 mm), n_D^{20} 1.5348; d_4^{20} 1.0163, which contained a mixture of 3-ethylphenol and 2,3-dimethylphenol. In addition, the catalyzates contained 2-octanone and 3-octanone (fraction with b.p. 70-71° (22 mm), n_D^{20} 1.4157; d_4^{20} 0.8231, yield ~ 30%) and, in very small amounts, ethylbenzene and *o*-xylene, which were determined spectroscopically.

The major portion (~ 60%) of the catalyzate of 2-*n*-propyl-5-acetylfuran consisted of the phenolic fraction with b.p. 122-123° (17 mm), d_4^{20} 0.9931; n_D^{20} 1.5272. It contained 3-*n*-propylphenol and 3-methyl-2-ethylphenol. Also isolated were 2-nonanone and 3-nonanone in the fraction with b.p. 84-86° (19 mm), n_D^{20} 1.4241; d_4^{20} 0.8281; semicarbazone: m.p. 118-119°. In the fraction with b.p. 71-78° (20 mm), *n*-propylbenzene and 1-methyl-2-ethylbenzene were detected spectroscopically.

The structures of the phenols were determined from the Raman spectra of the corresponding aromatic hydrocarbons, which were obtained as a result of reduction of the phenols in a flow system over Pt-C at 330-350°.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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

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