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CARBONYLATION OF TERMINAL OLEFINES BY CARBON MONOXIDE AND ALCOHOLS IN THE PRESENCE OF PALLADIUM PHOSPHIN COMPLEXES

Abstract. In order to develop new, effective and environmentally friendly methods for obtaining practically valuable esters of carboxylic acids, there was investigatedthe reaction of the hydroalkoxycarbonylation of a number of terminal olefins of normal structure (hexene-1, heptene-1, octene-1, nonen-1) and branched structure (isobutylene) with carbon monoxide and mono- and polyhydric alcohols in the presence of metal-complex catalysts based on phosphine complexes of palladium at low pressures of carbon monoxide (≤ 20 atm). Di- and tricomponent systems based on $PdCl_2$, $Pd(Acac)_2$, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$, containing free ligand (PPh_3) as a stabilizer and brönsted acid (TsOH) as promoter, were studied.It was shown that high catalytical activity of the systems is obtained by $PdCl_2$-PPh_3-TsOH,$PdCl_2(PPh_3)_2$-PPh_3-TsOH,$Pd(Acac)_2$-PPh_3-TsOH and $Pd(PPh_3)_4$-PPh_3-TsOH in studied reactions at low pressure of carbon monoxide.It has been found that the hydroaloxycarbonylation reaction of α-olefins of normal structure proceeds to form a mixture of products of a linear and branched structure, and in the case of a branched olefin (isobutylene), regioselectively to form a linear structure product.The influence of thevarious conditions of running the reaction and yields of the target products (ratio of initial reagents and the components of the catalytic systems,temperature,pressure of carbon monoxide,durationof the reaction)was studied.Optimal parameters of the reaction were found.The reaction of the hydroalkoxycarbonylation of isobutylene with carbon monoxide and polyhydric alcohols (ethylene glycol, glycerin) in the presence of the $Pd(Acac)_2$-PPh_3-TsOH system at low pressures of carbon monoxide (≤ 20 atm) was investigated.It has been established that the hydroalkoxycarbonylation of isobutylene with carbon monoxide and ethylene glycol takes place regioselectivelyat the extreme carbon atom, forming products of linear structure, mono- and diglycolides of isovaleric acid, independently of the ratio of the initial reactants.In the case of glycerol, the reaction also proceeds regioselectively at the extreme carbon atom, depending on the ratio of the initial reagents are formed mono- and di-, di- and tri- or mono-, di- and triglycerides of isovaleric acid.The results of these investigations formed the basis for the development of new, effective and environmentally friendly methods for the production of the widely used drugs "Novovalidolum", "Ethyl ester of α-bromizovaleric acid" and "Corvalolum-K".

Key words: palladium, phosphine ligands, carbon monoxide, carbonylation of α-olefins, homogenous catalysis.

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КАРБОНИЛИРОВАНИЕ ТЕРМИНАЛЬНЫХ ОЛЕФИНОВ МОНОКСИДОМ УГЛЕРОДА И СПИРТАМИ В ПРИСУТСТВИИ ФОСФИНОВЫХ КОМПЛЕКСОВ ПАЛЛАДИЯ