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Catalytic Hydroxycarbonylation of Isobutylene with Carbon Monoxide and Polyhydric Alcohols in the Presence of the Pd(acac)$_2$–PPh$_3$–TsOH System

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Abstract—The reaction of isobutylene hydroalcoxycarbonylation with CO and polyhydric alcohols (ethylene glycol, glycerol) in the presence of the catalytic system Pd(aacac)$_2$–PPh$_3$–TsOH has been investigated. It was found that carbonylation of isobutylene with CO in the presence of ethylene glycol yields a mixture of mono- and diglycol esters of isovaleric acid, irrespective of the initial reactant ratio. During the hydroalcoxycarbonylation of isobutylene with glycerol, either mono- and di- or mono-, di-, and triglycerides of isovaleric acid are formed depending on the reactant ratio.

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INTRODUCTION

Isobutylene as an accessible and inexpensive feedstock is of interest for synthesis of many practically useful compounds. Isobutylene carbonylation with carbon monoxide and alcohols under the conditions of homogeneous catalysis by transition metal complexes is an effective process for the manufacture of isovaleric acid esters, which exhibit biological activity and are used as ingredients of pharmaceuticals (validol, valocordin, etc.) [1].

It should be noted that, in all available works on the synthesis of carboxylic acids esters via the olefin hydroxycarbonylation reaction, short-chain monohydric aliphatic alcohols are mainly used as alcoholic reagents [2]. There is one communication on the synthesis of phenylcarboxylates via hydrophenoxycarbonylation [3]. Adaptation of this method to polyhydric alcohols with the purpose of production of carboxylic acid polyol esters is certainly of considerable practical interest. For example, the esters have found wide application as plasticizers, components of pharmaceuticals and cosmetics, wetting and emulsifying agents, etc. [4]. There is also a brief record of the use of palladium complexes [5] and several patents of the Japanese group [6–8] in which two-component catalytic systems based on cobalt, nickel, or rhodium chlorides; carboxylates; and carbonates and pyridine are claimed.

The purpose of the present work was investigation of the isobutylene hydroxycarbonylation reaction with carbon monoxide and polyhydric alcohols (ethylene glycol, glycerol) in the presence of the catalytic system Pd(Acac)$_2$–PPh$_3$–TsOH.

EXPERIMENTAL

A 0.035-g portion of Pd(acac)$_2$ (1.1×10^{-4} mol), 0.212 g (8.085×10^{-4} mol) of PPh$_3$, 0.263 g (1.386×10^{-3} mol) of TsOH, and 3.94 g (6.35×10^{-2} mol) of ethylene glycol or 5.858 g (6.35×10^{-2} mol) of glycerol were loaded into a 150-ml steel autoclave. The autoclave was hermetically closed, purged twice with CO for the removal of air from the system, and then filled with carbon monoxide up to a pressure of 1.0–1.1 MPa. Then, a calculated quantity of isobutylene (one- or twofold quantity relative to ethylene glycol; one-, two-, or threefold quantity relative to glycerol) was introduced into the autoclave, and the carbon monoxide pressure was increased to 2.0 MPa. Stirring and heating were switched on. The reaction mixture was stirred within 4 h at a temperature of 100°C and a pressure of 2.0 MPa. Then the autoclave was allowed to cool down to a room temperature and left for a night. The next day, after the pressure was released to atmospheric, the reaction mixture was fractionated in vacuo (1 mmHg). The desired products were separated from the obtained mixture of products with unreacted polyols by means of column adsorption chromatography on silica gel (0.005–0.04 mm). Chloroform and a chloroform : methanol blend (9 : 1 by volume) were used as eluents. The identity of the obtained products was determined by means of thin-layer chromatography, elemental analysis, and IR-spectroscopy.

The purity of the products was determined by thin-layer chromatography on Silufol (Czech Republic) in a chloroform : methanol (9 : 1 by volume) system of solvents or in chloroform. IR spectra were obtained for liquid compounds on a Nicolet 5700 spectrophotometer.

Isovaleric acid monoglycol ester. R_f = 0.22 (Silufol; CH_3Cl). Found, %: C 57.60; H 9.78. Calculated for $C_7H_{14}O_3$, %: C 57.5; H 9.7.

Isovaleric acid diglycol ester. R_f 0.52 (Silufol; CH_3Cl). Found, %: C 61.76; H 9.4. Calculated for $C_{12}H_{22}O_4$, %: C 62.6; H 9.6.

Isovaleric acid α-monoglyceride. R_f = Œ.39 ($CHCl_3$: CH_3OH = 9 : 1). Found, %: C 53.60, H 9.16. Calculated for $C_8H_{16}O_4$, %: C 54.53; H 9.15.

Isovaleric acid α,α'-diglyceride. R_f = 0.68 ($CHCl_3$: CH_3OH = 9 : 1). Found, %: C 59.99; H 9.29. Calculated for $C_{13}H_{24}O_5$, %: C 59.98; H 9.29.

Isovaleric acid triglyceride. R_f = 1.13 ($CHCl_3$: CH_3OH = 9 : 1). Found, %: C 63.00; H 9.44. Calculated for $C_{18}H_{32}O_6$, %: C 62.77; H 9.36.

RESULTS AND DISCUSSION

It was found that carbonylation of isobutylene by carbon monoxide in the presence of ethylene glycol and the catalytic system $Pd(Acac)_2$–PPh_3–TsOH does not depend on the ratio of the reactants (isobutylene, ethylene glycol) and yields a mixture of mono- and diglycol esters of isovaleric acid.

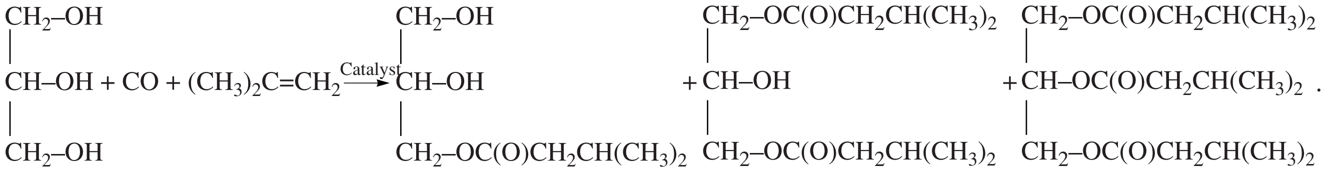
$$(CH_3)_2C{=}CH_2 + CO + HOCH_2CH_2OH \xrightarrow{\text{Catalyst}} (CH_3)_2CHCH_2C(O)OCH_2CH_2OH$$

$$+ (CH_3)_2CHCH_2C(O)OCH_2CH_2O(O)CCH_2CH(CH_3)_2$$

Catalyst = $Pd(Acac)_2$–PPh_3–TsO

At an [isobutylene] : [ethylene glycol] ratio of 1 : 1, mono- and disubstituted esters of ethylene glycol are formed with yields of 35.8 and 12.9%, respectively. At [isobutylene] : [ethylene glycol] = 2 : 1, the yield of monoglycol ester is 9.9% and that of diglycol ester of isovaleric acid amounts to 24.1%.

The IR spectra of the synthesized isovaleric acid glycol esters display typical absorption bands of esters: the intense carbonyl band at 1736.5 cm^{-1} (monoglycol ester) and 1739.1 cm^{-1} (diglycol ester), as well as the "ester band" (vibrations of the ester C–O–C group) at 1193.8 cm^{-1} (monoglycol ester) and 1189.7 cm^{-1} (diglycol ester). For monoglycol ester of isovaleric acid, there is an absorption band at 1098 cm^{-1} characteristic of a primary hydroxyl group of alcohols, as well as a broad absorption band of associated hydroxyl group at 3300–3500 cm^{-1}.



$$\begin{array}{l} CH_2\text{–}OH \\ | \\ CH\text{–}OH \\ | \\ CH_2\text{–}OH \end{array} + CO + (CH_3)_2C{=}CH_2 \xrightarrow{\text{Catalyst}} \begin{array}{l} CH_2\text{–}OH \\ | \\ CH\text{–}OH \\ | \\ CH_2\text{–}OC(O)CH_2CH(CH_3)_2 \end{array} + \begin{array}{l} CH_2\text{–}OC(O)CH_2CH(CH_3)_2 \\ | \\ CH\text{–}OH \\ | \\ CH_2\text{–}OC(O)CH_2CH(CH_3)_2 \end{array} + \begin{array}{l} CH_2\text{–}OC(O)CH_2CH(CH_3)_2 \\ | \\ CH\text{–}OC(O)CH_2CH(CH_3)_2 \\ | \\ CH_2\text{–}OC(O)CH_2CH(CH_3)_2 \end{array} .$$

Carbonylation of isobutylene with carbon monoxide in the presence of glycerol and the catalyst system $Pd(Acac)_2$–PPh_3–TsOH proceeds in several steps. According to available data, the secondary hydroxyl group of glycerol reacts more slowly than a primary one. At ratios of [isobutylene] : [glycerol] = 1 : 1 and 2 : 1, mono- and diglycerides are formed, and mono-, di-and triglycerides are formed when the ratio is 1 : 3. The maximum total yield of glycerides (23.3 %) was obtained at a ratio of [isobutylene] : [glycerol] = 2 : 1; the yields of monoglyceride and diglyceride make up 19.1 and 4.2%, respectively, in this case. The yields of mono-and diglycerides at [isobutylene] : [glycerol] = 1 : 1 are 9.3 and 1.1%, respectively. At a ratio of [isobutylene] : [glycerol] = 3 : 1, mono-, di-, and triglycerides were obtained with yields of 14.7, 3.0, and 0.4%, respectively.

Note that, in contrast to the known processes for the manufacture of glycerides of fatty acids by the direct esterification of the acids with glycerol and by transesterification of methyl (or ethyl) esters of fatty acids with glycerol when a mixture of α- and β-isomers of monoglycerides is formed [9, 10], the formation of the [alpha]-isomer alone is observed during the hydroxycarbonylation of isobutylene with carbon monoxide and glycerol.

The IR spectra of isovaleric acid glycerides are characterized by typical absorption bands of esters: the carbonyl band at 1735–1740 cm^{-1} and the "ester band" (stretching vibrations of the ester C–O–C group) at 1188–1191 cm^{-1}. For monoglyceride and diglyceride, there are absorption bands at 1051 and 1121 cm^{-1}, which are characteristic of primary and secondary alcoholic hydroxyls, and a broad absorption band of associated hydroxyl groups in the range of 3403–3466 cm^{-1}.

Thus, the feasibility of the synthesis of isovaleric acid esters with aliphatic polyols by means of alkoxycarbonylation of isobutylene in the presence of the catalytic system $Pd(Acac)_2$–PPh_3–TsOH was established. The reaction proceeds regioselectively at the terminal atom of isobutylene. Isovaleric acid monoglyceride is formed only in the form of the α-isomer.

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