How to Cite: Kudaibergenov, N.Zh., Shalmagambetov, K.M., Vavasori, A., Zhaksylykova, G.Zh., Kanapiyeva, F.M., Almatkyzy, P., Mamyrkhan, D.B., & Bulybayev, M. (2021) The use of Lewis acid $AlCl_3$ as a promoter in the Pd-complex catalytic system of the cyclohexene hydroethoxycarbonylation reaction. *Bulletin of the University of Karaganda – Chemistry, 102(2), 8-17.* https://doi.org/10.31489/2021Ch2/8-17

ORGANIC CHEMISTRY

UDC 547:326 https://doi.org/10.31489/2021Ch2/8-17

N.Zh. Kudaibergenov*[1], K.M. Shalmagambetov[1], A. Vavasori[2], G.Zh. Zhaksylykova[1], F.M. Kanapiyeva[1], P. Almatkyzy[1], D.B. Mamyrkhan[1], M. Bulybayev[1]

*[1]Center of Physical Chemical Methods of Research and Analysis, Al-Farabi Kazakh National University, Almaty, Kazakhstan; [2]Department of Molecular Science and Nanosystems, Ca' Foscari University Venice, Scientific Campus, Venezia, Italy (*Corresponding author's e-mail:n.zh.kudaibergenov@gmail.com)*

The use of Lewis acid $AlCl_3$ as a promoter in the Pd-complex catalytic system of the cyclohexene hydroethoxycarbonylation reaction

This paper presents the results of detailed studies of the possibility of using Lewis acid $AlCl_3$ as a promoter of the catalytic three-component system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ in the hydroethoxycarbonylation reaction of cyclohexene at low carbon monoxide pressures (2.5 MPa). As a result a high catalytic activity of the three-component system was established and the reaction proceeds regioselectively with the formation of ethyl ether of cyclohexanecarboxylic acid. The optimal conditions of the process have been elaborated (molar ratio of the starting reagents [Cyclohexene]:[Ethanol] = 1:1; molar ratio of the components of the catalytic system = = $[PdCl_2(PPh_3)_2]$:$[PPh_3]$:$[AlCl_3]$ = 1:6:9; carbon monoxide pressure P_{CO} = 2.5 MPa; process temperature T = 120 °C and reaction time τ = 5 h) at which the target product yield reaches 80.7 %. To identify the obtained ethyl ester of cyclohexane carboxylic acid gas chromatographic analysis and mass- and IR- spectra were carried out. Based on the data obtained, a possible mechanism of the reaction route of cyclohexene carbonylation with carbon monoxide and ethanol in the presence of the three-component system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ is proposed and discussed.

Keywords: cyclohexene, carbon monoxide, Pd-complex catalysts, phosphine ligands, aluminium (III) chloride, hydroalkoxycarbonylation, ethyl ester of cyclohexanecarboxylic acid, "Hydride" mechanism.

Introduction

Production technologies based on the use of carbon oxides are being developed recently throughout the world. Development of processes based on carbon monoxide use is motivated by a number of reasons. One of key reasons is the need to use alternative sources of raw materials. Starting from 40's of XIX century oil was the main source of raw material for chemical production, and petrochemicals production on its basis developed fast. However, a trend of crude production slowdown is observed today and effective processes that will be able to replace it are being searched for [1–3].

The carbonylation method is used, on an industrial scale, in the synthesis of carboxylic acids, hydroxy-acids, acid anhydrides, lactones, alcohols, ethers and esters, aldehydes and ketones. Many of these reactions have been well-studied and developed but a number of processes still undergo the search for catalyst systems with relatively high activity and selectivity.

It is possible to synthesize compounds with a large number of carbonyl groups having practical importance by carbonylation of unsaturated compounds. Interest to this reaction is preconditioned by the possibility of recovery of unsaturated compounds from non-petroleum raw material (natural gas, coal) [1–4].

The interaction of olefins with CO and H_2O leads to the formation of linear or branched carboxylic acids. Esters of carboxylic acids are obtained by replacing water with alcohol. The structure of the obtained esters depends primarily on the nature of the catalysts used, as well as the conditions of their use. Derivatives of

