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Abstract

Full Text

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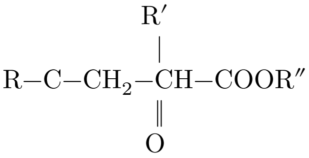
Catalytic Synthesis of Esters of γ-Ketocarboxylic Acids by the Method of Conjugated Hydrogenolysis

The new method of catalytic synthesis of esters of γ-ketocarboxylic acids described in our work[1] is based on the reaction of hydrogenolysis of the furan ring in esters of β-furylacrylic and β-furylpropionic acids. In this process, hydrogenation over Pt–C in the vapor phase makes it possible to obtain esters of γ-ketoenanthic acid and its α-alkyl-substituted homologs, as a result of hydrogenolysis of the furan ring at the C–O bond not adjacent to the side substituent.

As is known, the furan ring, in addition to hydrogenolysis at the C–O bond, can undergo so-called conjugated hydrogenolysis, in which simultaneous ruptures occur in pairs of three bonds: 1,5–4,5 and 1,5–3,4, as well as the C–O bond 1–5.

As a result, propyl, ethyl, and methyl groups are formed from the carbon atoms of the furan ring[2]. Hence it is clear how important conjugated hydrogenolysis is for synthesis based on furan compounds. In particular, its application to esters of β-furylpropionic acids (IV) opens the possibility of obtaining esters of γ-ketocarboxylic acids of three series: levulinic (V), γ-ketocaproic (VI), and γ-ketoenanthic (VII). Thus, if the formula of an ester of an α-substituted γ-ketocarboxylic acid is considered in general form as



$$R-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R'}{|}}{CH}-COOR''$$

then conjugated hydrogenolysis makes it possible to vary the structure of the radical R, changing its length from C_1 to C_3, while the structure of the radical

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[1] Reference number as printed in the source.

[2] Reference number as printed in the source.

R′ is determined by the structure of the ester of a carboxylic acid (II) taken into condensation with furfural (I):

$$\begin{array}{ccccccc} \text{(I)} & + & \text{(II)} & \longrightarrow & \text{(III)} & \xrightarrow[\text{Cu–Al}]{H_2} & \\ \text{furfural} & + & R'CH_2COOR'' & \longrightarrow & \text{furylidene ester} & \longrightarrow & \text{(IV)} \end{array}$$

$$\text{(IV)} \xrightarrow[\text{Ni–Al}]{H_2} \begin{cases} \xrightarrow{1,5-3,4} CH_3C(O)CH_2CH(R')COOR'' & \text{(V)} \\ \xrightarrow{1,5-4,5} CH_3CH_2C(O)CH_2CH(R')COOR'' & \text{(VI)} \\ \xrightarrow{1-5} CH_3CH_2CH_2C(O)CH_2CH(R')COOR'' & \text{(VII)} \end{cases}$$

In the present work, conjugated hydrogenolysis was investigated using two representatives of esters of β-furylpropionic acids and an ester of β-furylacrylic acid. Ethyl acetate (II, R = H) and methyl propionate (II, R = CH_3) were taken into condensation with furfural (I). The resulting condensation products—esters of β-furylacrylic acids

(III), as a result of selective hydrogenation of the double bond in the side chain, were converted into the corresponding esters of β-furylpropionic acids (IV), and the latter, upon hydrogenation in the vapor phase over a skeletal Ni—Al catalyst at 240°, underwent conjugated hydrogenolysis.

From ethyl β-furylpropionate (IV, R = H), the ethyl esters of levulinic (V, R = H), γ-ketocaproic (VI, R = H), and γ-ketoenanthic (VII, R = H) acids were obtained. From methyl α-methyl-β-furylpropionate (IV, R = CH_3), the methyl esters of α-methyllevulinic (V, R = CH_3), α-methyl-γ-ketocaproic (VI, R = CH_3), and α-methyl-γ-ketoenanthic (VII, R = CH_3) acids were obtained. In both cases the yields of the esters of levulinic, γ-ketocaproic, and γ-ketoenanthic acids were, respectively, 35, 20, and 35–40%. Thus, the same relative susceptibility to conjugated hydrogenolysis of the 1—5, 4—5, and 3—4 bonds is observed here as occurs in α-homologs of furan (^{2}) and furan alcohols (^{3}).

Esters of β-furylacrylic acids can also undergo conjugated hydrogenolysis. The hydrogenolysis products are obtained in the same quantitative ratio as in the case of esters of β-furylpropionic acids.

Experimental Part

Synthesis of starting substances. Ethyl β-furylacrylate and methyl α-methyl-β-furylacrylate were obtained by condensation of furfural with ethyl acetate or methyl propionate in the presence

Table 1

Properties of esters of γ-keto acids

Esters of γ-keto acids	Yield, %	B.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated
$CH_3C(=O)CH_2CH_2COOC_2H_5$	35	81—81.5 (10)	1.0112	1.4248	36.43	36.19
$CH_3CH_2C(=O)CH_2CH_2COOC_2H_5$	21	110—111 (16)	1.0013	1.4299	40.80	40.80
$CH_3CH_2CH_2C(=O)CH_2CH_2COOC_2H_5$	40	93 (5)	0.9801	1.4310	45.47	45.43
$CH_3C(=O)CH_2CH(CH_3)COOCH_3$	35	85—87 (15)	1.0089	1.4270	36.64	36.19
$CH_3CH_2C(=O)CH_2CH(CH_3)COOCH_3$	21	103—105 (20)	1.0005	1.4306	40.89	40.80
$CH_3CH_2CH_2C(=O)CH_2CH(CH_3)COOCH_3$	35	95—96 (11)	0.9790	1.4320	45.62	45.43

of metallic sodium by the method described by Hinz and co-workers (^{4}). Upon hydrogenation of the esters of β-furylacrylic acids in an autoclave over a skeletal copper-aluminum catalyst at 130°, ethyl β-furylpropionate was obtained, b.p. 94—95° (10 mm); n_D^{20} 1.4590, d_4^{20} 1.0562; MR_D 43.53. $C_9H_{12}O_3$. Calculated: MR_D 43.93, and methyl α-methyl-β-furylpropionate, b.p. 104—105° (15 mm); n_D^{20} 1.4560; d_4^{20} 1.0438; MR_D 43.80. $C_9H_{12}O_3$. Calculated: MR_D 43.93.

Catalysts. Skeletal Cu—Al and Ni—Al catalysts were prepared by leaching out part (about 50%) of the aluminum from copper-aluminum and nickel-aluminum alloys with a 10% sodium hydroxide solution, after which the catalysts were washed with water until neutral to phenolphthalein.

Experimental conditions. Conjugate hydrogenolysis of esters of β-furylacrylic, β-furylpropionic, and α-methyl-β-furylpropionic acids was carried out on a skeletal Ni—Al catalyst in the vapor phase at normal pressure in an excess of hydrogen at 235-245°. The starting material was fed into the catalytic tube at a space velocity of 0.1 h^{-1}. The catalyzates were dried with ignited magnesium sulfate and distilled at reduced pressure on an efficient column. The physical properties of the resulting esters of γ-keto acids are given in Table 1.

During hydrogenation of esters of β-furylacrylic and β-furylpropionic acids in the vapor phase on a skeletal Ni—Al catalyst at 240°, conjugate hydrogenolysis of the furan ring takes place, as a result of which the corresponding esters of levulinic, γ-ketocaproic, and γ-ketoenanthic acids are formed.

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