Table 2. Hydroethoxycarbonylation of isobutylene in the presence of the $Pd(acac)_2$–PPh_3–TsOH system. Amount of $Pd(acac)_2$ = 0.035 g (0.115 mmol). Molar ratio isobutylene : $Pd(acac)_2$ = 550

No.	Molar ratio of the reactants and catalyst components to $Pd(acac)_2$			Reaction conditions			Ethyl isovalerate yield, %
	Ethanol	PPh_3	TsOH	T, °C	p_{CO}, MPa	τ, h	
1	435	7	12	100	2.0	6	68.0
2	435	5	12	100	2.0	6	72.0
3	435	4	12	100	2.0	6	73.5
4	435	3	12	100	2.0	6	74.5
5	435	2	12	100	2.0	6	46.0
6	435	9	12	100	2.0	6	66.0
7	435	3	13	100	2.0	6	63.0
8	435	3	10	100	2.0	6	71.0
9	435	3	8	100	2.0	6	64.0
10	435	3	12	110	2.0	6	58.0
11	435	3	12	90	2.0	6	60.0
12	435	3	12	100	1.5	6	52.0
13	435	3	12	100	2.2	6	75.0
14	435	3	12	100	2.5	6	76.0
15	435	3	12	100	2.8	6	77.0
16	435	3	12	100	3.0	6	78.0
17	435	3	12	100	3.2	6	68.0
18	435	3	12	100	3.5	6	37.0
19	435	3	12	100	3.0	4	77.0
20	275	3	12	100	3.0	5	79.0
21	435	3	12	100	3.0	5	79.0
22	550	3	12	100	3.0	5	64.0
23	1100	3	12	100	3.0	5	25.4

dependence of the product yield on the carbon monoxide pressure and the reaction time is likewise nonmonotonic in character: a carbon monoxide pressure of 2.0 MPa (Table 1; entries 4, 11, and 12) and a reaction time of 4 h (Table 1; entries 4, 13, and 14) are the optimum values. The further increase in the pressure of carbon monoxide to 2.5 MPa sharply reduces the yield of the product to 39.7% (Table 1, entry 12), a development that is obviously caused by the competition between the olefin and carbon monoxide for the place in the coordination sphere of palladium complexes.

The reaction of hydroethoxycarbonylation of isobutylene with carbon monoxide and ethanol also proceeds regioselectively to give the linear product. The influence of the reaction conditions on the yield of the main product ethyl isovalerate (Table 2) was studied. The optimum ratio of the components of the catalytic system is $[Pd(Acac)_2]$: $[PPh_3]$: [TsOH] = 1 : 3 : 12 (Table 2, entries 1–9). Note that, unlike the case of hydromenthoxycarbonylation of isobutylene, a smaller quantity of triphenylphosphine is required for isobutylene hydroethoxycarbonylation, a difference that is obviously due, first of all, to the nature of the alcohol reagent. The dependences of the yield of the product on temperature (Table 2; entries 4, 10, and 11) and reaction time (Table 2; entries 16, 19, and 21) are nonmonotonic with a maximum at 100°C and 5 h, respectively. The pressure (Table 2; entries 4, 12–18) strongly affects the yield of the product. The product yield increases from 52 to 74.5% with an increase in the pressure from 1.5 to 2.0 MPa. Furthermore, the yield continuously increases by 3.5% with an increase in pressure from 2.0 to 3.0 MPa and, then, sharply falls to 37% at 3.5 MPa. The reactant ratio has a substantial effect on the yield of the product. The increase in the [isobutylene] : [ethanol] molar ratio from 0.5 to 2 was found to increase the yield of the product from 25.4 to 79.0% (Table 2, entries 20–23). From the data presented in the figure, it follows that the optimum molar ratio of these compounds is 0.8–1.0; in this case, the productivity of the catalytic system is ca. 330 mol/mol of Pd.

Thus, a high catalytic activity of the halogen-free ternary homogeneous catalytic system $Pd(Acac)_2$–PPh_3–TsOH in the reactions of isobutylene hydromen-