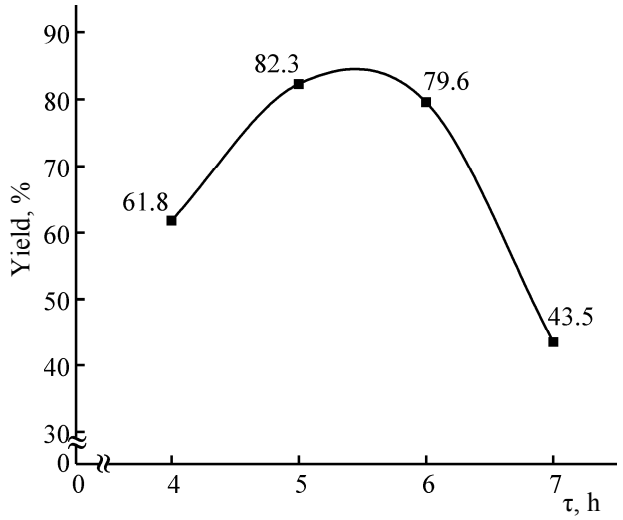

Fig. 3. The influence of the reaction duration on the yield of target products in the reaction of hydroethoxycarbonylation of hexene-1. $[C_6H_{12}] : [C_2H_5OH] : [PdCl_2(PPh_3)_2] : [PPh_3] : [AlCl_3] = 690 : 435 : 1 : 6 : 8$, $P_{CO} = 20$ atm, $T = 120°C$.

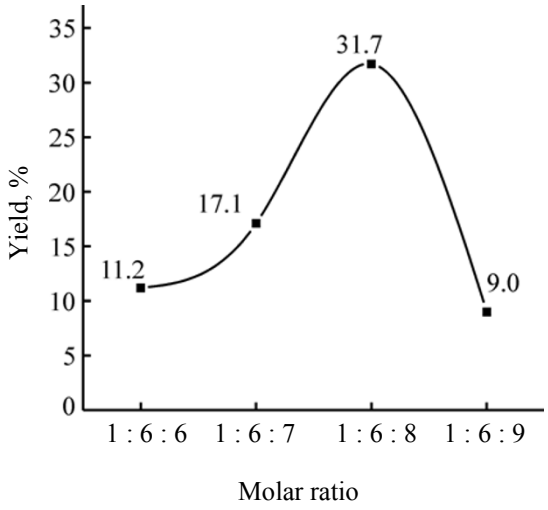

Fig. 4. The influence of $AlCl_3$ amount on the yield of target products in the reaction of hydroethoxycarbonylation of hexene-1. $[C_6H_{12}] : [C_2H_5OH] : [PdCl_2(PPh_3)_2] : [PPh_3] = 690 : 435 : 1 : 6$, $P_{CO} = 20$ atm, $T = 100°C$, $\tau = 5$ h.

catalyst (formation of palladium on carbon). The plots of the target products yield as a function of the carbon(II) oxide pressure and the reaction duration exhibited the extreme shape as well; the optimal conditions were as follows: $P_{CO} = 25$ atm (Fig. 2) and $\tau = 5$ h (Fig. 3). Further increase in the carbon(II) oxide pressure to 30 atm sharply reduced the target products yield, evidently due to the competing between the olefin and carbon(II) oxide for the sites in the coordination sphere of palladium. The molar fraction of $AlCl_3$ in the catalytic system also strongly affected the target products yield. The decrease in the $PdCl_2(PPh_3)_2$–$AlCl_3$ ratio from 1 : 6 to 1 : 8 led to the increase in the target products yield from 11.2 to 31.7% (Fig. 4); further increase in the $AlCl_3$ excess reduced the target products yield. The ratio of the starting reagents marginally affected the products yield (Fig. 5). Under the elaborated optimal conditions of the reaction the total yield of ethyl enanthate and ethyl 2-methylcapronate was 84.6%, with the products ratio being 77.8 : 22.2, respectively.

Similarly, we elucidated the effects of various factors on the yield of the products of hydroethoxycarbonylation of octene-1 in the presence of the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ system: ethyl pelargonate and ethyl 2-methylcaprylate (the table). The optimal conditions were found as follows: the reactants ratio $[C_8H_{16}] : [C_2H_5OH] : [Pd] : [PPh_3] : [AlCl_3] = 661 : 435 : 1 : 6 : 8$, temperature 120°C, reaction duration 5 h, and carbon(II) oxide pressure 25 atm. Under those conditions, total yield of the mentioned products equaled 93.8%, their ratio being 77.5 : 22.5 (GC–MS data).

Hydroesterification of α-olefins in the presence of the $PdCl_2(PPh_3)_2$–PPh_3 catalytic system containing $AlCl_3$ as the promotor likely occurred via the hydride mechanism, similarly to the case of hydroesterification of olefins in the presence of strong protic acids (*p*-TsOH and others). Being a strong Lewis acid, $AlCl_3$ likely interacted with ethanol to form the

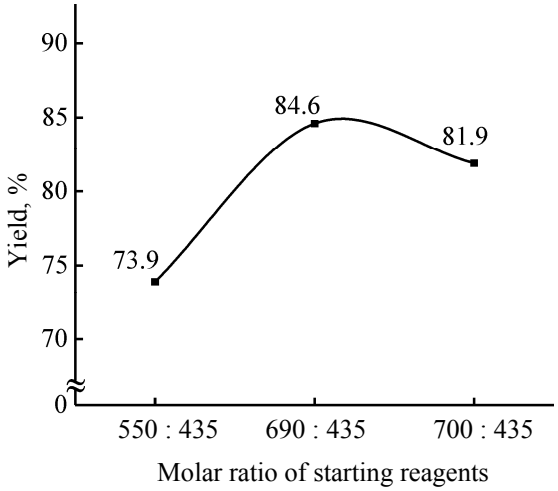

Fig. 5. The influence of molar ratio of the starting reagents on the yield of target products in the reaction of hydroethoxycarbonylation of hexene-1. $[C_6H_{12}] : [C_2H_5OH] : [PdCl_2(PPh_3)_2] : [PPh_3]:[AlCl_3] = 690 : 435 : 1 : 6 : 8$, $P_{CO} = 25$ atm, $T = 120°C$, $\tau = 5$ h.