

Hydroethoxycarbonylation of octane-1 in the presence of the $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$ system

Exp. no.	$[\text{C}_8\text{H}_{16}] : [\text{C}_2\text{H}_5\text{OH}] :$ $[\text{PdCl}_2(\text{PPh}_3)_2] : [\text{PPh}_3] : [\text{AlCl}_3]$	$T, ^\circ\text{C}$	$P_{\text{CO}}, \text{atm}$	τ, h	Products yield, %
1	550 : 435 : 1 : 6 : 8	100	20	5	12.7
2	661 : 435 : 1 : 6 : 8	100	20	5	21.9
3	750 : 435 : 1 : 6 : 8	100	20	5	14.5
4	661 : 435 : 1 : 6 : 8	100	20	3	8.5
5	661 : 435 : 1 : 6 : 8	100	20	4	19.5
6	661 : 435 : 1 : 6 : 8	100	20	6	18.2
7	661 : 435 : 1 : 6 : 8	100	15	5	14.3
8	661 : 435 : 1 : 6 : 8	100	25	5	33.5
9	661 : 435 : 1 : 6 : 8	100	30	5	72.5
10	661 : 435 : 1 : 6 : 8	110	25	5	73.3
11	661 : 435 : 1 : 6 : 8	120	25	5	93.8
12	661 : 435 : 1 : 6 : 8	130	25	5	85.6
13	661 : 435 : 1 : 6 : 6	120	25	5	86.4
14	661 : 435 : 1 : 6 : 7	120	25	5	87.9
15	690 : 435 : 1 : 6 : 9	120	25	5	82.5

$\text{H}^+[(\text{C}_2\text{H}_5\text{O})\text{AlCl}_3]^-$ complex serving as the proton source and the weakly coordinating conjugate anion $(\text{C}_2\text{H}_5\text{O})\text{AlCl}_3^-$. The possible mechanism of the process is given in Scheme 2 (the ligand surrounding and the stages of the formation of the intermediates with the charge transfer are omitted). The key stage is the formation of the HPd hydride complex giving rise to the well-known sequence of the catalytic transformations (the hydride mechanism).

The possibility of strong polarization of the O–H bonds in alcohols by $\text{Al}(\text{OTf})_3$ has been discussed in

[19]. The possibility of the hydride mechanism of hydromethoxycarbonylation of styrene in the presence of the $[\text{Pd}]\text{-PPh}_3$ systems containing aluminum triflate or aluminum methanesulfonate as the promoters (due to polarization of the O–H bond in methanol via its interaction with strong Lewis acids) has been suggested as well in [15, 16].

The synthesized compounds were identified using the data of IR and ^1H NMR spectroscopy. IR spectra of the prepared compounds contained the absorption bands of the ester group (C=O) stretching vibrations at

Scheme 2.

