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Abstract

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Catalytic Transformations of β-Furylpropionic and β-Furylacrylic Acids during Hydrogenation in the Vapor Phase

In the first studies devoted to the catalytic hydrogenation of furancarboxylic acids (pyromucic, β-furylacrylic) and their esters, the reaction was carried out in the liquid phase. The platinum catalyst used in this reaction proved effective both for hydrogenating the furan nucleus to tetrahydrofuran and for its hydrogenolysis ([1,2]). In the case of pyromucic acid, hydrogenolysis proceeds selectively at the C–O bond adjacent to the carboxyl group ([3]). On nickel catalysts, esters of furancarboxylic acids are readily hydrogenated to the corresponding tetrahydrofuran derivatives ([4]). Yu. K. Yur' ev and co-workers succeeded in reducing the furan ring in the molecule of an ester of pyromucic acid by hydrogenation in the vapor phase over a palladium catalyst ([5]). This result is explained by the highly specific action of the palladium catalyst, which, as is known, has an enhanced ability to hydrogenate double bonds in the furan ring. Usually, however, on other metals of Group VIII of the periodic system, hydrogenation in the vapor phase at elevated temperatures proceeds to the greatest extent in the direction of hydrogenolysis of the furan ring.

In our studies, new synthetic possibilities were revealed in the hydrogenation in the vapor phase, over platinum and skeletal nickel–aluminum catalysts, of esters of α-alkyl-β-furylacrylic and propionic acids. Esters of γ-ketocarboxylic acids are formed in high yields ([6,7]). The nature of the transformations depends on temperature. At 300°, the carbalkoxy group undergoes hydrogenolysis with formation of a carboxyl group and an aliphatic hydrocarbon. Cyclization then occurs to a lactone, and the latter is converted, as a result of hydrogenolysis, into a carboxylic acid. Therefore, under these conditions it is not possible to obtain lactones in satisfactory yields. But this result leads to a new formulation of the experiment: the investigation of the catalytic hydrogenation of β-furylacrylic and the corresponding propionic acids at lower temperatures, in order to avoid the secondary reaction of hydrogenolysis of lactones.

In the present work, β-furylacrylic and β-furylpropionic acids were subjected to hydrogenation in the vapor phase over Pt–C at 250, 265, and 300°. In accordance with previously established data on the influence of a carbalkoxy group on the direction of hydrogenolysis of the furan ring, when it is separated from the ring either by a system of single carbon-carbon bonds or by single and double bonds, hydrogenation of β-furylacrylic and β-furylpropionic acids shows a substantial difference in the degree of opening of the furan ring at one or another C–O bond. Hydrogenolysis of the C–O bond not adjacent to the side substituent proceeds more selectively (85-90%) in β-furylpropionic acid, whereas the furan ring in β-furylacrylic acid is opened at both C–O bonds to approximately the same extent. Comparing the action of carboxyl-

···and carboxyl groups on the direction of hydrogenolysis of the furan ring, one can see a noticeable decrease in the electron-withdrawing influence of the carboxyl group, which, in the hydrogenation of esters of β-furylacrylic acids, causes hydrogenolysis of the furan ring at the C–O bond adjacent to the substituent by 35-40%.

Hydrogenolysis of the furan ring in β-furylacrylic and β-furylpropionic acids leads to the same primary products. Cleavage of bond 1,5 gives γ-ketoenanthic acid, while cleavage of bond 1,2, after decarbonylation of the intermediate aldehydo acid, leads to the formation of caproic acid:

$$\text{(2-furyl)-}CH_2CH_2COOH \longrightarrow \begin{cases} CH_3CH_2CH_2C(=O)CH_2CH_2COOH, \\ [OHCCH_2CH_2CH_2CH_2CH_2COOH] \longrightarrow CH_3CH_2CH_2CH_2CH_2COOH + CO \end{cases}$$

γ-Ketoenanthic acid, to a greater or lesser extent depending on the temperature, cyclizes to an unsaturated lactone, which under hydrogenation conditions is converted into a saturated lactone:

$$CH_3CH_2CH_2C(=O)CH_2CH_2COOH \longrightarrow \begin{bmatrix} \text{unsaturated lactone} \\ C_3H_7\text{-substituted} \end{bmatrix} \xrightarrow{H_2} \text{5-propylbutyrolactone.}$$

This scheme shows that unsaturated lactones should be obtained in the greatest amount when the reaction is carried out under conditions of hydrogen deficiency; in this case, hydrogenolysis should apparently be conducted at high space velocities. Indeed, in the catalyst fraction with b.p. 88-90° at 7 mm and n_D^{20} 1.4320, obtained under these conditions, the presence of a lactone group and an unsaturated bond was proved by spectral methods. However, the unsaturated lactones could not be isolated in pure form.

Raising the temperature of the experiment is accompanied by a number of side reactions. At 300° 5-propylbutyrolactone undergoes hydrogenolysis with formation of enanthic acid; the latter and γ-ketoenanthic acid decarboxylate with formation of n-hexane and hexan-3-one; β-furylpropionic acid decarboxylates and, after hydrogenolysis of the intermediate ethylfuran, is also converted into hexan-3-one:

$$\text{5-propylbutyrolactone} \xrightarrow{H_2} CH_3CH_2CH_2CH_2CH_2CH_2COOH$$

$$CH_3CH_2CH_2CH_2CH_2CH_2COOH \xrightarrow{-CO_2} CH_3CH_2CH_2CH_2CH_2CH_3$$

$$CH_3CH_2CH_2C(=O)CH_2CH_2COOH \xrightarrow{-CO_2} CH_3CH_2CH_2C(=O)CH_2CH_3$$

$$\text{(2-furyl)-}CH_2CH_2COOH \xrightarrow{-CO_2} [\text{2-ethylfuran}] \longrightarrow CH_3CH_2CH_2C(=O)CH_2CH_3.$$

The greatest amount of 5-propylbutyrolactone is formed at 250° (52%), and of γ-ketoenanthic acid at 265° (42%).

Experimental Part

β-Furylacrylic acid was obtained according to the following scheme (^{8}):

$$\text{furfural} + CH_3COOK \longrightarrow \text{furyl-CH=CHCOOK} \longrightarrow \text{furyl-CH=CHCOOH}$$

β-Furylpropionic acid was obtained by hydrogenating β-furylacrylic acid in the presence of skeletal Ni–Al and Cu–Al catalysts in an autoclave in an alcohol medium at 70-80° in the former case and at 130-140° in the latter. β-Furylpropionic acid was obtained in yields of 65-70% and 55-60%, respectively. In addition, 25-30% of the ethyl ester of β-furylpropionic acid was also obtained. β-Furylpropionic acid had b.p. 134-136° at 12 mm and m.p. 58°.

Skeletal Ni–Al and Cu–Al catalysts and platinized carbon were prepared by the method described by us earlier (^{9}).

Table 1

Hydrogenolysis of β-furylpropionic acid on Pt–C (5% Pt)

Temp., °C	Space velocity, h^{-1}	Molar ratio of starting material to H_2	Catalyst yield, %	Degree of conversion, %	Hexanone-3	Caproic acid	5-Propylbutyrolactone	γ-Ketoenanthic acid
250	0.1	1 : 4	95.8	100	–	12.7	52.0	21.7
265	0.1	1 : 4	91.0	100	12.7	9.3	20.4	45.6
265	0.3	1 : 1.5	88.2	88.9	4.1	8.8	15.3	37.8
275	0.3	1 : 1.5	94.0	96.3	8.3	9.4	13.2	44.5
300	0.1	1 : 4	81.7	100	19.5	14.6	29.8	–
265*	0.1	1 : 5	80.6	100	14.6	40.0	30.0	9.0

* This line gives data on the hydrogenolysis of β-furylacrylic acid on Pt–C.

Hydrogenolysis of β-furylpropionic and β-furylacrylic acids. β-Furylpropionic and β-furylacrylic acids were passed over a catalyst–platinized carbon (5% platinum)–placed in a quartz tube at the temperatures and space velocities indicated in Table 1. The hydrogen flow rate was measured with a rheometer. The catalyzates were distilled on an efficient column in vacuum. During distillation the following were isolated: *n*-hexane with b.p. 68-70° and n_D^{20} 1.3839, identified by gas-liquid chromatography; hexanone-3 with b.p. 123° (752 mm), n_D^{20} 1.4000, d_4^{20} 0.8128, whose semicarbazone melted at 110° (from ethanol); 5-propylbutyrolactone with b.p. 112.5-113.5° (14 mm), n_D^{20} 1.4385 and d_4^{20} 0.9768; enanthic acid with b.p. 104° (7 mm), n_D^{20} 1.4232 and d_4^{20} 0.9182; and γ-ketoenanthic acid with m.p. 47-48° (from petroleum ether).

Caproic acid is constantly accompanied by impurities of the unsaturated lactone. The fraction with b.p. 88-90° (7 mm) contained, as shown by titration with alkali, 85% acid and had n_D^{20} 1.4229, d_4^{20} 0.9400.

The results of the experiments are given in Table 1.

On the basis of all the above, the following conclusions can be drawn: the hydrogenolysis in the vapor phase on platinized carbon of β-furylpropionic acid at 250, 265, 275, and 300° and of β-furylacrylic acid at 265° was investigated.

Hydrogenolysis of the furan ring in β-furylpropionic acid proceeds mainly at the C–O bond remote from the side substituent. The principal products are γ-ketoenanthic acid and 5-propylbutyrolactone.

Hydrogenolysis of β-furylacrylic acid proceeds at both ether bonds of the furan nucleus to approximately the same extent, as a result of which camphoric acid and 5-propylbutyrolactone are formed.

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