CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. Shuikin, V. M. Shostakovskii,

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. Shuikin,
V. M. Shostakovskii,
I. F. Bel’ skii

CATALYTIC ISOMERIZATION OF ESTERS OF β-TETRAHYDROFURYLPROPIONIC ACIDS

In our previous work, a new method was found for the synthesis of esters of γ-ketocarboxylic acids by catalytic hydrogenation in the vapor phase of esters of β-furylacrylic and β-furylpropionic acids. On a platinum catalyst, hydrogenolysis of the C—O bond not adjacent to the substituent takes place, and esters of γ-ketoenanthic acid and its α-alkyl-substituted homologs are formed (⁀1). On a skeletal nickel-aluminum catalyst, coupled hydrogenolysis of the furan ring occurs, and esters of levulinic, γ-ketocaproic, and γ-ketoenanthic acids are formed (⁀2).

It is known that formation of the propylcarbonyl group is possible both as a result of hydrogenolysis of the furan nucleus and as a result of isomerization of the tetrahydrofuran ring (⁀3). It therefore appears possible to carry out a catalytic synthesis of esters of γ-ketoenanthic acids and their α-homologs by applying the isomerization reaction of the corresponding esters of β-tetrahydrofurylpropionic acids. This reaction has been studied in the present work with respect to esters of β-tetrahydrofurylpropionic and α-methyl- and α-ethyl-β-tetrahydrofurylpropionic acids. The isomerization was carried out in the vapor phase over platinized carbon at 250–300°.

Opening of the tetrahydrofuran ring under these conditions proceeds in both directions to approximately the same extent. As a result of cleavage of the C—O bond 1,5, esters of γ-ketoenanthic acids are obtained, while cleavage of the C—O bond 1,2 gives esters of caproic acids (as a result of decarbonylation of the aldehydo-acid esters):

[scheme]

$$R = H,\ CH_3 \text{ and } C_2H_5$$
$$R' = CH_3 \text{ and } C_2H_5$$

Compared with hydrogenolysis of the furan ring, the isomerization reaction of the tetrahydrofuran ring proceeds with greater difficulty and at higher temperatures. Therefore, in our experiments the conversion of esters of

β-tetrahydrofurylpropionic acids was incomplete and amounted to 20–25% at 250°, and 60–65% at 275°. At 275° the yield of esters of γ-ketoenanthic acids was 40%, and that of esters of caproic acids 25%.

Since the isomerization reaction proceeds at higher temperatures than hydrogenolysis, and the catalyst contains a certain amount of adsorbed hydrogen, the principal reaction—isomerization of esters of β-tetrahydrofurylpropionic acids—is accompanied by a number of side processes, especially noticeable at 300° (overall conversion 75%). The main

a side reaction is hydrogenolysis of the carbalkoxy group, cyclization of the resulting γ-keto acid to a lactone, and hydrogenolysis of the latter to a carbonyl acid (^{1}).

Experimental Part

Ethyl ester of β-furylacrylic acid and methyl esters of α-methyl- and α-ethyl-β-furylacrylic acids were synthesized by condensation of furfural with ethyl acetate, methyl propionate, or methyl butyrate, respectively (^{4}).

Ethyl ester of β-tetrahydrofurylpropionic acid and methyl esters of α-methyl- and α-ethyl-β-tetrahydrofurylpropionic acids were obtained by hydrogenating the esters of the corresponding β-furylacrylic acids in an autoclave in the presence of Raney nickel in ethyl alcohol solution, first at 100°, and then at 150°.

Ethyl ester of β-tetrahydrofurylpropionic acid, b.p. 95—96° (7 mm), n_D^{20} 1.4404, d_4^{20} 1.0142; MR_D 44.78; $C_9H_{16}O_3$, calculated MR_D 44.85.

Methyl ester of α-methyl-β-tetrahydrofurylpropionic acid, b.p. 102—103° (14 mm), n_D^{20} 1.4418, d_4^{20} 1.0149, MR_D 44.87; $C_9H_{16}O_3$, calculated MR_D 44.85.

Methyl ester of α-ethyl-β-tetrahydrofurylpropionic acid, b.p. 100—101° (7 mm), n_D^{20} 1.4428, d_4^{20} 0.9975; MR_D 49.48; $C_{10}H_{18}O_3$, calculated MR_D 49.47.

The catalyst—platinized carbon—was prepared by impregnating activated birch charcoal with an aqueous solution of the calculated amount of chloroplatinic acid while cooling with ice, followed by reduction with 30% formalin in an alkaline medium. Excess KOH was removed by acidifying with hydrochloric acid to a weakly acidic reaction to Congo red. The catalyst obtained contained 5% finely dispersed platinum.

After each experiment the catalyst was regenerated in a stream of hydrogen at 275—300°.

Isomerization of the esters of β-tetrahydrofurylpropionic acids was carried out in the vapor phase over Pt—C at 250, 275, and 300°. The starting material was passed through at a space velocity of 0.1 h^{-1}. The catalyzates, dried by distillation on an efficient column, were separated into fractions corresponding to the individual substances.

Analysis of the fractions was carried out by gas-liquid chromatography on a 2.5 m column at 145°. Polyethylene glycol succinate (10%) deposited on Chromosorb W was used as the stationary phase. The carrier gas was helium.

From the catalyzates obtained by isomerization of 1) ethyl ester of β-tetrahydrofurylpropionic acid, 2) methyl ester of α-methyl-β-tetrahydrofurylpropionic acid, and 3) methyl ester of α-ethyl-β-tetrahydrofurylpropionic acid, the following were isolated, respectively:

1. Ethyl ester of caproic acid, b.p. 168° (750 mm), n_D^{20} 1.4073. Ethyl ester of γ-ketoenanthic acid, b.p. 111–112° (18 mm), n_D^{20} 1.4310.
2. Methyl ester of α-methylcaproic acid, b.p. 59–60° (17 mm), n_D^{20} 1.4090. Methyl ester of α-methyl-γ-ketoenanthic acid, b.p. 95–96° (11 mm), n_D^{20} 1.4320.
3. Methyl ester of α-ethylcaproic acid, b.p. 69–70° (17 mm), n_D^{20} 1.4149. Methyl ester of α-ethyl-γ-ketoenanthic acid, b.p. 104–105° (9 mm), n_D^{20} 1.4365.

On the basis of the foregoing, the following conclusions may be drawn: esters of β-tetrahydrofurylpropionic acids over Pt–C at 275° are isomerized

with ring opening at the C–O bond not adjacent to the substituent, into esters of γ-ketoenanthic acids.

Opening of the ring at the other C–O bond, together with decarbonylation of the intermediately formed esters of aldehyde acids, leads to the formation of esters of caproic acids.

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

Received
16 III 1964

REFERENCES CITED

1. I. F. Bel' skii, N. I. Shuikin et al., ZhOKh, **32**, 1030 (1962).
2. I. F. Bel' skii, N. I. Shuikin, V. M. Shostakovskii, DAN, **152**, 862 (1963).
3. N. I. Shuikin, I. F. Bel' skii, DAN, **120**, 548 (1958).
4. A. Hinz, G. Meyer, G. Schücking, Ber., **76B**, 676 (1943).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.