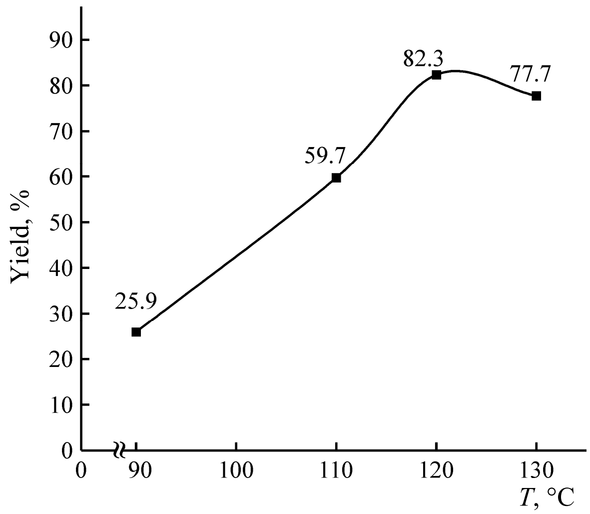

Fig. 1. The influence of temperature on the yield of target products in the reaction of hydroethoxycarbonylation of hexene-1. $[C_6H_{12}]$: $[C_2H_5OH]$: $[PdCl_2(PPh_3)_2]$: $[PPh_3]$: $[AlCl_3]$ = 690 : 435 : 1 : 6 : 8, P_{CO} = 20 atm, τ = 5 h.

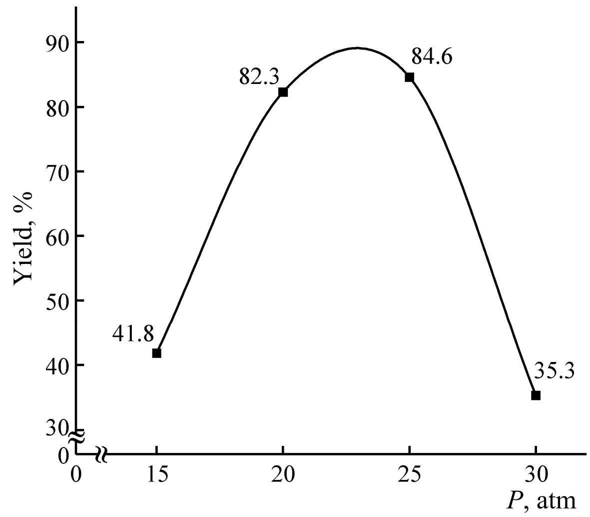

Fig. 2. The influence of carbon(II) oxide pressure on the yield of target products in the reaction of hydroethoxycarbonylation of hexene-1. $[C_6H_{12}]$: $[C_2H_5OH]$: $[PdCl_2(PPh_3)_2]$: $[PPh_3]$: $[AlCl_3]$ = 690 : 435 : 1 : 6 : 8, T = 120°C, τ = 5 h.

pentene-1, and it can substitute the conventionally used Brønsted acids. It has been noted that the use of $AlCl_3$ as the promotor of the $Pd(OAc)_2$–PPh_3 system under the tested conditions is inefficient. It has been reported in [16] that the $M(CH_3SO_3)_3$ and $M(OTsO)_3$ (M = Al, V, Fe, and Mo) Lewis acids prepared via the interaction of the corresponding metal oxides with methanesulfonic acid and *p*-toluenesulfonic acid have been used as the promotors of the catalytic systems based on palladium complexes in the reaction of hydromethoxycarbonylation of styrene. $InCl_3$ has been used as the promotor in the reaction of photolytic hydromethoxycarbonylation of bromoalkanes in the presence of the $Co(acac)_2$ complex [17].

We have earlier demonstrated that $AlCl_3$ can serve as promotor of catalytic systems based on phosphine palladium complexes in the reaction of hydroesterification of octene-1 [18]. In this work, we present the data of detailed study of various factors affecting the yield of hydroethoxycarbonylation of hexene-1 and octene-1 in the presence of the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ system containing $AlCl_3$ as the promotor.

It was found that hydroethoxycarbonylation of hexene-1 and octene-1 in the presence of the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ system led to the formation of two isomeric products, linear and branched (Scheme 1). The experiments were performed using a laboratory stainless steel pressure reactor. Since the isomeric esters could not be isolated due to the close boiling points, their content in the mixture was determined by means of chromato–mass spectrometry.

Figures 1–5 display the results of elucidation of the effect of various conditions of hexene-1 hydroethoxycarbonylation in the presence of the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ system on the yield of the target products: ethyl enanthate and ethyl 2-methylcapronate. Temperature, carbon(II) oxide pressure, the reaction duration, and the amount of $AlCl_3$ in the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalytic system were the major factors determining the process outcome. The increase in the reaction temperature from 90 to 120°C led to the increase in the target products yield from 25.9 to 82.3% (Fig. 1). Further increase in temperature reduced the target products yield due to the deactivation of the

Scheme 1.

$$CH_3(CH_2)_nCH{=}CH_2 + CO + C_2H_5OH \xrightarrow{\text{cat}} CH_3(CH_2)_mCH_2COOC_2H_5 + CH_3(CH_2)_nCH(CH_2OOC_2H_5)CH_3$$

cat = $PdCl_2(PPh_3)_2$—PPh_3—$AlCl_3$; n = 3, 5; m = 4, 6.