CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES

ХИМИЯ И ТЕХНОЛОГИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ

ISSN 2686-7575 (Online)
https://doi.org/10.32362/2410-6593-2023-18-1-29-37
UDC 66.095.62+544.47+547.326+544.478.1

RESEARCH ARTICLE

Combined process of cyclohexyl cyclohexanecarboxylate synthesis from cyclohexanol and CO catalyzed by the $Pd(OAc)_2$–PPh_3–*p*-toluenesulfonic acid system

Nadezhda T. Sevostyanova✉, Sergey A. Batashev, Anastasia S. Rodionova

Tula State Lev Tolstoy Pedagogical University, Tula, 300026 Russia
✉Corresponding author, e-mail: sevostyanova.nt@gmail.com

Abstract

Objectives. *To study the possibility of combining acid-catalytic cyclohexanol dehydration and alkoxycarbonylation of the formed cyclohexene with cyclohexanol and carbon(II) oxide in a single reactor in order to achieve high yields of the target cyclohexyl cyclohexanecarboxylate product using the* $Pd(OAc)_2$–PPh_3–*p-toluenesulfonic acid catalytic system.*
Methods. *The combined process took place in a toluene medium in a periodic steel reactor designed to operate at elevated pressure, equipped with a glass insert, a magnetic stirrer, and a sampler, as well as gas input and discharge devices. The reaction mass with the components of the catalytic system was placed in a glass reactor inside a steel autoclave. The reaction mass samples obtained during the combined process were analyzed by gas–liquid chromatography with a flame ionization detector.*
Results. *The possibility of combining cyclohexanol dehydration catalyzed by p-toluenesulfonic acid monohydrate and formed cyclohexene alkoxycarbonylation with cyclohexanol and CO during catalysis by the* $Pd(OAc)_2$–PPh_3–*p-toluenesulfonic acid system in a single reactor was demonstrated. Under mild conditions (temperature 110°C; CO pressure 2.1 MPa), the target product yield reached 64.8% in 5 h. However, the combined process is complicated by the formation of a cyclohexanecarboxylic acid by-product formed as a result of the cyclohexyl cyclohexanecarboxylate hydrolysis and the cyclohexene hydroxycarbonylation.*

Conclusions. *The reactions of intramolecular acid-catalytic cyclohexanol dehydration and formed cyclohexene alkoxycarbonylation catalyzed by the* $Pd(OAc)_2$*–*PPh_3*–p-toluenesulfonic acid system can be combined in a single reactor. p-Toluenesulfonic acid can simultaneously act as a catalyst for the cyclohexanol dehydration and a co-catalyst of the palladium–phosphine system of cyclohexene alkoxycarbonylation. The involvement of cyclohexene, representing a product of reversible cyclohexanol dehydration, in the alkoxycarbonylation reaction is a factor in shifting the dehydration reaction equilibrium towards the formation of cyclohexene. Cyclohexanecarboxylic acid is a by-product of the proposed combined process. A factor in the reduction of target product yield is water formed as a result of cyclohexanol dehydration due to the involvement of the latter in the hydrolysis reaction and the course of the cyclohexene hydroxycarbonylation.*

Keywords: *combined process, alcohol dehydration, alkene alkoxycarbonylation, palladium–phosphine system, strong protonic acid*

For citation: Sevostyanova N.T., Batashev S.A., Rodionova A.S. Combined process of cyclohexyl cyclohexanecarboxylate synthesis from cyclohexanol and CO catalyzed by the $Pd(OAc)_2$–PPh_3–*p*-toluenesulfonic acid system. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2023;18(1):29–37 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2023-18-1-29-37

НАУЧНАЯ СТАТЬЯ

Совмещенный процесс синтеза циклогексилциклогексанкарбоксилата из циклогексанола и CO, катализируемый системой $Pd(OAc)_2$–PPh_3–*n*-толуолсульфокислота

Н.Т. Севостьянова✉, С.А. Баташев, А.С. Родионова

Тульский государственный педагогический университет им. Л.Н. Толстого, Тула, 300026 Россия
✉Автор для переписки, e-mail: sevostyanova.nt@gmail.com

Аннотация

Цели. *Изучение возможности совмещения в одном реакторе реакций кислотнокаталитической дегидратации циклогексанола и алкоксикарбонилирования образующегося циклогексена циклогексанолом и оксидом углерода (II). Установление возможности достижения высоких выходов целевого продукта – циклогексилциклогексанкарбоксилата – в мягких условиях при катализе системой* $Pd(OAc)_2$*–*PPh_3*–n-толуолсульфокислота.*

Методы. *Совмещенный процесс изучался в среде толуола в периодическом стальном реакторе, рассчитанном на работу при повышенном давлении, снабженном стеклянной вставкой, магнитной мешалкой, пробоотборником, устройствами ввода и сброса газов. Реакционная масса с компонентами каталитической системы помещалась в стеклянный реактор внутри стального автоклава. Отбираемые в ходе совмещенного процесса пробы реакционной массы анализировали методом газо-жидкостной хроматографии с пламенно-ионизационным детектором.*

Результаты. *Показана возможность совмещения в одном реакторе дегидратации циклогексанола, катализируемой моногидратом n-толуолсульфокислоты, и алкоксикарбонилирования образующегося циклогексена циклогексанолом и CO при катализе системой* $Pd(OAc)_2$*–*PPh_3*–n-толуолсульфокислота. В мягких условиях (температура 110 °C,* *давление CO 2.1 МПа) выход целевого продукта достигал 64.8% за 5 ч. Установлено, что совмещенный процесс осложняется образованием побочного продукта – циклогексанкарбоновой кислоты – в результате гидролиза циклогексилового эфира циклогексанкарбоновой кислоты и гидроксикарбонилирования циклогексена.*

Выводы. *Реакции внутримолекулярной кислотнокаталитической дегидратации циклогексанола и алкоксикарбонилирования образующегося циклогексена, катализируемого системой $Pd(OAc)_2$–PPh_3–п-толуолсульфокислота, могут быть совмещены в одном реакторе. п-Толуолсульфокислота может одновременно выполнять функции катализатора дегидратации циклогексанола и сокатализатора палладий-фосфиновой системы алкоксикарбонилирования циклогексена. Вовлечение циклогексена – продукта обратимой реакции дегидратации циклогексанола – в реакцию алкоксикарбонилирования является фактором смещения равновесия реакции дегидратации в сторону образования циклогексена. Побочным продуктом предлагаемого совмещенного процесса является циклогексанкарбоновая кислота. Вода, образующаяся в результате дегидратации циклогексанола, является фактором снижения выхода целевого продукта, что обусловлено вовлечением последнего в реакцию гидролиза и протеканием реакции гидроксикарбонилирования циклогексена.*

Ключевые слова: *совмещенный процесс, дегидратация спирта, алкоксикарбонилирование алкена, палладий-фосфиновая система, сильная протонная кислота*

Для цитирования: Севостьянова Н.Т., Баташев С.А., Родионова А.С. Совмещенный процесс синтеза циклогексилциклогексанкарбоксилата из циклогексанола и CO, катализируемый системой $Pd(OAc)_2$–PPh_3–*п*-толуолсульфокислота. *Тонкие химические технологии*. 2023;18(1):29–37. https://doi.org/10.32362/2410-6593-2023-18-1-29-37

INTRODUCTION

The alkoxycarbonylation of alkenes with alcohols and CO represents an alternative one-step method for obtaining esters from available raw materials, as opposed to the traditionally implemented esterification of carboxylic acids with alcohols. CO is isolated from synthesis gas, which can be obtained not only from oil and natural gas, but also from coal, as well as biomass waste, thus potentially comprising a renewable raw material source. In the alkoxycarbonylation of alkenes, homogeneous palladium–phosphine catalytic systems are considered the most active and selective, since they make it possible to obtain target products, esters, under mild conditions in high yields [1–9]. As a rule, the only by-products produced in these reactions are isomeric esters. Thus, in the alkoxycarbonylation of alkenes catalyzed by palladium compounds, the principle of atom conservation is observed, which underlies the development of resource-saving, low-waste chemical technologies offering a high level of environmental safety.

However, in some cases, alkenes are less accessible reagents than the corresponding alcohols. Although alcohols can be used as carbonylation substrates to obtain carboxylic acids and esters, these reactions take place under more severe conditions than the alkoxycarbonylation of alkenes. Thus, in industry, ethylene methoxycarbonylation is the first stage in the synthesis of methyl methacrylate according to *Lucite*'s Alpha technology, catalyzed by a palladium–phosphine system using a mixture of CO and ethylene with a total pressure of 1.0 MPa at a temperature of 80°C [2, 3]. At the same time, the carbonylation of methanol in the industrial processes of Monsanto and Cativa, carried out with catalysis by rhodium and iridium catalysts, respectively, requires maintaining a temperature of 150–200°C and a CO pressure of 3–6 MPa [10].

The objectives of this work were:

1) to study the possibility of combining in a single reactor (Fig. 1) acid catalytic dehydration of cyclohexanol (compound **1**, reaction (1)) and alkoxycarbonylation of the formed cyclohexene (compound **2**) with cyclohexanol and CO (reaction (2)) catalyzed by the $Pd(OAc)_2$–PPh_3–*p*-toluenesulfonic acid (TsOH) system;

2) to establish the possibility of achieving high yields of the target product—cyclohexyl cyclohexanecarboxylate (CHCHC, compound **3**)—under mild conditions (Fig. 1) during catalysis by the indicated catalytic system.

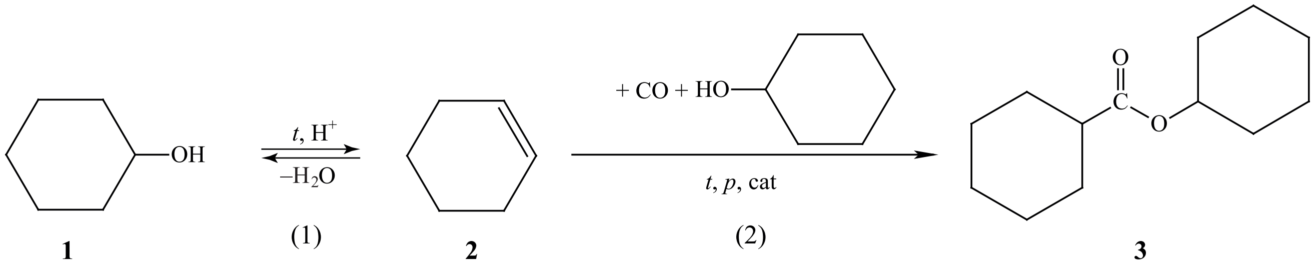

Fig. 1. Scheme for the synthesis of cyclohexyl cyclohexanecarboxylate.

The organization of processes based on the combination of two reactions in a single reactor is aimed at promoting the use of cheap and available raw materials, as well as avoiding the need to isolate and purify of the intermediate product, thus becoming a factor in reduced capital and energy costs during its subsequent implementation. As a result, the developed processes are characterized by increased efficiency, resource saving, and environmental safety.

The process under study (reactions (1), (2)) is a model one, since the alkoxycarbonylation of cyclohexene catalyzed by palladium–phosphine systems is not complicated by the formation of any by-products, including isomeric esters. The target product of this process, comprising CHCHC and other esters of cyclohexanecarboxylic acid, can be used as an additive to various types of fuels [11], an intermediate in the synthesis of medicinal substances [11, 12], plasticizers [13, 14], and components of cosmetics [15].

$Pd(OAc)_2$ [4, 16], $PdCl_2$ [6, 7], and $Pd(PPh_3)_2Cl_2$ [17] are most often used as catalytic precursors in alkoxycarbonylation of alkenes. Previously, using $Pd(PPh_3)_2Cl_2$ in combination with promoting additives PPh_3 and TsOH, we obtained product **3** in the combined process under study with a yield of 86.8% in 320 min at a ratio of cyclohexanol and TsOH of 2.5 : 1.0 (mol). When this catalytic system was supplemented with the addition of sodium *p*-tosylate as a possible agent for binding water and generating in situ additional amounts of TsOH, the yield of the target product was more than 99% for the same time at a ratio of the amount of cyclohexanol and total amounts of TsOH and TsONa 1.6 : 1.0 (mol) [18, 19]. However, for an industrially important process, it is desirable to achieve high yields of the target product in a shorter time with minimal use of various additives, as well as, if possible, without them. As shown earlier [17], the Cl^- anions of the catalytic precursor negatively affect the rate of alkoxycarbonylation. In this regard, at this stage of the study of the possibility of implementing the combined process of dehydration and alkoxycarbonylation, $Pd(OAc)_2$ was used in combination with the addition of promoters: PPh_3, one of the most active monophosphines, and TsOH, representing one of the strong organic acids previously used in the alkoxycarbonylation of cyclohexene [16–21].

EXPERIMENTAL

The combined process was studied in a toluene medium in a periodic steel reactor designed to operate at elevated pressure, equipped with a magnetic stirrer, a sampler, and gas inlet and outlet devices. The reaction mass with the components of the catalytic system $Pd(OAc)_2$, PPh_3 and *p*-toluenesulfonic acid monohydrate $TsOH{\cdot}H_2O$ was placed in a glass reactor inside a steel autoclave. During the experiments, the temperature was maintained at 110°C, the CO pressure was 2.1 MPa, and the initial concentrations of cyclohexanol and components of the catalytic system were: $C_0(C_6H_5OH) = 0.50$ M, $C_0(Pd(OAc)_2) = 2.0{\cdot}10^{-3}$ M, $C_0(PPh_3) = 2.0{\cdot}10^{-2}$ M, $C_0(TsOH{\cdot}H_2O) = (0.14–0.28)$ M. A detailed experimental technique is described in [16].

Samples of the reaction mass taken during the combined process were analyzed by gas–liquid chromatography on a Crystallux 4000M chromatograph (*SPF Metakhrom*, Russia) with a flame ionization detector and an argon carrier gas (carrier gas flow rate 1.0 mL/min; flow division 1 : 60). The evaporator and detector temperatures were 300°C and 320°C, respectively. Separation of the components of the reaction mixture was carried out in an Optima-5 capillary column (*Macherey-Nagel*, Germany) 30 m × 0.32 mm in size with a film thickness of 0.35 μm in the temperature programming mode: in the range of 120–220°C, the heating rate was 20 deg/min, in the range of 220–280°C, the heating rate is 8 deg/min, the isothermal regime is 280°C for 2.5 min. Peak areas were calculated using the NetChrom V 2.1 program (*SPF Metachrom*, Russia). Peaks in chromatograms were identified by retention time by comparison with the retention times of standard samples of substances. The concentrations of substances **1**–**3** and cyclohexanecarboxylic acid (by-product **4**) were calculated by the internal standard method, which was *o*-xylene. The internal standard was introduced at a constant concentration into a solution of cyclohexanol in toluene before the start of the experiment.

RESULTS AND DISCUSSION

According to the results of the analysis of samples of the reaction mass, it can be seen that cyclohexene is formed as an intermediate product of the studied combined process. Along with the main product, the formation of by-product **4** was recorded.

Typical curves for consumption of cyclohexanol (starting compound **1**) and accumulation of cyclohexene (intermediate product **2**), as well as cyclohexanecarboxylate (target product **3**) and cyclohexanecarboxylic acid (by-product **4**), are shown in Fig. 2.

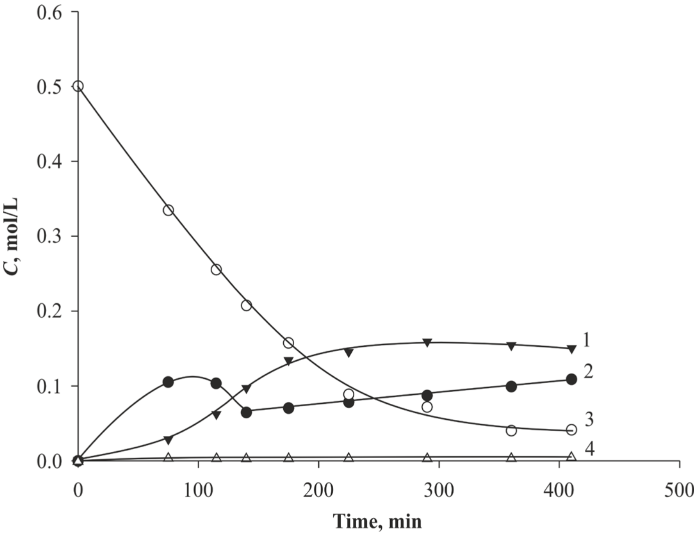

Fig. 2. Curves of reagent consumption and accumulation of intermediate, target and by-products in the combined model process at C(TsOH) = 0.280 M: 1 – product **3** accumulation; 2 – intermediate product **2** accumulation; 3 – reagent **1** consumption; 4 – product **4** accumulation.

Table below shows the results of the experiments performed with varying the concentration of TsOH and the constancy of the remaining parameters of the system. It can be seen that an increase in the TsOH concentration from 0.140 to 0.200 M was accompanied by an increase in the yield of target product **3** from 17.2% (0.043 M) to 64.0% (0.160 M). An increase in the initial concentration of TsOH to 0.28 M led to a reduction in the time to reach the maximum yield of product **3** (64.8%) to 5 h. The total concentration of free cyclohexene and cyclohexene entered in carbonylation reaction with the formation of products **3** and **4** increased with an increase in the concentration of TsOH.

Table. Results of experiments on varying the concentration of TsOH as a component of the Pd(OAc)$_2$–PPh$_3$–TsOH catalytic system of the combined model process of the cyclohexanol dehydration and the resulting cyclohexene alkoxycarbonylation

Experiment number	C(TsOH), M	Time*, min	C(1), M	C(2)**, M	C(3), M	C(4), M	C(2)***, M
1	0.140	450	0.355	0.045	0.043	0.004	0.092
2	0.200	450	0.143	0.034	0.160	0.003	0.197
3	0.250	420	0.112	0.058	0.160	0.004	0.222
4	0.280	290	0.073	0.091	0.162	0.004	0.257

*Time to reach the highest concentration of the product **3**.

**Concentration of free cyclohexene.

***Total concentrations of free cyclohexene and cyclohexene entered in carbonylation reactions with the formation of products 3 and **4**.

The formation of cyclohexanecarboxylic acid is apparently due to the presence of water in the reaction mass, which is released in reaction (1) and enters into the reactions of hydroxycarbonylation of cyclohexene (Fig. 3, reaction (3)) and hydrolysis of CHCHC (Fig. 4, reaction (4)).

Reaction (4) can be catalyzed by the strong protic acid TsOH. Hydroxy- and alkoxy-carbonylation reactions can be catalyzed by the same systems, including a palladium precursor, an organophosphine, and a strong protic acid [23, 24]. At the same time, most researchers rely on the hydride mechanism for both reactions [4–9, 16, 17, 20–24].

Based on current understandings of the acid catalysis of alcohol dehydration and the hydride mechanism of alkoxycarbonylation, a further increase in $C_0(TsOH \cdot H_2O)$ can be expected to lead to an increase in the combined CHCHC synthesis rate [16]. However, from the point of view of the industrial implementation of the process, a further increase in the concentration of $TsOH \cdot H_2O$ seems unlikely due to high concentrations of strong protic acids in the reaction mass being undesirable due to corrosion of steel equipment. Therefore, research should be continued in the direction of determining the optimal conditions for the combined process to ensure the achievement of high yields of CHCHC without increasing the concentration of a strong protic acid. One of these approaches involves the use of organodiphosphines, which are more active promoters than monophosphines for palladium catalysts of alkoxycarbonylation [1, 16].

CONCLUSIONS

The possibility of combining intramolecular acid catalytic dehydration of cyclohexanol and alkoxycarbonylation of the resulting cyclohexene during catalysis by the $Pd(OAc)_2$–PPh_3–*p*-toluenesulfonic acid system has been established. In the combined process carried out, *p*-toluenesulfonic acid simultaneously served as a catalyst for the dehydration of cyclohexanol and as a cocatalyst for the palladium–phosphine system of cyclohexene alkoxycarbonylation. Due to the involvement of cyclohexene—a product of the reversible cyclohexanol dehydration reaction—in the alkoxycarbonylation reaction, the equilibrium of the dehydration reaction was shifted towards the formation of cyclohexene; as a result, the total conversion of cyclohexanol reaching 85%. Further studies of the combined process should be carried out in the direction of finding optimal conditions that ensure the achievement of high yields of CHCHC without increasing the concentration of strong protic acid.

Acknowledgments

The study was supported by the Russian Science Foundation, grant No. 22-23-00102, https://rscf.ru/project/22-23-00102/.

Authors’ contributions

N.T. Sevostyanova – concept of the study, the idea of organizing the combined process, the analysis and interpretation of the data obtained, and writing of the text of the article.

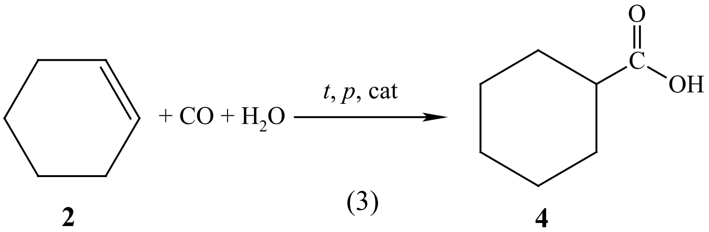

Fig. 3. Scheme for hydroxycarbonylation of cyclohexene.

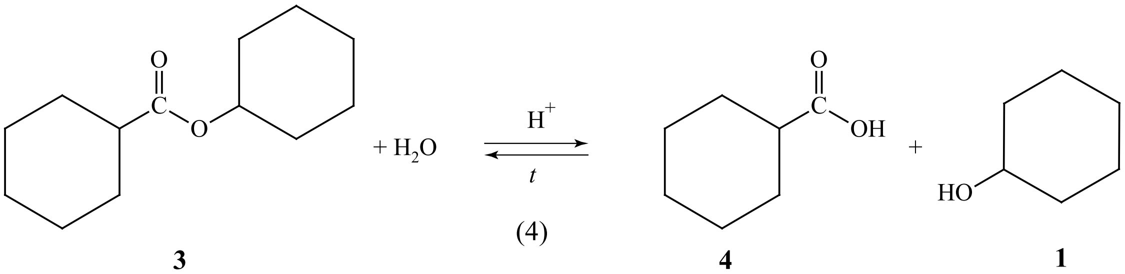

Fig. 4. Scheme for the hydrolysis of cyclohexyl cyclohexanecarboxylate.

S.A. Batashev – chromatographic analysis of the reaction mass, analysis and interpretation of the data obtained, and participation in writing the text of the article.

A.S. Rodionova – experimental studies of the combined process with sampling the reaction mass, calculation on the results of experiments, and participation in writing the text of the article.

The authors declare no conflicts of interest.

REFERENCES

1. Biermann U., Bornscheuer U., Feussner I., Meier M.A.R., Metzger J.O. Fatty Acids and their Derivatives as Renewable Platform Molecules for the Chemical Industry. *Ang. Chem. Int. Ed.* 2021;60(37):20144−20165. https://doi.org/10.1002/anie.202100778

2. Tullo A.H. A unique methyl methacrylate plant in Singapore owes its success to a handful of British chemists. *Chemical & Engineering News*. 2009;87(42). URL: https://cen.acs.org/articles/87/i42/New.html (Accessed November 30, 2022).

3. Nomura K., Awang N.W.B. Synthesis of bio-based aliphatic polyesters from plant oils by efficient molecular catalysis: a selected survey from recent reports. *ACS Sustainable Chem. Eng*. 2021;9(16):5486–5505. https://doi.org/10.1021/acssuschemeng.1c00493

4. Liu Y., Mecking S. A synthetic polyester from plant oil feedstock by functionalizing polymerization. *Angew. Chem. Int. Ed*. 2019;58(11):3346−3350. https://doi.org/10.1002/anie.201810914

5. Herrmann N., Köhnke K., Seidensticker T. Selective product crystallization for concurrent product separation and catalyst recycling in the isomerizing methoxycarbonylation of methyl oleate. *ACS Sustainable Chem. Eng*. 2020;8(29):10633–10638. https://doi.org/10.1021/acssuschemeng.0c03432

6. Nifant'ev I.E., Sevostyanova N.T., Batashev S.A., Vinogradov A.A., Vinogradov A.A., Churakov A.V., Ivchenko P.V. Synthesis of methyl β-alkylcarboxylates by Pd/diphosphine-catalyzed methoxycarbonylation of methylenealkanes $RCH_2CH_2C(R){=}CH_2$. *Appl. Catal. A: Gen.* 2019;581:123–132. https://doi.org/10.1016/j.apcata.2019.05.030

7. Nifant'ev I., Bagrov V., Vinogradov A., Vinogradov A., Ilyin S., Sevostyanova N., Batashev S., Ivchenko P. Methylenealkane-based low-viscosity ester oils: synthesis and outlook. *Lubricants*. 2020;8(5):50–59. https://doi.org/10.3390/lubricants8050050

9. Akiri S.O., Ojwach S.O. Methoxycarbonylation of olefins catalysed by homogeneous palladium(II) complexes of (phenoxy)imine ligands bearing alkoxy silane groups. *Inorganica Chim. Acta*. 2019;489:236–243. https://doi.org/10.1016/j.ica.2019.02.025

10. Kalck P., Le C., Serp B.P. Recent advances in the methanol carbonylation reaction into acetic acid. *Coord. Chem. Rev.* 2020;402:213078. https://doi.org/10.1016/j.ccr.2019.213078

11. Lapidus A.L., Pirozhkov S.D. Catalytic synthesis of organic compounds by the carbonylation of unsaturated hydrocarbons and alcohols. *Russ. Chem. Rev*. 1989;58(2):117–138. https://doi.org/10.1070/RC1989v058n02ABEH003430

[Original Russian Text: Lapidus A.L., Pirozhkov S.D. Catalytic synthesis of organic compounds by the carbonylation of unsaturated hydrocarbons and alcohols. *Uspekhi Khimii*. 1989;58(2):197–233 (in Russ.). URL: https://www.uspkhim.ru/RCR3430pdf]

12. Hoffmann U., Jansen M., Reents R., Stahr H. *Process for cyclohexanecarboxylic acid derivatives*: US Pat. 20090253927 A1. Publ. 08.10.2009.

13. Colle K., Stanat J.E., Reinoso J.J., Godwin A.D. *C_7-C_{12} Secondary alcohol esters of cyclohexanoic acid*: WO Pat. 2009/070398 A1. Publ. 04.06.2009.

14. Godwin A.D. *Co-plasticizer systems*: WO Pat. 2009/085453 A2. Publ. 09.07.2009.

15. Jenni K., Springer O. *Cosmetic and dermatological formulations including phenoxyalkyl esters*: US Pat. 20100068160 A1. Publ. 18.03.2010.

16. Nifant'ev I.E., Sevostyanova N.T., Averyanov V.A., Batashev S.A., Vorobiev A.A., Toloraya S.A., Bagrov V.V., Tavtorkin A.N. The concentration effects of reactants and components in the $Pd(OAc)_2$ / *p*-toluenesulfonic acid / trans-2,3-bis(diphenyl-phosphinomethyl)-norbornane catalytic system on the rate of cyclohexene hydrocarbomethoxylation. *Appl. Catal. A: Gen.* 2012;449:145–152. https://doi.org/10.1016/j.apcata.2012.09.020

17. Aver'yanov V.A., Sevost'yanova N.T., Batashev S.A., Nesolenaya S.V. Mechanism of the catalytic effect of the $Pd(PPh_3)_2Cl_2$-PPh_3-*p*-toluenesulfonic acid system on cyclohexene hydrocarbalkoxylation in cyclohexanol. *Pet. Chem*. 2006;46(6):405–414. https://doi.org/10.1134/S0965544106060053

[Original Russian Text: Aver'yanov V.A., Sevost'yanova N.T., Batashev S.A., Nesolenaya S.V. Mechanism of the catalytic effect of the $Pd(PPh_3)_2Cl_2$-PPh_3-*p*-toluenesulfonic acid system on cyclohexene hydrocarbalkoxylation in cyclohexanol. *Neftekhimiya*. 2006;46(6):435–445 (in Russ.). URL: https://www.elibrary.ru/item.asp?id=9466418]

18. Sevostyanova N.T, Batashev S.A. One-pot cyclohexyl cyclohexanecarboxylate synthesis from cyclohexanol and CO at catalysis by $Pd(PPh_3)_2Cl_2$ / PPh_3 / *p*-toluenesulfonic acid system. *Chemistry of Organoelement Compounds and Polymers 2019*: *Proceedings of the International Conference*. 2019. P. 239. URL: http://irbiscorp.spsl.nsc.ru/fulltext/WORKS/2019/Abstracts.pdf

19. Sevostyanova N.T, Batashev S.A. Rodionova A.S., Kozlenko D.K. Combined process of cyclohexyl cyclohexanecarboxylate synthesis from cyclohexanol and CO. In: *Sovremennaya Khimicheskaya Fizika: Sbornik Tezisov 34 Simpoziuma* (*Modern Chemical Physics: Collection of Abstracts of the 34th Symposium*). 2022. P. 170 (in Russ.). URL: http://www.chemicalphysics.ru/?page_id=1360

20. Vavasori A., Cavinato G., Toniolo L. Effect of a hydride source (water, hydrogen, *p*- toluenesulfonic acid) on the hydroesterification of ethylene to methyl propionate using a $Pd(PPh_3)_2(TsO)_2$ (TsO = *p*-toluenesulfonate anion) catalyst precursor. *J. Mol. Catal. A: Chemical*. 2001;176(1–2):11–18. https://doi.org/10.1016/S1381-1169(01)00235-7

21. Vavasori A., Toniolo L., Cavinato G. Hydroesterification of cyclohexene using the complex $Pd(PPh_3)_2(TsO)_2$ as catalyst precursor: Effect of a hydrogen source (TsOH, H_2O) on the TOF and a kinetic study (TsOH: *p*-toluenesulfonic acid). *J. Mol. Catal. A: Chemical*. 2003;191(1):9–21. https://doi.org/10.1016/S1381-1169(02)00358-8

22. Li J., Ren W., Dai J., Shi Y. Palladium-catalyzed regio- and enantioselective hydroesterification of aryl olefins with CO gas. *Org. Chem. Front*. 2018;5(1):75–79. https://doi.org/10.1039/C7QO00622E

23. Brennführer A., Neumann H., Beller M. Palladium-catalyzed carbonylation reactions of alkenes and alkynes. *ChemCatChem.* 2009;1(1):28–41. https://doi.org/10.1002/cctc.200900062

24. Neumann H., Brennführer A., Beller M. An efficient and practical sequential one-pot synthesis of suprofen, ketoprofen and other 2-arylpropionic acids. *Adv. Synth. Catal.* 2008;350(14–15):2437–2442. https://doi.org/10.1002/adsc.200800415

About the authors:

Nadezhda T. Sevostyanova, Cand. Sci. (Chem.), Associate Professor, Senior Researcher, Head, Research and Production Center "Himreaktivdiagnostika," Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: sevostyanova.nt@gmail.com. RSCI SPIN-code 9239-7136, Scopus Author ID 25643582900, ResearcherID M-8567-2014, https://orcid.org/0000-0002-3499-2226

Sergey A. Batashev, Cand. Sci. (Chem.), Associate Professor, Senior Researcher, Research and Production Center "Himreaktivdiagnostika," Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: tulapharma@gmail.com. RSCI SPIN-code 8241-9789, Scopus Author ID 14071256200, ResearcherID N-1405-2018, https://orcid.org/0000-0001-7537-7740

Anastasia S. Rodionova, Researcher, Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: rodionova.nastia@ya.ru. Scopus Author ID 57189375048, https://orcid.org/0000-0002-0896-5208

Об авторах:

Севостьянова Надежда Тенгизовна, к.х.н., доцент, старший научный сотрудник, руководитель научно-производственного центра «Химреактивдиагностика», ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: sevostyanova.nt@gmail.com. Scopus Author ID 25643582900, ResearcherID M-8567-2014, SPIN-код РИНЦ 9239-7136, https://orcid.org/0000-0002-3499-2226

Баташев Сергей Александрович, к.х.н., доцент, старший научный сотрудник научно-производственного центра «Химреактивдиагностика», ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: tulapharma@gmail.com. SPIN-код РИНЦ 8241-9789, Scopus Author ID 14071256200, ResearcherID N-1405-2018, https://orcid.org/0000-0001-7537-7740

Родионова Анастасия Сергеевна, исполнитель по гражданско-правовому договору реализации гранта Российского научного фонда, ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: rodionova.nastia@ya.ru. Scopus Author ID 57189375048, https://orcid.org/0000-0002-0896-5208

The article was submitted: October 12, 2022; approved after reviewing: November 30, 2022; accepted for publication: January 24, 2023.

Translated from Russian into English by H. Moshkov
Edited for English language and spelling by Thomas A. Beavitt