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ETHOXYCARBONYLATION OF PENTENE-1 IN THE PRESENCE OF $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ SYSTEM

Shalmagambetov K.M.[1]***, Zhaksylykova G.J.***[1]***, Kanapieva F.M.***[1]***,***
Kudaibergenov N.J.[1]***, Abyzbekova G.M.***[2]

[1]*Al-Farabi Kazakh National University, Almaty, Kazakhstan*
[2]*Korkyt Ata Kyzylorda University, Kyzylorda, Kazakhstan*
E-mail: banu.81@mail.ru

Abstract: *Introduction:* Reactions based on CO allow the synthesis of almost all oxygen-containing organic compounds, which are important raw materials for obtaining practically valuable products of wide consumption. Alkoxycarbonylation of olefins with CO and various alcohols in the presence of metal complex catalysts synthesizes esters of carboxylic acids in one step. *The purpose:* In accordance with previously synthesized ethyl esters of enanthic and 2-methylcaproic acids in the reaction of ethoxycarbonylation of hexene-1 with CO in the presence of the catalytic system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ in this work we planned to synthesize ethyl esters of capronic and 2-methylvalerian acids by hydroethoxycarbonylation of pentene-1 with CO in the presence of the same catalytic system. *Methodology*: The autoclave was sealed and then filled with CO to 1.5 MPa pressure. The pressure of CO was brought to 2.0 MPa, the temperature was raised to 100^0C for 1 hour and at this pressure and temperature the reaction mixture was stirred for 5 h. *Results and discussion*: Experimental results show that the reaction proceeds with the formation of two isomeric products of linear (EECA) and branched structure (EE-2-MVA). Optimal reaction conditions have been found, at which the yield of the target products (sum of isomeric esters of EECA and EE-2-MVA) reaches 74.72 %. *Conclusion:* The catalytic activity of the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ containing $AlCl_3$ as a promoter in the reaction of ethoxycarbonylation of pentene-1 has been established. The reaction proceeds with the formation of two isomeric products of linear (EECA) and branched structure (EE-2-MVA).

Key words: pentene-1, carbon oxide(II), alcohols, ethoxycarbonylation, metal complex catalysts

Shalmagambetov Kairzhan Mustafinovich	*Doctor of chemical sciences, Head of the laboratory, e-mail: kairshan@yandex.ru, ORCID ID: https://orcid.org/0000-0002-5660-9208*
Zhaksylykova Gulbanu Zhaksylykova	*Candidate of chemical sciences, associate professor, senior researcher, e-mail: banu.81@mail.ru, ORCID ID: https://orcid.org/0000-0003-2390-0688*
Kanapiyeva Fatima Mukhidinovna	*Candidate of chemical sciences, senior researcher, e-mail: fatima31@mail.ru,ORCID ID: https://orcid.org/0000-0002-9829-3117*
Kudaibergenov Nurbolat Zharylkasinuly	*Doctor of philosophy (PhD) in chemistry, senior researcher, e-mail: nuka1991@mail.ru, ORCID ID: https://orcid.org/0000-0002-4641-6779*
Abyzbekova Gulmira Mynbayevna	*Candidate of chemical sciences, senior researcher, e-mail: abizgul@mail.ru, ORCID ID: https://orcid.org/0000-0003-3721-1322*

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1. Introduction

Palladium-catalyzed carbonylation of olefins has been of industrial interest for about five decades, as confirmed by several papers [1]. Syntheses of most organic compounds based on carbon oxide (II) is an extensive and topical part of modern organic synthesis. A wide range of oxygen-containing organic compounds, which are valuable raw materials for obtaining medicines, pesticides, plastic masses, synthetic fibers, etc., can be obtained on the basis of carbon oxide (II). The vast majority of carbon oxide (II) based syntheses are catalytic [2].

Carboxylic acids and their derivatives (esters, anhydrides, amides, metal salts, etc.) are high volume products and chemical intermediates. There are several known ways of obtaining carboxylic acids and their derivatives by carbonylation catalyzed by transition metals. Although oxidative carbonylation is sometimes also called hydrocarboxylation or hydroetherification, it differs significantly in that an oxidizer, usually air, is required to re-oxidize Pd^0 formed in stoichiometric amounts to $Pd^{2+\cdot}$In addition, the catalytic system also contains a catalyst, usually a copper salt, to catalyze the conversion of Pd^0/Pd^{2+}, thereby closing the catalytic cycle and stabilizing the Pd-catalyst [3-4].

Recently, Reppe carbonylation has received considerable attention. This process is very versatile because it can transform not only olefins but also acetylenes and dienes. It can also transfer a large variety of functional groups, which makes it attractive in organic synthesis. The main agents are CO and a nucleophile, usually water, alcohol, or acid, yielding a wide range of saturated or unsaturated acids, esters, or anhydrides, respectively. When the nucleophile is water or alcohol, the process is called hydrocarboxylation or hydroetherification, respectively. Hydroetherification is sometimes also called hydroalkoxycarbonylation or hydrocarbalkoxylation [3].

Oxidative carbonylation of unsaturated hydrocarbons catalyzed by $PdCl_2(PPh_3)_2$ can produce acids and their derivatives in a single step, but has the disadvantage of producing complex product mixtures, lower yields of the target product, and the need for complex separation processes. Despite these disadvantages, Union Oil has developed a process to convert ethylene to acrylic acids, and ARCO has announced the commercial availability of its technology to convert butadiene to adipic and sebacic acids. It was reported in [3] that Pd(II)-monophosphine complexes like $[PdCl_2(PPh_3)_2]$ in combination with HCl were active, although under rather harsh pressure conditions (300-700 bar). Subsequently, it was found that the reaction could be carried out at much lower pressures. This fact prompted several research groups, including us [3-9].

α-Olefins (alkenes) unsaturated acyclic hydrocarbons contained in petroleum and natural gas products are widely used in petrochemical synthesis to obtain plastic materials, some synthetic rubbers, ester chemical fibers and other industrially important products due to their high reactivity, availability and cheapness [10-11]. There are few publications about the use of Lewis acids metal complex catalysts as promoters in the carbonylation reaction of organic substrates with carbon oxide (II) [12-13]. In [13] it was found that some Lewis acids like

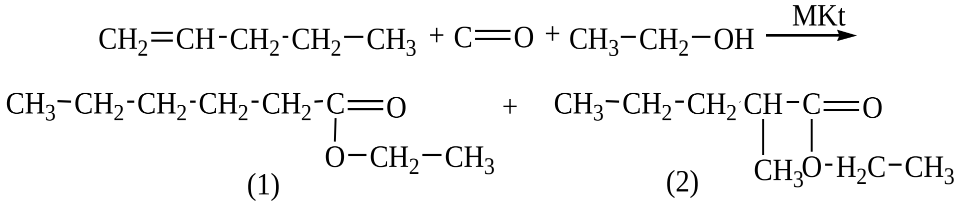
$Al(CF_3SO_3)_3$ and $Al(CH_3SO_3)_3$ are effective as promoters of palladium complex based catalytic systems in styrene and pentene-1 hydroetherification reactions and they can replace the Brensted acids traditionally used for this purpose. It is noted that the use of $AlCl_3$ as a promoter of metal complex catalysts in these reactions is ineffective.

The catalytic activity of the three-component $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ system containing Lewis acid ($AlCl_3$) as a promoter in the ethoxycarbonylation of pentene-1 was studied in the present work.

2. Results and discussion

We studied the catalytic activity of the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ with dry aluminum chloride as a metal complex catalyst promoter in the alkoxycarbonylation reaction of pentene-1 by Reppe synthesis.

In this work, we investigated the catalytic activity of metal complex catalyst promoters for the hydroesterification reaction of pentene-1.



$$CH_2{=}CH\text{-}CH_2\text{-}CH_2{-}CH_3 + C{=}O + CH_3{-}CH_2{-}OH \xrightarrow{MKt}$$

$$\underset{(1)}{CH_3{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle O{-}CH_2{-}CH_3}{\underset{|}{C}}{=}O} \quad + \quad \underset{(2)}{CH_3{-}CH_2\text{-}CH_2\,\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\underset{\displaystyle O\text{-}H_2C{-}CH_3}{\underset{|}{C}}{=}O}$$

MKt – $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$

1 – ethyl ester of caproic acid;
2 – ethyl ester of 2-methylvaleric acid

In order to compare Brensted and Lewis acids in this work, we used several types of promoters. Para-toluenesulfonic acid was used as Brensted acid. Aluminum trichloride was used as an example of Lewis acids.

Before that, Brensted acids were almost entirely investigated in scientific works, and Lewis acids have been of interest only in recent years. The reaction was found to proceed with the formation of two products (linear - ethyl ester of caproic acid (EECA) and branched - ethyl ester of 2-methylvaleric acid (EE-2-MVA)). Since the boiling points of these two isomers (EECA=168^0C, EE-2-MVA=152-153^0C) are very close, their yield ratios were determined on an Agilent 7890A/5975C chromato-mass spectrometer (USA) and an IR-Prestige 21 IR spectrometer by Shimadzu (Japan). The results of the chromato-mass spectrometer and IR-spectrum are shown.

The activity of $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ three-component catalytic system with a promoter in the form of aluminum trichloride in the reaction of ethoxycarbonylation of pentene-1 by Reppe was studied. The reaction conditions (catalytic system components ratio, CO pressure, temperature, reaction time) were determined and the effect of the target products (EECA and EE-2-MVA) on the yield of the target product was studied.

The ratio of the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ and the reagent ratio in the ethoxycarbonylation reaction of pentene-1 at low pressure of CO were studied. The pressure of CO as was investigated earlier was 2.0 MPa or 20 atm, the temperature required for the reaction was 100^0C, the time required for the reaction was 5 h.

Molar ratios of reagents [pentene-1]:[ethanol] in the ratio $[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]=1:6:7$ in ethoxycarbonylation reaction of pentene-1 at low CO pressure have been determined. As a result, in the ratio [pentene-1]:[ethanol]=435:550, the target yield was 61.16%, the linear yield was 50.92%, and the branched yield was 10.24%. The results of the experiment are presented below in Table 1.

Table 1 - Investigation of molar ratio of reactants at $[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3])=1:6:7$ in ethoxycarbonylation reaction of pentene-1 and low pressure of CO (P_{CO}=2.0 MPa, T=100^0C, τ=5 h)

№	Reagent molar ratio pentene-1:ethanol	EECA* and EE-2-MVA**, % (mass.)total yield	Yield, % (mass.)	
			Yield EECA*, % (mass.)	Yield EE-2-MVA**, % (mass.)
1	550:435	44.94	36.09	8.85
2	550:550	50.69	40.65	10.04
3	435:550	61.16	50.92	10.24
4	435:740	60.86	48.13	12.73
Notes: 1 EECA* - Ethyl ester of caproic acid. 2 EE-2-MVA** - Ethyl ester of 2-methylvaleric acid.				

After studying the molar ratios of reactants in the reaction of ethoxycarbonylation of pentene-1 at low pressure of CO the relationships of three-component system ($[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$) were studied. As a result, it was found that the optimum ratio of the three-component catalytic system $[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$ is 1:7:9, the total product yield is 68.74%, the linear product is 57.06%, and the branched product is 11.68%. The results of the experiment are given below in the Tables 2-3.

Table 2 – Investigation of the PPh_3molar ratios in the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ in the reaction of ethoxycarbonylation of pentene-1 at a low pressure of CO (P_{CO}=2.0 MPa, T=100^0C, τ=5 h)

№	Molar ratio of catalysts	EECA* and EE-2-MVA**,% (mass.)total yield	Yield, % (mass.)	
			Yield EECA*, % (mass.)	Yield EE-2-MVA**,% (mass.)
1	$PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$(1:5:7)	50.06	39.83	10.23
2	$PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$(1:6:7)	61.16	50.92	10.24
3	$PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$(1:7:7)	62.32	50.38	11.94
4	$PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$(1:8:7)	50.73	40.81	9.92
Notes: 1 EECA* - Ethyl ester of caproic acid. 2 EE-2-MVA** - Ethyl ester of 2-methylvaleric acid.				

Table 3 - Investigation of $AlCl_3$ molar ratio in the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ in the ethoxycarbonylation reaction of pentene-1 at low pressure of CO (P_{CO}=2.0 MPa, T=100^{0}C, τ=5 h)

№	Molar ratio of catalysts $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$	EECA* and EE-2-MVA**, % (mass.) total yield	Yield, % (mass.)	
			Yield EECA*, % (mass.)	Yield EE-2-MVA**, % (mass.)
1	1:7:5	66.72	55.53	11.19
2	1:7:7	67.04	55.59	11.45
3	1:7:9	68.74	57.06	11.68
4	1:7:12	57.09	44.76	12.33
Notes: 1 EECA* - Ethyl ester of caproic acid. 2 EE-2-MVA** - Ethyl ester of 2-methylvaleric acid.				

After investigation of molar ratios of reactants in ethoxycarbonylation reaction of pentene-1 at low pressure of carbon oxide (II) [pentene-1]:[ethanol]=435:550 three-component system $[PdCl_2(PPh_3)_2]$:$[PPh_3]$:$[AlCl_3]$=1:7:9 the optimum temperature of process has been determined. As a result, it was found that the optimum temperature of the process was 100 ^{0}C. The total yield of the products was 68.74%, the yield of the linear product was 57.06% and the branched product was 11.68%. The results of the experiment are presented below in Table 4.

Table 4 – Investigation of the temperature effect on the yield of the target product in the presence of the three-component system $[C_5H_{10}]$:$[C_2H_5OH]$: $[PdCl_2(PPh_3)_2]$:$[PPh_3]$:$[AlCl_3]$ in the ethoxycarbonylation reaction of pentene-1 at low pressure of CO (P_{CO}=2.0 MPa, τ=5 h)

№	Temperature, °C	EECA* and EE-2-MVA**, % (mass.) total yield	Yield, % (mass.)	
			Yield EECA*, % (mass.)	Yield EE-2-MVA**, % (mass.)
1	90	52.3	42.9	9.4
2	100	68.74	57.06	11.68
3	105	60.3	44.62	15.68
4	110	50.41	42.03	8.38
Notes: 1 EECA* - Ethyl ester of caproic acid. 2 EE-2-MVA** - Ethyl ester of 2-methylvaleric acid.				

Molar ratios of reagents in ethoxycarbonylation reaction of pentene-1 at low pressure of CO [pentene-1]:[ethanol]=435:550, three-component system $[PdCl_2(PPh_3)_2]$:$[PPh_3]$:$[AlCl_3]$=1:7:9 and process temperature were studied, then influence of duration of reaction was studied. As a result, it was found that the optimum duration of the process was 7 h. The total yield was 72.74%, the linear product was 59.06% and the branched product was 13.68%. The results of the experiment are presented below in Table 5.

Table 5 – Investigation of the influence of process duration effect on yield of target product in presence of three-component system $[C_5H_{10}]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]=435:550:1:7:9$ in ethoxycarbonylation reaction of pentene-1 at low pressure of CO (P_{CO}=2.0 MPa, T=100 ^{0}C)

№	Time of the reaction, h	EECA* and EE-2-MVA**, % (mass.) total yield	Yield, % (mass.)	
			EECA*, % (mass.)	EE-2-MVA**, % (mass.)
1	5	68.74	57.06	11.68
2	6	70.56	58.06	12.5
3	7	72.74	59.06	13.68
4	8	71.7	60.6	11.1
5	9	63.9	53.7	10.2
Notes: 1 EECA* - Ethyl ester of caproic acid. 2 EE-2-MVA** - Ethyl ester of 2-methylvaleric acid.				

Molar ratios of reactants in the reaction of ethoxycarbonylation of pentene-1 at low pressure of CO [pentene-1]:[ethanol]=435:550, three-component system $[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$ =1:7:9, after studying the process flowing temperature the influence of pressure was investigated. As a result, it was found that the pressure, which showed the optimal result, was 2.0 MPa. The total yield was 72.74%, the yield of the linear product was 59.06% and the branched product was 13.68%. The results of the experiment are presented below in Table 6.

Table 6 - Investigation of process pressure effect on yield of target product in the presence of three-component system $[C_5H_{10}]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]: [PPh_3]:[AlCl_3]=435:550:1:7:9$ in ethoxycarbonylation reaction of pentene-1 at low pressure of CO (τ = 7 h, T=100^{0}C)

№	Study of system effect on pressure, atm	EECA* and EE-2-MVA**, % (mass.) total yeild	Yield, % (mass.)	
			Yield EECA*, % (mass.)	Yield EE-2-MVA**, % (mass.)
1	15	66.21	55.02	11.19
2	20	72.74	59.06	13.68
3	25	62.57	50.21	12.36
4	30	55.34	44.82	10.52
Notes: 1 EECA* - Ethyl ester of caproic acid. 2 EE-2-MVA** - Ethyl ester of 2-methylvaleric acid.				

Thus, the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ with aluminum trichloride promoter in the ethoxycarbonylation of pentene-1 at low pressure of CO (>20 atm) was found to exhibit catalytic activity. Optimal conditions for the process were found ($[C_5H_{10}]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]:[PPh_3]: [AlCl_3]=435:550:1:7:9$; T=100^{0}C; P_{CO}=2.0 MPa; τ = 7 h); the total product yield reached 74.72%, the linear product-ethyl ester of caproic acid–59.06%, and the branched product-ethyl ester of 2-methylvaleric acid–13.68%.

IR and chromatography-mass spectroscopy of obtained products

The IR spectra of the product obtained by the reaction of ethoxycarbonylation of pentene-1 with carbon oxide (II) and ethanol in the presence of catalytic system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$.

The IR spectrum shows 1738.4 cm^{-1} clear absorption bands of wavelength 1 (complex ether group C=O), 1033-1300 cm^{-1} clear absorption bands characterizing wavelength 1 ("ether bands") and 2857-2928 cm^{-1} absorption bands of CH-, CH_2 - and CH_3 groups (CH_3, CH_2 and CH - groups).

The yield ratios (EECA + EE-2-MVA) of Agilent 7890A/5975C (USA) chromatography-mass spectrometer of two products obtained by the reaction of ethoxycarbonylation with ethanol and carbon oxide (II) in the presence of $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ catalytic system, which showed high yield within promoters.

3. Experimental part

Pentene-1 and dichlorobis(triphenylphosphine)palladium, SIGMA-ALDRICH triphenylphosphine, absolute ethanol, reactive aluminum trichloride and carbon (II) oxide without special purification were used as initial reagents. The experiments were performed without the use of solvents in a laboratory autoclave-type unit made of stainless steel. Due to proximity of boiling points of isomeric products (esters) of linear and branched structure, their separation by fractional distillation is impossible, their ratio was determined by chromatography on Agilent 7890A/5975C (USA) chromatography-mass spectrometer. Chromatographic conditions: 7890A gas chromatograph with 5975C mass-selective detector from Agilent; mobile phase (carrier gas) - helium; evaporator temperature 300 ^{0}C, flow drop (Split) 1000:1; column thermostat temperature, beginning 40^{0}C (1 min), temperature rise 5 ^{0}C per minute, end 250 ^{0}C, at this temperature held 1 min, total analysis time 44 min; ionization mode of mass-detector by electronic shock. HP-FFAP capillary chromatographic column, column length 30 m, inner diameter 0.25 mm, fixed phase - nitroterephthalic acid modified with polyethylene glycol.

Identification of the synthesized compounds was performed by infrared spectroscopy. IR spectra were taken on a single-beam infrared spectrometer "Nicolet 5700" of Termo Electron Corporation (USA) in the region of 400-4000 cm^{-1}.

Ethoxycarbonylation of pentene-1. In a 100 ml steel autoclave, equipped with an agitator and a carbon oxide (II) injection device, 2.23 g ($3.17*10^{-2}$ mol) of pentene-1, 1.16 g ($2.51*10^{-2}$ mol) of ethanol, 0.091 g ($3.46*10^{-4}$ mol) of PPh_3, 0.054 g ($4.04*10^{-4}$ mol) of $AlCl_3$, 0.041 g ($5.77*10^{-5}$ mol) of $PdCl_2(PPh_3)_2$. Ratio of initial reagents and component of catalytic system ($[C_5H_{10}]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$) is equal to 550:435:1:6:7.

The autoclave was sealed, purged 2 times with carbon oxide (II) to remove air from it, and then filled with CO to 1.5 MPa pressure. After that stirring and heating were switched on. The pressure of CO was brought to 2.0 MPa, the temperature was raised to 100 ^{0}C for 1 h and at this pressure and temperature the reaction mixture was stirred for 5 h. Then it was cooled to r.t. The reaction mixture was fractionated under vacuum. As a result the total yield reached 74.72%, the linear product - ethyl ester of caproic acid is equal 59.06% and the branched product - ethyl ester of 2 - methylvaleric acid – 13.68%.

4. Conclusion

The catalytic activity of the three-component system $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ containing $AlCl_3$ as a promoter in the reaction of ethoxycarbonylation of pentene-1 has been established. The reaction proceeds with the formation of two isomeric products of linear (EECA) and branched structure (EE-2-MVA). Optimal reaction conditions have been found, at which the yield of the target products (sum of isomeric esters of EECA and EE-2-MVA) reaches 74.72 %.

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Conflict of Interest: The authors declare no conflict of interest.

ПЕНТЕН-1-ДІ $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ ЖҮЙЕСІ ҚАТЫСЫНДА ЭТОКСИКАРБОНИЛДЕУ

Шалмағамбетов Қ.М.[1], Жақсылықова Г.Ж.[1], Қанапиева Ф.М.[1], Құдайбергенов Н.Ж.[1], Абызбекова Г.М.[2]

[1]әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан
[2]Қорқыт ата атындағы Қызылорда университеті, Қызылорда, Қазақстан
E-mail: banu.81@mail.ru

Түйіндеме. *Кіріспе.* Көміртегі тотығына негізделген реакциялар барлық дерлік оттегі бар органикалық қосылыстарды синтездеуге мүмкіндік береді, олар іс жүзінде құнды өнімдерді алу үшін маңызды шикізат болып табылады. Олефиндерді СО және әртүрлі спирттермен алкоксикарбонилдеу арқылы металлкомплексті катализаторлардың қатысуымен карбон қышқылдарының эфирлерін бір сатыға синтездеуге мүмкіндік береді.
Бұл жұмыстың мақсаты. Бұрын синтезделген энанта және 2-метилкапрон қышқылының этил эфирлеріне сәйкес $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ каталитикалық жүйесінің қатысуымен гексен-1 СО этоксикарбонилдену реакциясында осы жұмыста ұқсас каталитикалық жүйенің қатысуымен пентен-1 СО гидроэтоксикарбонилдену реакциясымен капрон және 2-метилвалериан қышқылдарының этил эфирлерінің синтездері жоспарланған. *Әдістеме.* Автоклав саңылаусызданып, содан кейін СО-ны 1.5 МПа қысымына дейін толтырылды. СО қысымы 2.0 МПа дейін жеткізілді, температура 1 сағат ішінде 100^{0}С дейін көтерілді және бұл қысым мен температурада реакция қоспасы 5 сағат бойы араластырылды. *Нәтижелер мен талқылау.* Тәжірибе нәтижелері реакцияның сызықтық (КҚЭЭ) және тармақталған құрылымды (2-МВҚЭЭ) екі изомерлік өнімінің түзілуімен жүретінін көрсетті. Реакцияның оңтайлы шарттары табылды, онда мақсатты өнімдердің шығымы (КҚЭЭ және 2-МВҚЭЭ изомерлік эфирлерінің қосындысы) 74.72% жетті. *Қорытынды.* Пентен-1 этоксикарбонилдену реакциясында промотор ретінде $AlCl_3$ бар $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ үш компонентті жүйесінің каталитикалық белсенділігі анықталды. Реакция сызықтық (КҚЭЭ) және тармақталған құрылымды (2-МВҚЭЭ) екі изомерлі өнімінің пайда болуымен жүретіндігі анықталды.

Түйінді сөздер: пентен-1, көміртек оксиді (II), спирттер, этоксикарбонилдеу, металлкомплексті катализаторлар.

Шалмағамбетов Қайыржан Мустафинович	*Химия ғылымдарының докторы, лаборатория меңгерушісі*
Жаксылыкова Гүлбану Жаксылыковна	*Химия ғылымдарының кандидаты, доцент, аға ғылыми қызметкер*
Канапиева Фатима Мухидиновна	*Химия ғылымдарының кандидаты, аға ғылыми қызметкер*
Құдайбергенов Нұрболат Жарылқасынұлы	*PhD, аға ғылыми қызметкер*
Абызбекова Гүлмира Мыңбайқызы	*Химия ғылымдарының кандидаты, аға ғылыми қызметкер*

ЭТОКСИКАРБОНИЛИРОВАНИЕ ПЕНТЕНА-1 В ПРИСУТСТВИИ СИСТЕМЫ $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$

Шалмагамбетов К.М.[1], Жаксылыкова Г.Ж.[1], Канапиева Ф.М.[1],
Кудайбергенов Н.Ж.[1], Абызбекова Г.М.[2]

[1]Казахский национальный университет им. аль-Фараби, Алматы, Казахстан
[2]Кызылординский университет им. Коркыт Ата, Кызылорда, Казахстан
E-mail: banu.81@mail.ru

Резюме: *Введение.* Реакции на основе СО позволяют синтезировать практически все кислородсодержащие органические соединения, которые являются важным сырьем для получения практически ценных продуктов широкого потребления. Алкоксикарбонилирование олефинов с помощью СО и различных спиртов в присутствии металлокомплексных катализаторов синтезирует сложные эфиры карбоновых кислот в одну стадию. *Цель работы.* В соответствии с ранее синтезированными этиловыми эфирами энантовой и 2-метилкапроновой кислот в реакции этоксикарбонилирования гексена-1 с СО в присутствии каталитической системы $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ в данной работе запланированы синтезы этиловых эфиров капроновой и 2-метилвалериановой кислот реакцией гидроэтоксикарбонилирования пентена-1 с СО в присутствии аналогичной каталитической системы. *Методология.* Автоклав герметизировали и затем заполнили СО до давления 1,5 МПа. Давление СО доводили до 2,0 МПа, температуру повышали до 100^{0}С в течение 1 ч и при этом давлении и температуре реакционную смесь перемешивали в течение 5 ч. *Результаты и обсуждение.* Результаты экспериментов показывают, что реакция протекает с образованием двух изомерных продуктов линейной (ЭЭКК) и разветвленной структуры (ЭЭ-2-МВК). Найдены оптимальные условия реакции, при которых выход целевых продуктов (сумма изомерных эфиров ЭЭКК и ЭЭ-2-МВК) достигает 74.72 %. *Заключение.* Установлена каталитическая активность трехкомпонентной системы $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$, содержащей $AlCl_3$ в качестве промотора, в реакции этоксикарбонилирования пентена-1. Реакция протекает с образованием двух изомерных продуктов линейного (ЭЭКК) и разветвленного строения (ЭЭ-2-МВК).

Ключевые слова: пентен-1, оксид углерода (II), спирты, этоксикарбонилирование, металлокомплексные катализаторы

Шалмагамбетов Кайыржан Мустафинович	*Доктор химических наук, заведущий лабораторией*
Жаксылыкова Гулбану Жаксылыковна	*Кандидат химических наук, доцент, старший научный сотрудник*

Канапиева Фатима Мухидиновна	*Кандидат химических наук, старший научный сотрудник*
Кудайбергенов Нурболат Жарылкасынулы	*PhD, старший научный сотрудник*
Абызбекова Гулмира Мынбайкызы	*Кандидат химических наук, старший научный сотрудник*

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