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<https://orcid.org/0000-0003-2390-0688>

<https://orcid.org/0000-0002-5660-9208>

<https://orcid.org/0000-0002-4641-6779>

<https://orcid.org/0000-0002-9829-3117>

<https://orcid.org/0009-0007-2072-5884>

<https://orcid.org/0000-0002-7550-4989>

<https://orcid.org/0009-0006-5444-4266>

<https://orcid.org/0009-0003-5149-2957>

## HYDROETHOXYCARBONYLATION OF CYCLOPENTENE IN THE PRESENCE OF A THREE-COMPONENT $\text{PdCl}_2(\text{PPh}_3)_2$ - $\text{PPh}_3$ - $\text{AlCl}_3$ SYSTEM



**G.Zh. ZHAKSYLYKOVA**, Candidate of Chemical Sciences, Associate Professor, Associate Professor of the Department of Physical Chemistry, Catalysis and Petrochemistry, [banu.81@mail.ru](mailto:banu.81@mail.ru)



**K.M. SHALMAGAMBETOV**, Doctor of Chemical Sciences, Head, laboratory "Petrochemical Syntheses" of the Center for Physico-Chemical Methods of Research and Analysis, [kairshan@yandex.ru](mailto:kairshan@yandex.ru)



**N.ZH. KUDAIBERGENOV**, PhD, Senior Lecturer of the Department of Physical Chemistry, Catalysis and Petrochemistry, [nuka1991@mail.ru](mailto:nuka1991@mail.ru)



**F.M. KANAPIYEVA**, Candidate of Chemical Sciences, Senior Lecturer of the Department of Physical Chemistry, Catalysis and Petrochemistry, [fatima31@mail.ru](mailto:fatima31@mail.ru)

**M.E. BULYBAEV**, Doctoral student, lecturer of the Department of Physical Chemistry, Catalysis and Petrochemistry, [marat.bulybayev14@gmail.com](mailto:marat.bulybayev14@gmail.com)

**N. BOLATKYZY**, master's student, [nbolatkyzy98@gmail.ru](mailto:nbolatkyzy98@gmail.ru)

**A. AZIMBAY**, Bachelor, [abzal\\_azimbay@icloud.com](mailto:abzal_azimbay@icloud.com)

**E.A. ALIKEEVA**, Master's student, [alua.alikeyeva@gmail.ru](mailto:alua.alikeyeva@gmail.ru)

AL-FARABI KAZAKH NATIONAL UNIVERSITY  
Republic of Kazakhstan, 050040, Almaty, 71 al-Farabi Ave.

*Carbon monoxide-based synthesis is an extensive and promising branch of organic synthesis. The interest in this area is primarily due to the wide synthetic capabilities of C1 chemistry, as well as the gradual depletion of traditional sources of hydrocarbon raw materials and the rise in the cost of petroleum products. In this regard, the development of new processes based on alternative sources of raw materials is an urgent task.*

*The synthesis of carbon monoxide is currently becoming increasingly important for several reasons. Firstly, CO is an important raw material for the production of many chemical compounds, such as methanol, formaldehyde, acetone, etc. These compounds are widely used in various industries, including the production of plastics, dyes, medicines and other products. Secondly, CO synthesis can be used to produce hydrogen from biomass or other renewable sources, which makes this process more environmentally friendly and sustainable compared to traditional methods of hydrogen production based on the use of fossil fuels. Third, CO synthesis plays an important role in the production of clean energy.*

*This article reported on the study of the activity of the three-component catalytic system  $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$  in the reaction of hydroethoxycarbonylation of cyclopentene with ethanol at low pressure of carbon monoxide ( $P=25 \text{ atm.}$ ).*

*The optimal parameters of the process of hydroethoxycarbonylation of cyclopentene with the ternary system  $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$  have been determined. At the molar ratio of the initial reagent  $[\text{C}_5\text{H}_8]:[\text{C}_2\text{H}_5\text{OH}]=2:1$ , at the molar ratio of the component of the catalytic system  $[\text{Pd}]:[\text{PPh}_3]:[\text{AlCl}_3]$  in the ratio 1:6:10 and at  $T=120^\circ\text{C}$ ,  $P_{\text{CO}}=25 \text{ atm.}$  and reaction duration  $\tau=6$  hours, ethylcyclopentanecarboxylate was synthesized with a yield of 75.74%.*

**KEY WORDS:** cyclopentene, carbon monoxide, ethanol, dichlorbis(triphenylphosphine) palladium (II), aluminum chloride (III), triphenylphosphine, hydroalkoxycarbonylation, carbonylation.

## ГИДРОЭТОКСИКАРБОНИЛИРОВАНИЕ ЦИКЛОПЕНТЕНА В ПРИСУТСТВИИ ТРЕХКОМПОНЕНТНОЙ СИСТЕМЫ $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$

**Г.Ж. ЖАКСЫЛЫКОВА**, кандидат химических наук, ассоц. профессор, доцент кафедры физической химии, катализа и нефтехимии, [banu.81@mail.ru](mailto:banu.81@mail.ru)

**К.М. ШАЛМАГАМБЕТОВ**, доктор химических наук, зав. лабораторией «Нефтехимические синтезы» Центра физико-химических методов исследования и анализа, [kairshan@yandex.ru](mailto:kairshan@yandex.ru)

**Н.Ж. КУДАЙБЕРГЕНОВ**, PhD по химии, ст. преподаватель кафедры физической химии, катализа и нефтехимии, [nuka1991@mail.ru](mailto:nuka1991@mail.ru)

**Ф.М. КАНАПИЕВА**, кандидат химических наук, ст. преподаватель кафедры физической химии, катализа и нефтехимии, [fatima31@mail.ru](mailto:fatima31@mail.ru)

**М.Е. БУЛЫБАЕВ**, докторант, преподаватель кафедры физической химии, катализа и нефтехимии, [marat.bulybayev14@gmail.com](mailto:marat.bulybayev14@gmail.com)

**Н. БОЛАТКЫЗЫ**, магистрант, [nbolatkyzy98@gmail.ru](mailto:nbolatkyzy98@gmail.ru)

**А. АЗИМБАЙ**, бакалавр, [abzal\\_azimbay@icloud.com](mailto:abzal_azimbay@icloud.com)

**Е.А. АЛИКЕЕВА**, магистрант, [alua.alikeyeva@gmail.ru](mailto:alua.alikeyeva@gmail.ru)

КАЗАХСКИЙ НАЦИОНАЛЬНЫЙ УНИВЕРСИТЕТ ИМ. АЛЬ-ФАРАБИ  
Республика Казахстан, 050040, г. Алматы, пр. аль-Фараби 71

Синтезы на основе монооксида углерода является обширной и перспективной отраслью органического синтеза. Интерес к этой области обусловлен прежде всего широкими синтетическими возможностями химии C1, а также постепенным истощением традиционных источников углеводородного сырья и удорожанием нефтепродуктов. В этой связи актуальной задачей является разработка новых процессов на основе альтернативных источников сырья.

Синтез монооксида углерода в настоящее время приобретает все большее значение по нескольким причинам. Во-первых, СО является важным сырьем для производства многих химических соединений, таких как метанол, формальдегид, ацетон и т. д. Эти соединения широко используются в различных отраслях промышленности, включая производство пластмасс, красителей, лекарств и других продуктов. Во-вторых, синтез СО может использоваться для производства водорода из биомассы или других возобновляемых источников, что делает этот процесс более экологически чистым и устойчивым по сравнению с традиционными методами производства водорода, основанными на использовании ископаемого топлива. В-третьих, синтез СО играет важную роль в производстве чистой энергии.

В данной статье сообщалось об изучении активности трехкомпонентной каталитической системы  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  в реакции гидроэтоксикарбонилирования циклопентена этанолом при низком давлении монооксида углерода ( $P=25$  атм.).

Определены оптимальные параметры процесса гидроэтоксикарбонилирования циклопентена трехкомпонентной системой  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$ . При мольном соотношении исходного реагента  $[C_5H_8]:[C_2H_5OH]=2:1$ , при мольном соотношении компонента каталитической системы  $[Pd]:[PPh_3]:[AlCl_3]$  в соотношении 1:6:10 и при  $T=120^\circ C$ ,  $PCO=25$  атм. и продолжительностью реакции  $\tau=6$  часов синтезирован этилциклопентанкарбоксилат с выходом 75,74%.

**КЛЮЧЕВЫЕ СЛОВА:** циклопентен, монооксид углерода, этанол, дихлоробис(трифенилфосфин)палладий (II), хлорид алюминия (III), трифенилфосфин, гидроалкоксикарбонилирование, карбонилирование.

## ҮШ КОМПОНЕНТТІ $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$ ЖҮЙЕСІНІҢ ҚАТЫСЫНДА ЦИКЛОПЕНТЕНДІ ГИДРОЭТОКСИКАРБОНИЛДЕУ

Г.Ж. ЖАҚСЫЛЫҚОВА, химия ғылымдарының кандидаты, қауымдастырылған профессор, [banu.81@mail.ru](mailto:banu.81@mail.ru)

К.М. ШАЛМАҒАМБЕТОВ, химия ғылымдарының докторы, [kairshan@yandex.ru](mailto:kairshan@yandex.ru)

Н.Ж. ҚҰДАЙБЕРГЕНОВ, PhD, [nuka1991@mail.ru](mailto:nuka1991@mail.ru)

Ф.М. КАНАПИЕВА, химия ғылымдарының кандидаты, [fatima31@mail.ru](mailto:fatima31@mail.ru)

М.Е. БУЛЫБАЕВ, PhD докторанты, [marat.bulybayev14@gmail.com](mailto:marat.bulybayev14@gmail.com)

Н. БОЛАТҚЫЗЫ, магистрант, [nbolatkyzy98@gmail.ru](mailto:nbolatkyzy98@gmail.ru)

А. АЗИМБАЙ, бакалавр, [abzal\\_azimbay@icloud.com](mailto:abzal_azimbay@icloud.com)

Е.А. АЛИКЕЕВА, магистрант, [alu.alikeyeva@mail.ru](mailto:alu.alikeyeva@mail.ru)

ӘЛ-ФАРАБИ АТЫНДАҒЫ ҚАЗАҚ ҰЛТТЫҚ УНИВЕРСИТЕТІ  
Қазақстан Республикасы, 050040, Алматы қ., әл-Фараби даңғылы 71

Көміртек монооксиді негізіндегі синтез органикалық синтездің кең және перспективалы саласы болып табылады. Бұл салаға қызығушылық ең алдымен – C1-химияның кең синтетикалық мүмкіндіктеріне, сондай-ақ көмірсутек шикізаттарының дәстүрлі көздерінің біртіндеп сарқылуы және мұнай өнімдерінің қымбаттауымен байланысты. Осыған

байланысты баламалы шикізат көздері негізінде жаңа процестерді әзірлеу өзекті міндет болып табылады.

Көміртек монооксиді синтезі қазіргі уақытта бірнеше себептерге байланысты маңыздылығы арта түсуде. Біріншіден, СО метанол, формальдегид, ацетон және т.б. сияқты көптеген химиялық қосылыстарды өндіру үшін маңызды шикізат болып табылады. Бұл қосылыстар әртүрлі салаларда, соның ішінде пластмасса, бояғыш, дәрі-дәрмек және басқа да өнімдер өндірісінде кеңінен қолданылады. Екіншіден, СО синтезі биомассадан немесе басқа жаңартылатын көздерден сутекті өндіру үшін пайдаланылуы мүмкін, бұл қазба отындарын пайдалануға негізделген сутекті өндірудің дәстүрлі әдістерімен салыстырғанда бұл процесті экологиялық таза және тұрақты етеді. Үшіншіден, СО синтезі таза энергия өндіруде маңызды рөл атқарады.

Бұл мақалада циклопентенді көміртек монооксидінің төмен қысымында ( $P=25$  атм.) этанолмен гидроэтоксикарбонилдеу реакциясындағы  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  үш компонентті каталитикалық жүйесінің активтілігі зерттеліп, циклопентенді гидроэтоксикарбонилдеу реакцияларында  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  жүйесі жоғары каталитикалық белсенділік көрсететіндігі зерттелгені баяндалды.

Циклопентенді үшкомпонентті  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  жүйесі қатысында гидроэтоксикарбонилдеу процесінің тиімді параметрлері анықталды. Бастапқы реагенттердің  $[C_5H_8]:[C_2H_5OH]=2:1$  мольдік қатынасында, каталитикалық жүйе компоненттерінің  $[Pd]:[PPh_3]:[AlCl_3]$  мольдік қатынасының  $1.6:10$  мөлшерінде және  $T=120^\circ C$ -та,  $PCO=25$  атм. қысымда және реакцияның жүру ұзақтығы  $\tau=6$  сағатта  $75,74\%$  шығыммен этилциклопентанкарбоксилат синтезделіп алынды.

**КІЛТТІК СӨЗДЕР:** циклопентен, көміртек монооксиді, этанол, дихлробис(трифенилфосфин)палладий (II), алюминий (III) хлориді, трифенилфосфин, гидроалкоксикарбонилдеу, карбонилдеу.

**I**ntroduction. In 1938, the German chemist Walter Reppe discovered the carbonylation of unsaturated compounds. Today, this method, called the Reppe synthesis, has become a popular method for obtaining organic compounds [1]. An important advantage of the Reppe synthesis is the possibility of obtaining unsaturated carboxylic acids and their derivatives in one stage with a high purity of the product. Reppe synthesis is an important method in industry, especially in the production of medicines and other biologically active substances. In addition, this method can be used to obtain aldehydes, ketones, and polymeric materials such as polycarbonates and polyurethanes [2-6]. After the discovery of the Rolen and Reppe reaction in the 1940s, the carbonylation reactions involving transition metals discovered by Heck and others in the 1970s were accelerated by the discovery of cross-combination reactions of carbonyl groups, and their scope expanded significantly. Since then, scientific progress in this field has been enormous, in particular due to the development of selective and efficient catalysts.

Carbonylation is a general term for many reactions in which carbon monoxide is added to an organic molecule. Carbonylation reactions are one of the most important processes in organic chemistry, since they are used to synthesize many industrial and medical compounds, such as aldehydes, ketones, esters, and amides [7]. Hydroformylation reactions have enabled the development of many valuable methods for the direct introduction of carbonyl groups into organic molecules due to their ability to coordinate and activate carbon monoxide. However, the Oxo and Rehlen methods use carbon monoxide under high pressure, the reaction is carried out at high temperature, and highly toxic compounds are used as catalysts. At present, the development of highly active catalysts based on Pd,

Ru, Rh and Pt and catalysts based on other transition metals has made it possible to carry out carbonylation reactions under much milder and safer conditions.

Carbonylation reactions in the presence of metals of variable valence have become an area of intensive research in synthetic organic chemistry in the last decade. Metal complexes such as Co, Ni, Fe, Ru, Rh, Os, Ir, Pt, Pd exhibit high catalytic activity in hydroalkoxycarbonylation reactions of alkenes and other unsaturated compounds [8–11].

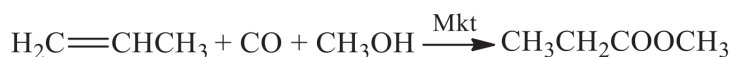
Palladium complexes promoted by free ligand-forming agents and strong protic acids are the most promising catalysts for hydroalkoxycarbonylation reactions. Carbonylation reactions in the presence of palladium complexes significantly enriched the methods for obtaining carbonyl compounds [12–14]. The alkoxycarbonylation reactions in the presence of palladium make it possible to effectively convert unsaturated compounds, CO, and alcohols into the corresponding derivatives of carboxylic acids [15–17].

Palladium complexes have a number of advantages over other catalysts in hydroalkoxycarbonylation reactions. These advantages include high activity, selectivity and resistance to reaction conditions. Carbon monoxide can serve as an ideal ligand for catalysts based on Pd(0) and Pd(II), since it can act as a  $\sigma$ -donor and  $\pi$ -acceptor [18]. As a result, the palladium center forms relatively stable intermediates with reagents that are sufficiently reactive in subsequent reactions of the catalytic cycle [19].

In the *olefin carbonylation reaction* in the presence of metal complex catalysts, olefins react with alcohol and carbon monoxide to form esters of carboxylic acids.

In this reaction, olefins are added to the active catalyst, and then the alcohol reacts with the complex formed on the catalyst. The CO molecule enters the molecule of the alkylated product and forms the desired carbonyl product [14].

An example of olefins olefins olefins is the reaction of propylene in the presence of rhodium (Rh) catalysts [20]:



*The carbonylation reaction of cycloolefins* is a reaction in which carbon monoxide is reacted with cyclic hydrocarbons having a double bond in the ring system, such as cyclohexene, cyclopentadiene and diene rubbers. The reaction proceeds under pressure of carbon monoxide and in the presence of catalysts, usually metal complex catalysts. The carbonylation process can take place in the liquid or gas phase at temperatures up to about 150°C. As a result, complex carboxylic acids, aldehydes, and ketones are obtained [21–22].

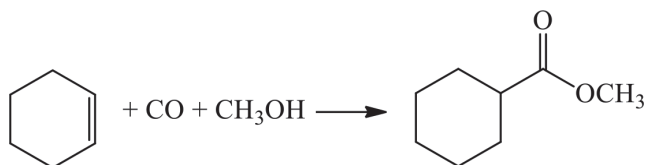
Cycloolefin carbonylation products are used in various industries, including pharmaceuticals, plastics, synthetic rubbers, dyes, perfumes, and others. b. wide range of applications in manufacturing. The carbonylation reaction of cycloolefins is complex and requires careful control of the reaction conditions to obtain the desired products. In addition, the process can lead to the formation of unexpected by-products that degrade the quality of the final product. Therefore, to obtain high-quality products such as carboxylic acids, it is necessary to precisely control such reaction parameters as pressure, temperature, catalyst concentration, and reaction time using optimal catalysts [21].

Thus, the carbonylation of cycloolefins is an important process for the synthesis of high quality products. It is widely used in industry and continues to attract the attention of



researchers in connection with the search for new, more efficient methods for the synthesis of complex carbon compounds.

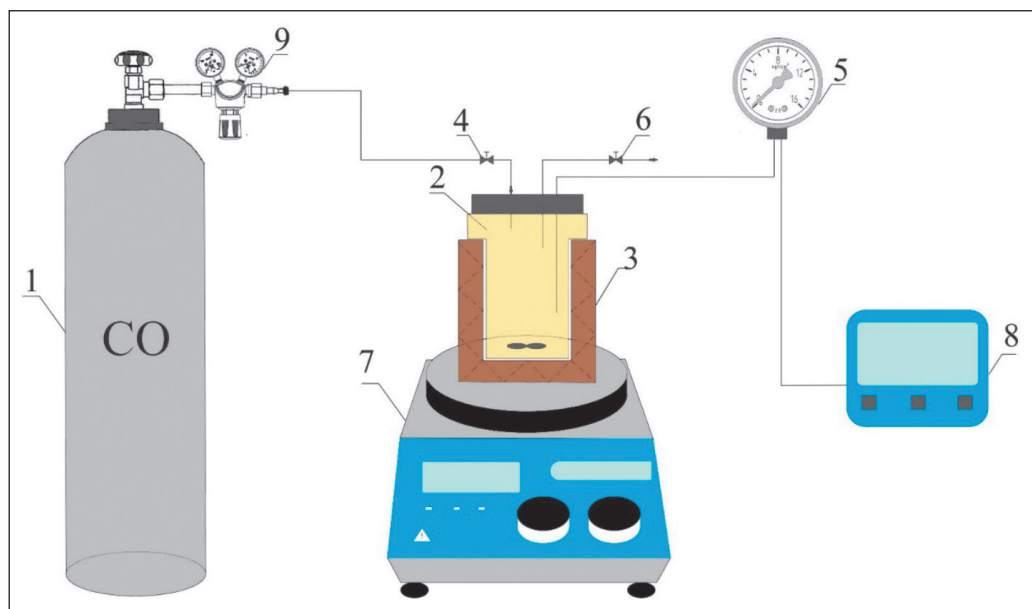
Sergei Batashev and other scientists [23] performed hydromethoxycarbonylation reactions of cyclohexene in the presence of  $\text{Pd}(\text{OAc})_2/\text{trans-2,3-bis}(\text{diphenylphosphinomethyl})\text{norbornene}/p\text{-toluenesulfonic acid (TsOH)}$  at 378 K with  $[\text{HPd}(\text{CO})_2\text{Ots}]$  by compared with the diphosphine complex,  $[\text{HPd}(\text{TBDPN})(\text{CH}_3\text{OH})]\text{OTs}$  showed higher stability.



As a rule, the optimal reaction time for each particular hydroalkoxycarbonylation reaction should be determined experimentally, taking into account the specific reaction conditions and the choice of catalysts. This contributes to achieving the maximum yield of the target product, minimizing the formation of by-products, and increasing the efficiency of the hydroalkoxycarbonylation reaction.

**Materials and research methods.** Experiments on the hydroethoxycarbonylation of cyclopentene of the  $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$  system were carried out in a laboratory autoclave without the use of a solvent.

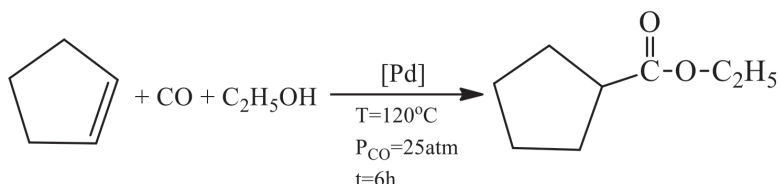
$\text{PdCl}_2(\text{PPh}_3)_2$  0,08 g ( $1,14 \times 10^{-4}$  mol),  $\text{PPh}_3$  0,180 g ( $6,84 \times 10^{-4}$  mol),  $\text{AlCl}_3$  0,152 g ( $10,26 \times 10^{-4}$  mol), ethanol 2,289 g ( $4,96 \times 10^{-2}$  mol) and cyclopentene 6,76 g ( $9,92 \times 10^{-2}$  mol) were added to a 100 ml steel autoclave equipped with a magnetic stirrer and a device



**Figure 1 – Scheme of a laboratory setup for carrying out the reaction of hydroalkoxycarbonylation of olefins on metal complex catalysts**

for introducing carbon monoxide. The ratio of the initial reagents and components of the catalytic system ( $[C_5H_8]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$ ) = 870:435:1:6:10. The autoclave was sealed and pumped three times with carbon monoxide to remove the air inside it and with 15 atm was filled to pressure. Then a magnetic mixer and an electric heater were added, which increased the temperature to 120 °C and the carbon monoxide pressure to 25 atm within 1 hour. At this set temperature and pressure, the reaction mixture was intensively mixed for 5 hours. Then it is cooled to room temperature, and the reaction mixture is fractionated at atmospheric pressure. As a result of distillation, 5,359 g (75.74 %) of the product was obtained.

**Results and discussion.** *Hydroethoxycarbonylation of cyclopentene in the ternary system  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$*



Activation of the three-component  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  catalytic system containing  $AlCl_3$  as a promoter was investigated in the reaction of cyclopentene carbon monoxide and ethanol hydroethoxycarbonylation, and high catalytic activation of the  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  system was detected at low carbon monoxide pressure ( $P_{CO} = 25$  atm) for this reaction. It is proved that the reaction proceeds with the formation of cyclopentanecarboxylic acid ethyl ether, due to the coincidence of physical properties, i.e. boiling point and refractive index values, with reference data.

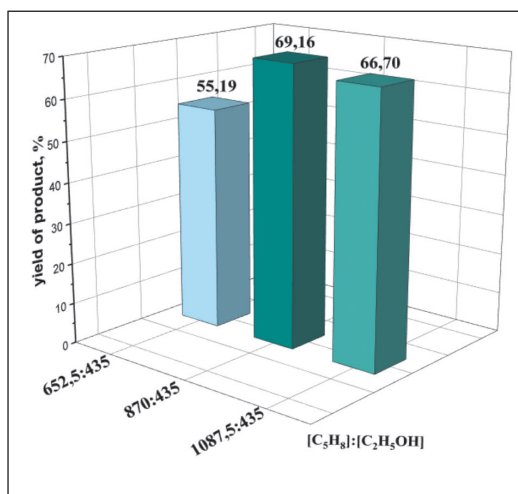
It was found that the yield of the target product is influenced by the reaction conditions: temperature, CO pressure, the proportion of the initial reagents, the ratio of the components of the catalytic system and the duration of the reaction.

Influence of the molar ratios of the initial reagents on the yield of the reaction product

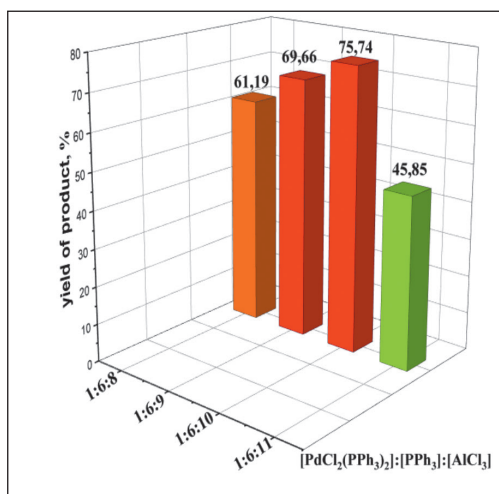
The influence of the ratio of primary reagents on the yield of the target product in the reaction of hydroethoxycarbonylation of cyclopentene with ethanol under reduced pressure of carbon monoxide was studied, and the results of the experiments are presented in *Table 1* and in *Figure 2*.

**Table 1 – Study of the effect of molar ratios of the starting reagents in the hydroethoxycarbonylation reaction of cyclopentene on the product yield**

Ratio of initial reagents $[C_5H_8]:[C_2H_5OH]$	The ratio of the components of the catalytic system $[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$	Reaction conditions			General output, % (mass.)
		T, °C	$P_{CO}$ , atm	$\tau$ , hour	
652,5:435	1:6:9	120	25	6	55,19
870:435	1:6:9	120	25	6	69,66
1087,5:435	1:6:9	120	25	6	66,70



**Figure 2 – The effect of molar ratios of initial reagents on the output of products**



**Figure 3 – The effect of the ratio of the components of the catalytic system on the output**

As a result of the experiments, it became known that a change in the molar ratio of the initial reagents has a great influence on the yield of the reaction product. The change in the molar ratio of primary reagents - cyclopentene and ethanol from [C<sub>5</sub>H<sub>8</sub>]:[C<sub>2</sub>H<sub>5</sub>OH]=652.5:435 to 1087.5:435 was taken into account. It has been established that an important factor affecting the yield of the target product is the change in the concentration of cyclopentene. Molar ratios were studied between 652.5:435 and 870:435 resulting in an increase from 55.19 % to 69.16 %. As a result of a further increase in the ratio of primary reagents [C<sub>5</sub>H<sub>8</sub>]:[C<sub>2</sub>H<sub>5</sub>OH] to 1087.5:435, the product yield decreased to 66.7 %. Based on the results obtained, it was determined that the molar ratio of the most optimal primary reagents is [C<sub>5</sub>H<sub>8</sub>]:[C<sub>2</sub>H<sub>5</sub>OH] = 870:435.

***Influence of the ratio of the components of the catalytic system on the yield of the product***

The effect of the molar ratio of the components of the PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-PPh<sub>3</sub>-AlCl<sub>3</sub> catalytic system on the yield of the product formed as a result of the cyclopentene hydrotoxicarbonylation reaction under such conditions [C<sub>5</sub>H<sub>8</sub>]:[C<sub>2</sub>H<sub>5</sub>OH] = 870:435, T = 120 °C, P<sub>CO</sub> = 25 atm., τ = 6 h. was investigated. The results of the study are presented in Table 2 and Figure 3.

**Table 2 – Study of the influence of the ratio of the components of the catalytic system on the yield of the product in the reaction of hydroethoxycarbonylation of cyclopentene**

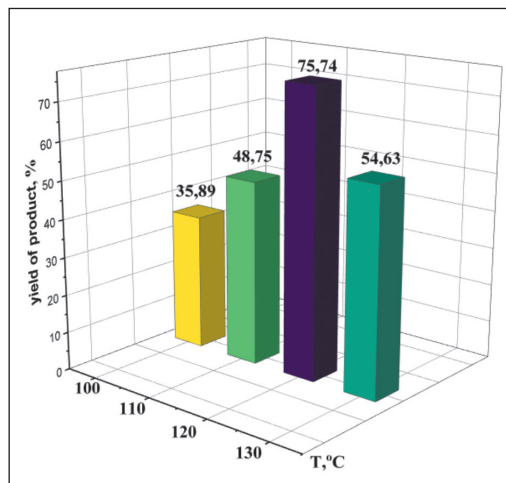
Ratio of initial reagents [C <sub>5</sub> H <sub>8</sub> ]:[C <sub>2</sub> H <sub>5</sub> OH]	The ratio of the components of the catalytic system [PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]:[PPh <sub>3</sub> ]:[AlCl <sub>3</sub> ]	Reaction conditions			General output, % (mass.)
		T, °C	P <sub>CO</sub> , atm	τ, hour	
870:435	1:6:8	120	25	6	61,19
870:435	1:6:9	120	25	6	69,66
870:435	1:6:10	120	25	6	75,74
870:435	1:6:11	120	25	6	45,85



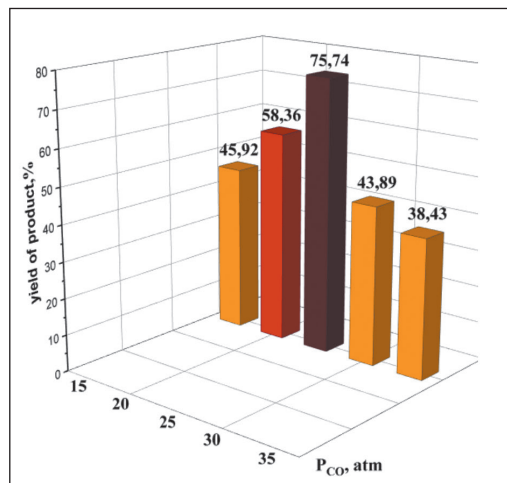
It has been established that the use of a Lewis acid, aluminum (III) chloride, as a promoter increases the activity of the catalytic system. Changing the ratio of  $[\text{PdCl}_2(\text{PPh}_3)_2]:[\text{PPh}_3]:[\text{AlCl}_3]$  from 1:6:8 to 1:6:11, i.e. an increase in the concentration of the promoter led to the yield of the ratio of the target product from 61.19 % to 1:6:10 led to an increase to 75.74 %, a further increase in the ratio to 1:6:11 showed a decrease in the yield of the product by 45.85 %. Based on the results obtained, it was found that the optimal molar ratio of the components of the catalytic system is 1:6:10.

***The effect of temperature, reaction time, and CO pressure on the yield of the reaction product***

The molar ratio of primary reactants and components of the catalytic system for the hydroethoxycarbonylation reaction of cyclopentene under reduced pressure of carbon monoxide ( $P_{\text{CO}} = 25 \text{ atm}$ ) ( $[\text{C}_5\text{H}_8]:[\text{C}_2\text{H}_5\text{OH}]:[\text{Pd}]:[\text{PPh}_3]:[\text{AlCl}_3] = 870:435:1:6:10$ ), after finding the most optimal values, the effect of temperature on the carbonylation reaction was studied, and it became known that temperature has a significant effect on the yield of the target product. The results of the experiment are presented in *Table 3* and *Figure 4*.



**Figure 4 – The effect of temperature on the product yield**



**Figure 5 – The effect of CO pressure on the product yield**

The experiment was carried out in the temperature range of 100-130 °C and the temperature change in the yield of the reaction product of hydroethoxycarbonylation of cyclopentene was determined. An increase in the reaction temperature from 100 °C to 120 °C increased the yield of the target product from 35.89 % to 75.74 %, a further increase in temperature to 130 °C increased the yield of the target product, which led to its decrease by 54.63 %.

Based on the obtained research results, it is known that the most optimal temperature for the reaction of hydroethoxycarbonylation of cyclopentene is 120 °C.

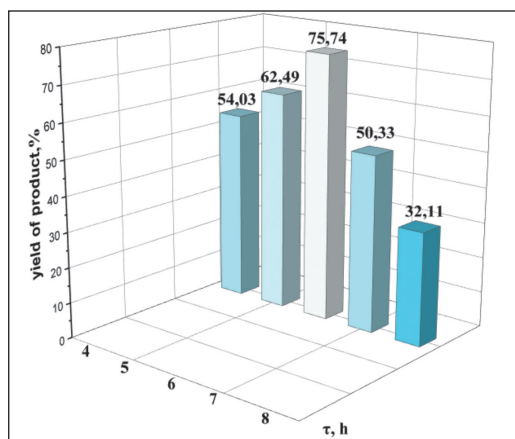
Since the reactions of carbonylation of cyclopentene with ethanol proceed directly in the presence of carbon monoxide, the magnitude and magnitude of the supplied pressure of CO is considered one of the main influencing factors. During the study 15; 20; 25; 30; the

**Table 3 – Study of the effect of temperature, reaction time and CO pressure on the yield of the reaction product of cyclopentene gyroethoxycarbonylation**

Ratio of initial reagents [C <sub>5</sub> H <sub>8</sub> ]:[C <sub>2</sub> H <sub>5</sub> OH]	The ratio of the components of the catalytic system [PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]:[PPh <sub>3</sub> ]:[AlCl <sub>3</sub> ]	Reaction conditions			General output, % (mass.)
		T, °C	P <sub>CO</sub> , atm	τ, hour	
870:435	1:6:10	100	25	6	35,89
870:435	1:6:10	110	25	6	48,75
870:435	1:6:10	120	25	6	75,74
870:435	1:6:10	130	25	6	54,63
870:435	1:6:10	120	15	6	45,92
870:435	1:6:10	120	20	6	58,36
870:435	1:6:10	120	30	6	43,89
870:435	1:6:10	120	35	6	38,43
870:435	1:6:10	120	25	4	54,03
870:435	1:6:10	120	25	5	62,49
870:435	1:6:10	120	25	7	50,33
870:435	1:6:10	120	25	8	32,11

influence of CO pressure 35 atm on the yield of the target product was investigated and it was found that a pressure of 25 atm is effective for hydroethoxycarbonylation reactions of cyclopentene (the yield of the target product is 75.74 %). Increasing the process pressure from 15 atm to 25 atm led to an increase in the yield of the target product from 45.92 % to 75.74 %. It has been established that a further increase in CO pressure to 30 atm and 35 atm leads to a decrease in the yield of the target product to 43.89 and 38.43 %, respectively. The results of the experiment are presented in *Table 3* and *Figure 5*.

In addition, as a result of the hydroethoxycarbonylation reaction of cyclopentene, the ratio of the content of the initial reagents and components of the catalytic system ([C<sub>5</sub>H<sub>8</sub>]:[C<sub>2</sub>H<sub>5</sub>OH]:[Pd]:[PPh<sub>3</sub>]:[AlCl<sub>3</sub>] = 870:435:1:6:10) and the most effective values of the reaction parameters (T=120 °C, P<sub>CO</sub>=25 atm), the effect of the duration of the reaction on the carbonylation reaction was studied. The results of the experiment are presented in *Table 3* and *Figure 6*.



**Figure 6 – The effect of reaction duration on output**


It was found that the cyclopentene hydroethoxycarbonylation reaction was carried out with a time interval of 4-8 hours and had a great influence on the yield of the cyclopentene hydro-oxycarbonylation reaction product. An increase in the reaction time from 4 to 6 hours led to an increase in the target yield of the product from 54.03 % to 75.74 %. It is known that a further increase in the reaction time to 7 and 8 hours leads to a decrease in the target yield of the product by 50.33 % and 32.11 %, respectively.

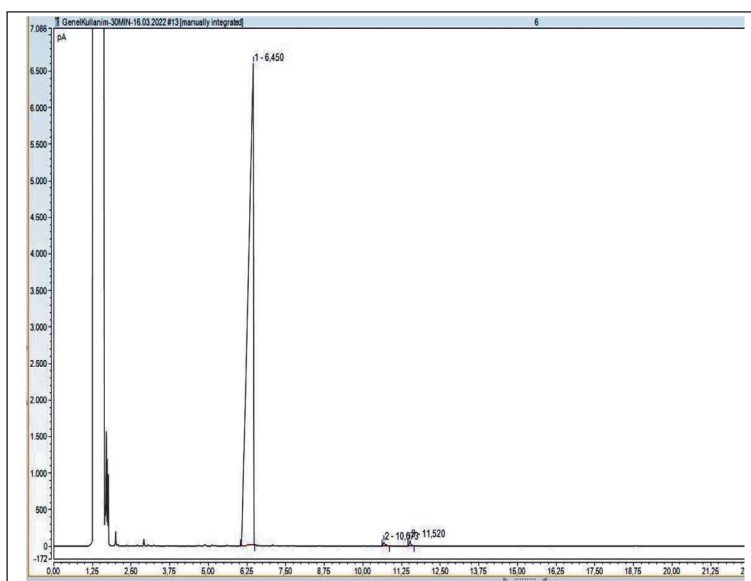
It is known that the optimal duration of the reaction for the process of hydrotoxicarbonylation of cyclopentene occurring at the parameters  $[C_5H_8]:[C_2H_5OH] = 870:435$ ,  $[Pd]:[PPh_3]:[AlCl_3] = 1:6:10$ ,  $T = 120\text{ }^\circ\text{C}$ ,  $P_{CO}=25\text{ atm}$ , determined by the results of the above study, is 6 h was.

Thus, the ternary system  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  with  $AlCl_3$  as a promoter has a high catalytic activity in the reaction of hydroethoxycarbonylation of cyclopentene in the presence of carbon monoxide, which it exhibits. Molar ratio of primary reactants and components of the catalytic system to the yield of the reaction product of hydroethoxycarbonylation of cyclopentene with respect to the catalytic system  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$ . The effect of parameters such as temperature, CO pressure, and reaction time was studied. As a result, the following effective parameters were determined:  $PCO = 25\text{ atm}$ ,  $T=120\text{ }^\circ\text{C}$ ,  $\tau = 6\text{ hours}$ ,  $[C_5H_8]:[C_2H_5OH]:[Pd]:[PPh_3]:[AlCl_3]=870:435:1:6:10$ . As a result of the hydroethoxycarbonylation reaction under the found optimal conditions, the product yield was 75.74 %.

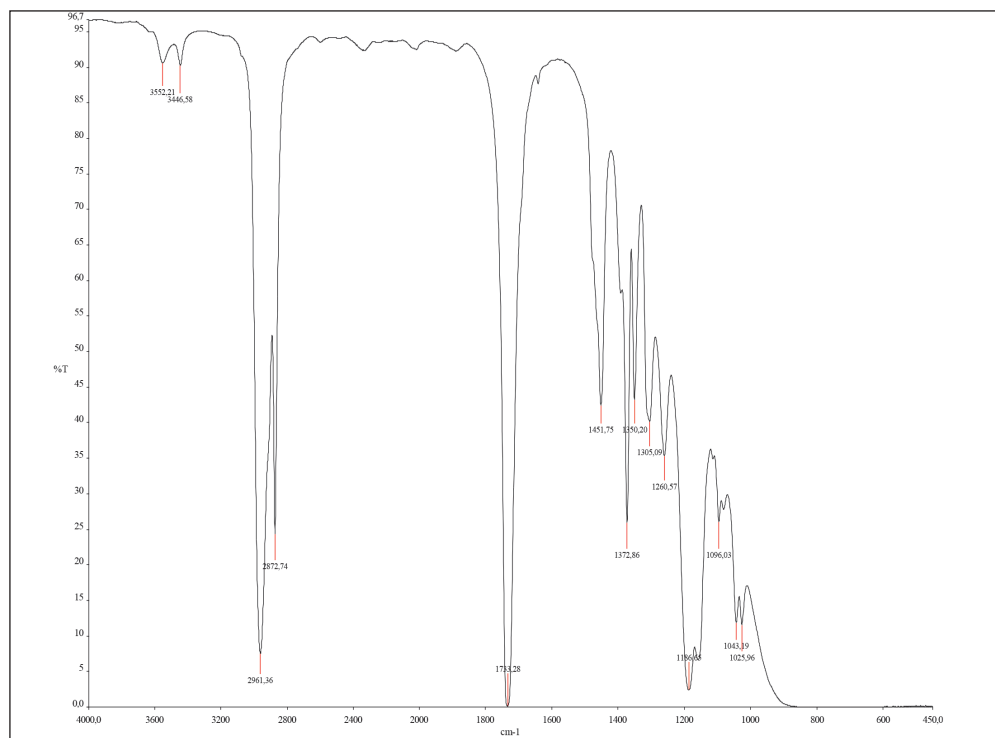
The fractionated product was analyzed and identified by GCh. Basically, at a retention time of 6450 minutes, a change in the value of the total ion current by  $pA = 6793$  was observed, which in turn indicates that the target product, ethylcyclopentanecarboxylate, contains ions proportional to this value (1-unreacted cyclopentene; 2 - ethylcyclopentanecarboxylate; 3 - containing a 99 % standard solution of ethylcyclopentanecarboxylic acid with ether). The result of the analysis of the product obtained as a result of the hydroethoxycarbonylation reaction of cyclopentene under certain optimal parameters is shown in *Figure 7*.

The IR spectrum of the ethylcyclopentanecarboxylate product obtained as a result of the synthesis was recorded (*Figure 8*). In the spectrum, the absorption bands at  $3552.21\text{ cm}^{-1}$  and  $3446.58\text{ cm}^{-1}$  indicate the presence of an O-H bond of the carboxylic acid, and the absorption band at  $1733.28\text{ cm}^{-1}$  indicates the presence of a C=O bond. From the absorption band at  $1260.57\text{ cm}^{-1}$ , vibrations of the C-O bond of the aromatic ether can be observed.

**Conclusion.** The activity of the three-component catalytic system  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  in the reaction of hydroethoxycarbonylation of cyclopentene carbon monoxide at low pressure was studied and it was found that the  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$  system exhibits high catalytic activity in the reactions of hydroethoxycarbonylation of cyclopentene. The effective parameters of the hydroethoxycarbonylation process were determined for the first time in relation to the cyclopentene three-component system  $PdCl_2(PPh_3)_2-PPh_3-AlCl_3$ . At the molar ratio of the initial reagent  $[C_5H_8]:[C_2H_5OH] = 2:1$ , at the molar ratio of the component of the catalytic system  $[Pd]:[PPh_3]:[AlCl_3]$  in the amount of 1:6:10 and at  $T=120\text{ }^\circ\text{C}$ ,  $P_{CO}=25\text{ atm}$ . under pressure and reaction time  $\tau=6\text{ hours}$ , ethylcyclopentanecarboxylate was synthesized with a yield of 75.74 %. 



**Figure 7 – Chromatogram of the product of hydroethoxycarbonylation of cyclopentene of the  $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPH}_3\text{-AlCl}_3$  system in optimal parameters**



**Figure 8 – IR spectrum of the reaction product of hydroethoxycarbonylation of cyclopentene of the  $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPH}_3\text{-AlCl}_3$  system**

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