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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 $\tau = 5$ 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.

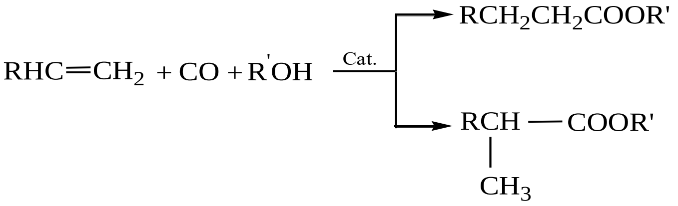
Introduction

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 esters of carboxylic acids are mainly linear and α-branched, and synthesized with the participation of catalysts based on metals of group VIII of the Periodic Table [5, 6].

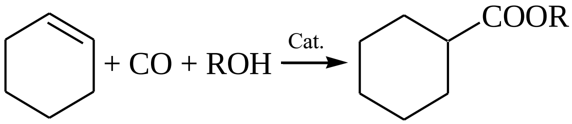


R= H, Alk, Ar Cat. = metal complex catalysts

Currently, many studies have been carried out in the field of hydroesterification of alkenes [7–20] and the degree of their transformation and sensitivity has been studied. Works [3, 17] have studied the influence of various factors on carbonylation processes (at 70–95 °C, 1–4 MPa, for 3 hours) of primary alkenes, such as propene, isobutylene, pentene-1, hexene-1, heptene-1, octene-1, and other terminal alkenes in the presence of $(PPh_3)_2PdCl_2$–$SnCl_2$ catalysts. Output of obtained esters varies within limits of 70–95, depending on structure of the used catalyst system.

Most of recent researches are focused on the processes of carbonylation of hexane-1, octane-1, decene-1, and dodecene-1. In particular, hexene-1 was carbonylated in the presence of the $PdCl_2$-$6PPh_3$-5p-TsOH system at 125 °C and a pressure of 0.8 MPa [18, 19] as well as in the presence of the $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ system at 120 °C and a pressure of 2.5 MPa for 5 hours [12]. As a result, 84–93.8 % of the product was obtained with a selectivity of 98 %. In order to increase the selectivity with respect to linear esters, the systems $PdCl_2$–monophosphine ligand–LiCl–Lewis acid were used in the reaction of hydromethoxycarbonylation of alkenes [20]. The process was found to be influenced by parameters such as CO pressure, solvents and the nature of the catalyst. 1-Dodecene was hydromethoxycarbonylated with a $PdCl_2$–$P(p\text{-}C_6H_4\text{-}OCH_3)_3$–LiCl–$SnCl_2$ catalyst ($T = 110$ °C, $P_{CO} = 2.4$ MPa, 22 h) in a high yield (93 %). The results of the carbonylation of octene-1 and tetradecene-1 in the presence of the same catalytic system were obtained with high efficiency (96 %) within 22 hours. Previous works on the carbonylation of octene-1 together with methanol and CO in the presence of the $Pd(CH_3COO)_2$–PPh_3–p-TsOH system at 80 °C and a pressure of 2.1 MPa showed a yield of 74 %, and the conversion of the substrate was achieved in 3.5 hours [12]. Most of the studies mentioned above aimed at increasing the yields of linear isomers, which is the main problem in the carbonylation of alkenes, since the practical value of the resulting linear isomer of the product is very high.

Currently, cyclic carboxylic acids and their esters obtained from cycloolefins with carbon monoxide and alcohols or phenols are an important raw material for the synthesis of pharmaceuticals and flavorings. Therefore, more work is underway to find effective catalysts and optimal parameters for their preparation, as well as research on kinetics and thermodynamics [6, 21–29].



R= H, Alk, Ar Cat. = metal complex catalysts

Esters of carboxylic acids are widely used in practice as pesticides, solvents in varnishes, dyes, flavours in perfume compositions, additives to various types of fuel, additives to polymeric materials, etc. [30–31]. One of the most important qualities is their use as semi-finished products in chemical and pharmaceutical synthesis [5, 6]. Some esters are components of pharmaceuticals.

Based on the studies of the above literature, it is possible to conclude that the processes of carbonylation of unsaturated compounds, especially olefins, is the most effective method for the synthesis of various organic compounds of great practical importance. Compared to other methods for the production of carboxylic acid esters, hydroalkoxycarbonylation of olefins has a number of advantages, such as single-stage processes, the availability of raw materials, the possibility of influencing the reaction by changing the nature of the metal-complex catalyst and the conditions of the process, which determines that the conduct on an industrial scale is in all respects advantageous.

Experimental

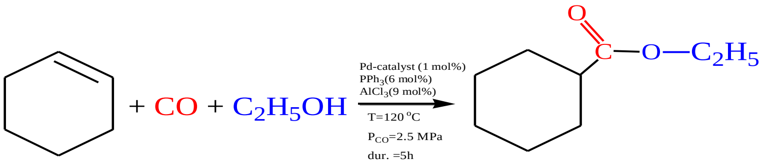
Primary reagents, features and methods of their study. Reagents produced by SIGMA-ALDRICH (bis(triphenylphosphine)palladium (II) dichloride, cyclohexene (purity 99 %), triphenylphosphine, aluminium trichloride), absolute ethyl alcohol, carbon monoxide reagent without superrefining (CO) were used as primary reagents.

Equipments. Experiments were conducted in a steel laboratory autoclave reactor (capacity 100 ml) equipped with a mixer and heater. The target product (ethyl ester of cyclohexanecarboxylic acid) was identified by gas chromatography on an Agilent 7890A/5975C mass-spectrometer (USA). Chromatography conditions were as follows: gas chromatograph 7890A with mass-selective detector 5975C produced by Agilent, helium mobile phase (gas carrier), evaporation temperature 300 ºC, flow shift (Split) 1000:1. Also, column heating with initial oven temperature 40 °C (1 min), temperature increase 5 ºC per minute and final value 250 ºC that is maintained for 1 minute were used. Total analysis time was 44 minutes and mass detector ionization was carried out by electron impact method. A capillary chromatographic column HP-FFAP was also used; the column length was 30 m, the inner diameter was 0.25 mm, the stationary phase was nitrophthalic acid modified with polyethylene glycol.

Hydroethoxycarbonylation of cyclohexene. 0.08 g (1.14×10^{-4} mol) $PdCl_2(PPh_3)_2$, 0.180 g (6.84×10^{-4} mol) PPh_3, 0.122 g (9.12×10^{-4} mol) $AlCl_3$, 2.289 g (4.96×10^{-2} mol) ethanol and 4.067 g (4.96×10^{-2} mol) of cyclohexene were placed into a steel autoclave reactor (100 ml) equipped with a mixer and carbon monoxide injection device. Ratio of primary reagents and components of catalyst system was $[C_6H_{10}]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$ = 435:435:1:6:9. The reactor was sealed. To remove air inside of it, it is blown through with carbon monoxide three times and filled with carbon monoxide until pressure reaches 1.5 MPa. Then, mixer and heater are turned on and within 1 hour temperature is increased up to 120 °C, and carbon monoxide pressure grew up to 2.5 MPa. At a given temperature and pressure the reaction mixture is intensively stirred for 5 hours. Then it is cooled to room temperature and reaction mixture fractionation is carried out at atmospheric pressure. As a result of distillation, 6.244 g (80.7 %) of ethyl ester of cyclohexanecarboxylic acid was obtained.

Results and discussion

The reaction of cyclohexene hydroethoxycarbonylation in the presence of $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalyst system has the following form:



The activity of the three-component catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$, which contains $AlCl_3$ as a promoter, was studied in the hydroethoxycarbonylation of cyclohexene at low pressure (P_{CO} = 2.5 MPa) of carbon monoxide. A high catalytic activity of the catalytic system with respect to this reaction was found. Cyclohexanecarboxylic acid ethyl ester formation reaction was confirmed by reference data for such characteristics as GC/MS analysis, boiling point, and refractive index.

The effect of the reaction conditions (temperature, CO pressure, molar ratio of primary reagents, ratio of the components of the catalytic system and reaction time) on the yield of the target product has been established (Table 1).

Table 1 shows the results of the influence of various conditions on the yield of ethyl ester of cyclohexanecarboxylic acid as the target product of the reaction of hydroethoxycarbonylation of cyclohexene in the presence of the system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$. Temperature, pressure of carbon monoxide, reaction time, and the amount of $AlCl_3$ in the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalytic system were the main factors determining the outcome of the process. An increase in the reaction temperature from 110 to 130 °C led to an increase in the yield of target products from 65.8 to 80.7 %. A further increase in temperature reduces the yield of target products due to catalyst deactivation (formation of palladium on carbon). The graphs of the yield of the target products depending on the pressure of carbon monoxide and the duration of the reaction also have an extreme form. Optimal conditions are P_{CO} = 2.5 MPa, τ = 5 h. A further increase in the pressure of carbon monoxide to 3.0 MPa sharply reduces the yield of the target products. Apparently, that is due to competition between the olefin and carbon monoxide behind the center of the palladium focal point. The molar ratio of $AlCl_3$ in the catalytic system also strongly affects on the yield of the target products. An increase in the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ ratio from 1:8 to 1:9 led to an increase in the yield of target products from 72.6 to 80.7 %; a further increase in the excess of $AlCl_3$ reduces the yield of the target product. No solvents were used in this reaction, and the ratio of the starting reagents affected the product yield. With the ratio $[C_8H_{10}]:[C_2H_5OH]$ = 661:435, the product yield is 72.3 %; further reduction to $[C_8H_{10}]:[C_2H_5OH]$ = 435:435 gives the highest product yield of 80.7 %, but further reduction to $[C_8H_{10}]:[C_2H_5OH]$ = 217.5:435 reduces the yield of the target product.

Table 1

Hydroethoxycarbonylation of cyclohexene in the presence of the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ system

Exp. no.	$[C_8H_{10}]:[C_2H_5OH]$	$[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$	T, °C	P_{CO}, MPa	τ, h	Product yield, %
1	661:435	1:6:9	120	2.5	5	72.3
2	435:435	1:6:9	120	2.5	5	80.7
3	217.5:435	1:6:9	120	2.5	5	55.6
4	435:435	1:6:8	120	2.5	5	72.6
5	435:435	1:6:10	120	2.5	5	74.2
6	435:435	1:6:9	130	2.5	5	66.7
7	435:435	1:6:9	110	2.5	5	65.8
8	435:435	1:6:9	120	3.0	5	68.0
9	435:435	1:6:9	120	2.0	5	43.4
10	435:435	1:6:9	120	2.5	4	68.5
11	435:435	1:6:9	120	2.5	6	77.2

Thus, it was found that the three-component catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$, which contains $AlCl_3$ as a promoter in the carbonylation reaction of cyclohexene at a low carbon monoxide pressure (2.5 MPa), exhibits high catalytic activity. As a result, the following effective parameters were identified: $[C_6H_{10}]:[C_2H_5OH]:[Pd]:[PPh_3]:[AlCl_3]$ = 435:435:1:6:9, P_{CO} = 2.5 MPa, T = 120 ºC, τ = 5 h. Under the developed optimal reaction conditions, the yield of ethyl ester of cyclohexanecarboxylic acid was 80.7%.

The study and identification of the fractionated product was carried out as mentioned above (experimental part), by gas chromatography method (shown in Figure 1). On the chromatogram we can observe a change in the value of the total ion current at the 19th minute of exposure, which, in turn, indicates the presence of the target product – ethyl ester of cyclohexanecarboxylic acid (at the 1st minute — unreacted ethanol; at the 3rd minute — unreacted cyclohexene).

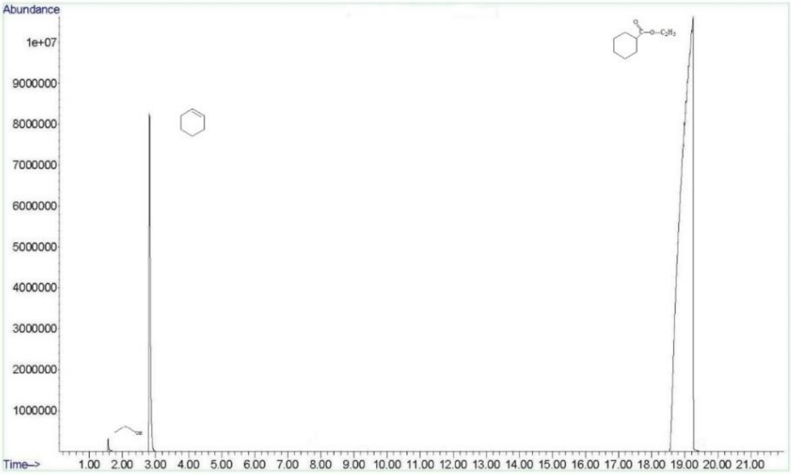


Figure 1. GC analysis of target product

Along with the hydroethoxycarbonylation of cyclohexene in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ with $AlCl_3$ in its composition as a promoter, there can also be a “hydride” mechanism, reminiscent of the carbonylation process, which occurs in the presence of strong hydrogen acids (p-TsOH, etc.).

The mechanism of the reaction of hydroethoxycarbonylation of cyclohexene can proceed in the same way as the mechanism of hydroethoxycarbonylation of octene-1 in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ [7].

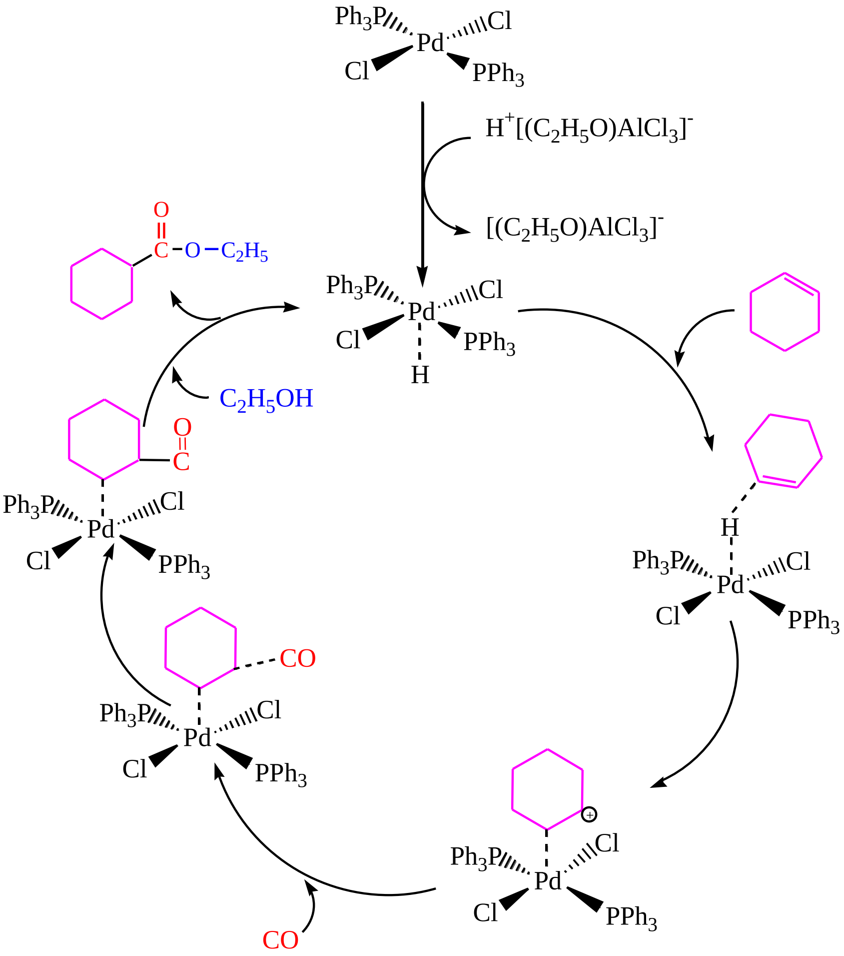


Figure 2. “Hydride” mechanism of cyclohexene hydroesterification reaction

The mechanism of cyclohexene hydroesterification in the presence of three-component $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalyst system is shown in Figure 2. The stage of HPd hydride complex formation is the main stage of the process. This complex gives the possibility of further catalytic cycle. When ethanol interacts with aluminum (III) chloride, which is a strong Lewis acid, it is possible to get the formation of $H^+[C_2H_5OAlCl_3]^-$ proton and $[C_2H_5OAlCl_3]^-$ of weakly coordinating anions complexes. The polarization of O-H bonds in alcohol under the action of strong Lewis acids allows the process to take place according to the hydride mechanism.

Conclusions

The activity of the three-component catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ with $AlCl_3$ in its composition as a promoter in the carbonylation reaction of cyclohexene with carbon monoxide and ethanol was investigated. A high catalytic activity of this catalytic system was found. The effect of process conditions, such as components of catalyst system ratio and primary reagents mole ratio, temperature, CO pressure, reaction time on the result of the hydroethoxycarbonylation reaction of cyclohexene in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ at low carbon monoxide pressure was studied. Optimal parameters were identified: $[C_6H_{10}]:[C_2H_5OH]:[Pd]:[PPh_3]:[AlCl_3] = 435:435:1:6:9$, $P_{CO} = 2.5$ MPa, $T = 120$ °C, $\tau = 5$ h. The possibility of cyclohexanecarboxylic acid ethyl ester synthesizing at these parameters with a yield of 80.7 %

was investigated. Ethyl ether of cyclohexanecarboxylic acid is of great practical importance as flavoring agents, food additives in food, pharmaceutical and other industries.

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Циклогексенді гидроэтоксикарбонилдеу реакциясының Pd-комплексті каталитикалық жүйесінде $AlCl_3$ Льюис қышқылын промотор ретінде қолдану

Мақалада көміртек оксидінің төмен қысымында (2,5 МПа) циклогексенді гидроэтоксикарбонилдеу реакциясында үш компонентті $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ каталитикалық жүйесінің промоторы ретінде $AlCl_3$ Льюис қышқылын пайдалану мүмкіндігінің зерттеу нәтижелері келтірілген. Нәтижесінде үш компонентті жүйенің жоғары каталитикалық белсенділігі және реакция региоселективті циклогексанкарбон қышқылының этил эфирін түзе отырып жүретіндігі анықталды. Процестің оңтайлы шарттары табылып (бастапқы реагенттердің моль қатынасы [Циклогексен]:[Этанол] = 1:1; каталитикалық жүйе компоненттерінің молярлық қатынасы = $[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$ = 1:6:9; P_{CO} көміртегі тотығының қысымы = 2,5 МПа; процесс температурасы T = 120 °C және реакция уақыты τ = 5 сағ), онда мақсатты өнімнің шығымы 80,7 % жетті. Алынған циклогексанкарбон қышқылының этил эфирін анықтау үшін газохроматографиялық талдау жүргізіліп, масс- және ИҚ-спектрлері түсірілді. Алынған мәліметтер негізінде үш компонентті $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ жүйесінің қатысуымен циклогексеннің көміртек оксиді және этанолмен карбонилдеу реакциясының мүмкін болатын механизмі ұсынылды және талқыланды.

Кілт сөздер: циклогексен, көміртек моноксиді, Pd-комплексті катализаторлар, фосфинді лигандтар, алюминий (III) хлориді, гидроалкоксикарбонилдеу, циклогексанкарбон қышқылының этил эфирі, «гидридтік» механизм.

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Использование кислоты Льюиса $AlCl_3$ в качестве промотора в Pd-комплексной каталитической системе в реакции гидроэтоксикарбонилирования циклогексена

В статье представлены результаты детальных исследований возможности использования кислоты Льюиса $AlCl_3$ в качестве промотора каталитической трехкомпонентной системы $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ в реакции гидроэтоксикарбонилирования циклогексена при низких давлениях монооксида углерода (2,5 МПа). Установлены высокая каталитическая активность трехкомпонентной системы и региоселективное протекание реакции с образованием этилового эфира циклогексанкарбоновой кислоты. Разработаны оптимальные условия процесса (мольное соотношение исходных реагентов [циклогексен]:[этанол] = 1:1; молярное соотношение компонентов каталитической системы = [$PdCl_2(PPh_3)_2$]:[PPh_3]:[$AlCl_3$] = 1:6:9; давление монооксида углерода P_{CO}=2,5 МПа; температура процесса Т = 120 °С и время реакции τ = 5 ч), при которых выход целевого продукта достигает 80,7 %. Для идентификации полученного этилового эфира циклогексанкарбоновой кислоты проведен газохроматографический анализ и сняты масс- и ИК- спектры. На основании полученных данных предложен и обсужден возможный механизм протекания реакции карбонилирования циклогексена монооксидом углерода и этанолом в присутствии трехкомпонентной системы $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$.

Ключевые слова: циклогексен, моноксид углерода, Pd-комплексные катализаторы, фосфиновые лиганды, хлорид алюминия (III), гидроалкоксикарбонилирование, этиловый эфир циклогексанкарбоновой кислоты, гидридный механизм.

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