

1737  $\text{cm}^{-1}$  and C–O–C stretching vibrations at 1033–1300  $\text{cm}^{-1}$ ) and of the CH, CH<sub>2</sub>, and CH<sub>3</sub> groups ( $\approx$ 729, 1300–1462, 2800–3000  $\text{cm}^{-1}$ ). The <sup>1</sup>H NMR parameters (CDCl<sub>3</sub>) of the products of hexene-1 hydroethoxycarbonylation corresponded to the linear product containing the admixture of the branched one. The most weak-field range of the spectrum contained a quartet at 4.12 ppm ( $J = 7.3$  Hz) assigned to the methylene group of the ethyl substituent. The protons of the adjacent methyl group resonated at 1.25 ppm (triplet,  $J = 7.3$  Hz). The most upfield range of the spectrum contained the signals of the methyl group of the acid part (0.88 ppm, triplet,  $J = 5.3$  Hz). The protons of the methylene group adjacent to the carbonyl one were found at 2.28 ppm (triplet,  $J = 7.3$  Hz). The multiplet at 1.62 ppm was assigned to the methylene protons at the C<sup>5</sup> atom; other methylene groups (those at the C<sup>2</sup>, C<sup>3</sup>, and C<sup>4</sup> atoms) were assigned to the multiplet around 1.29 ppm. The admixture of the branched isomer (ethyl  $\alpha$ -methylcapronate) was identified by the presence of the doublet signal of the methyl groups at the C<sup>5</sup> atom at 1.13 ppm ( $J = 6.8$  Hz) and the multiplet signal of the methine proton at the C<sup>5</sup> atom at 2.4 ppm ( $J = 8.0$  Hz). The signals of other protons of the branched product were overlapped by those of the major linear product (ethyl enanthoate).

In summary, we observed high catalytic activity of the PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–PPh<sub>3</sub>–AlCl<sub>3</sub> three-component system containing AlCl<sub>3</sub> as the promotor in the reaction of hydroethoxycarbonylation of hexene-1 and octene-1. The reaction occurred with the formation of a pair of isomeric products: the linear and the branched ones. The optimal conditions of the reactions were elaborated, and the yield of the target products (isomeric esters) reached 84.6 (for hexene-1) and 93.8% (for octene-1).

## EXPERIMENTAL

The following chemicals were used as received: hexene-1, octene-1, and dichlorobis(triphenylphosphine)palladium (Sigma-Aldrich), anhydrous ethanol, aluminum trichloride, and carbon dioxide without special purification. Triphenylphosphine ("pure," Chemapol) was recrystallized from ethanol.

The experiments were performed without solvents, using a stainless-steel laboratory pressure reactor. The ratio of the isomeric esters (linear and branched) was determined by chromatography using an Agilent 7890A/5975C chromatomass spectrometer (USA) (ionization by electron impact, capillary column HP-

FFAP, column length 30 m, inner diameter 0.25 mm, nitroterephthalic acid modified with polyethylene glycol as the stationary phase).

IR spectra were recorded using a Nicolet 5700 single-beam spectrometer (ThermoElectron Corporation, USA) at 400–4000  $\text{cm}^{-1}$ . <sup>1</sup>H NMR spectra were recorded using a Bruker DPX 400 instrument.

**Hydroethoxycarbonylation of hexene-1.** A mixture of 6.637 g ( $7.89 \times 10^{-2}$  mol) of hexene-1, 2.289 g ( $4.97 \times 10^{-2}$  mol) of ethanol, 0.080 g ( $11.42 \times 10^{-5}$  mol) of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.180 g ( $6.85 \times 10^{-4}$  mol) of PPh<sub>3</sub>, and 0.122 g ( $9.14 \times 10^{-4}$  mol) of AlCl<sub>3</sub> was charged into a 100 mL stainless steel reactor equipped with a stirrer and a carbon(II) oxide injecting device. The pressure reactor was sealed, deaerated by flushing with carbon(II) oxide for three times, and filled with carbon(II) oxide to a pressure of 10 at; then stirring and heating were switched on. The temperature was increased to 100°C during 1 h, the pressure was up to 25 at, and the reaction mixture was stirred under those conditions during 5 h. Then the vessel was cooled down to ambient, and the reaction mixture was separated by fractionation. Yield 7.0 g (84.6%) of a mixture of ethyl enanthoate and ethyl 2-methylcapronate (77.8 : 22.2). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1737 (C=O), 1033–1300 [CH<sub>2</sub>C(O)O], 729 (CH), 1300–1462 (CH<sub>2</sub>), 2800–3000 (CH<sub>3</sub>). **Ethyl enanthoate.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 4.12 q (2H, CH<sub>3</sub>CH<sub>2</sub>O,  $J = 7.3$  Hz), 1.25 t (3H, CH<sub>3</sub>CH<sub>2</sub>O,  $J = 7.3$  Hz), 0.88 t [3H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>C(O)O,  $J = 5.3$  Hz], 1.29 m [6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C(O)O], 1.62 m [2H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)O], 2.28 t [2H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>C(O)O,  $J = 7.3$  Hz]. **Ethyl 2-methylcapronate.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 1.13 d [3H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)C(O)O,  $J = 6.8$  Hz], 2.4 m [1H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)C(O)O].

**Hydroethoxycarbonylation of octene-1** was performed similarly using 5.6 g ( $5.02 \times 10^{-2}$  mol) of octene-1, 1.52 g ( $3.3 \times 10^{-2}$  mol) of ethanol, 0.053 g ( $7.59 \times 10^{-5}$  mol) of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.119 g ( $4.55 \times 10^{-4}$  mol) of PPh<sub>3</sub>, and 0.081 g ( $6.07 \times 10^{-4}$  mol) of AlCl<sub>3</sub>. Yield 5.76 g (93.8%) of a mixture of ethyl pelargonate and ethyl 2-methylcaprylate (77.5 : 22.5). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1738 (C=O), 1033–1260 [CH<sub>2</sub>C(O)O], 740 (CH), 1340–1462 (CH<sub>2</sub>), 2868–2957 (CH<sub>3</sub>).

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