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PREPARATION OF MONOCYCLIC DIESTERS OF GLYCEROL

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Abstract: *The reaction of cyclohexene addition to glycerol in the presence of boron trifluoride etherate to obtain a simple cyclohexyl-2-glyceride ether was carried out. Also, the reaction of esterification of the obtained cyclohexyl-2-glyceride with C₁-C₅ monobasic saturated carboxylic acids in the presence of a heterogeneous catalyst KU-2-8 (H-form) was studied. The influence of various factors on the yield of cyclohexyl-2-glyceride and the ester formate obtained on its basis has been studied, and optimal reaction conditions have been found. As a result, appropriate esters with yields 71 -91% were obtained. Physicochemical properties of the synthesized esters were determined and their structure identified.*

Keywords: *glycerin, cyclohexene, cyclohexyl glyceride, esterification, monocyclic diesters, formate*

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Introduction

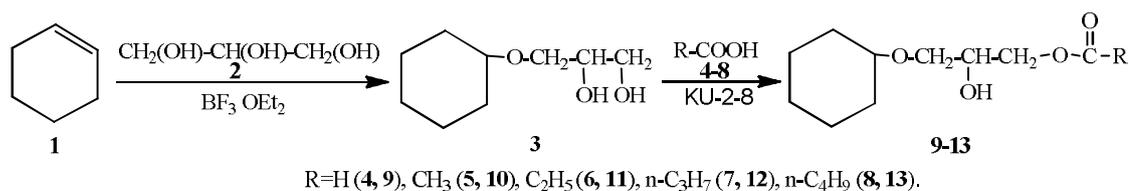
Over the past 20 years, there has been an unprecedented breakthrough in the biodiesel industry worldwide that led to an excess of glycerin. The growing demand for biodiesel has resulted in overproduction of glycerol to reduce commercial prices for glycerol [1]. Note that global growth in biodiesel production is expected to result in the production of more than 42 billion liters of crude glycerin by 2020 [2]. The traditional use of glycerin includes textiles (24%), food and drinks (21%), cosmetics and toiletries (18%), medicines (18%), tobacco (6%), paper and printing (5%), etc. It is necessary to find new conversion routes for this chemical to avoid market saturation [3]. The main processes for the synthesis of glycerol ethers which are used as fuel additives, increase the octane number and improve the properties of gasoline, are esterification of glycerol with monohydric alcohols, as well as transesterification of esters and addition of unsaturated hydrocarbons [4, 5].

It has to be kept in mind that the esterification of glycerol with carboxylic acids leads to the preparation of mono-, di- and tri-esters of glycerol. Monoesters of glycerol can be also synthesized by transesterification of glycerides. Monoesters of glycerol and their derivatives are widely used as emulsifiers in the food, pharmaceutical and cosmetic industries [6–9].

In recent years, as a result of the addition of diols to bicyclic olefins, a number of cyclic ethers have been obtained and their properties studied [10]. It revealed that they have antiseptic properties and can be used for preparation of drugs to treat fungal diseases [11].

Continuing research in this area, we studied the preparation of monocyclic ether of glycerol in the presence of a homogeneous catalyst BF₃•OEt₂ and mixed diesters based on them, by reaction of addition C₁-C₅ monobasic saturated carboxylic acids to it.

Scheme



In the first stage the reaction of addition of glycerol to cyclohexene in the presence of a $\text{BF}_3 \cdot \text{OEt}_2$ catalyst was carried out. In order to find optimal conditions for the synthesis of cyclohexyl-2-glyceride, the influence of various factors on the yield of ether was studied.

When studying the effect of temperature on yield **3**, it found that as the reaction temperature rises from 80 to 90 °C (τ -2 h, $\text{BF}_3 \cdot \text{OEt}_2$ - 0.5%), the yield of cyclohexyl-2-glyceride grows as well - from 42 to 47%, while its further growth up to 100 °C does not result in a significant increase in the yield of ether. At 90 °C, the effect of a molar ratio of reacting components of **1:2** in the range of 1:1-1:1.4 was studied to reveal that with their ratio of 1:1.2, the highest ether yield is 51%.

The influence of the amount of catalyst on the formation of ether was studied in the range of 0.5–2%. The most effective amount of catalyst is 1.3%, so the amount of catalyst (τ -2 h), the yield of cyclohexyl-2-glyceride is 55%.

The effect of the reaction time (2-6 h) on the yield of ether was also studied, and it has been found that the greatest yield is achieved with a reaction time of 4 hours

The optimal reaction conditions are as follows: temperature 90 °C, the molar ratio of the raw components **1: 2** = 1:1.2, the amount of catalyst $\text{BF}_3 \cdot \text{OEt}_2$ 1.3 wt. %, reaction time 4 hours. The yield of ether **3** is 70%.

At the second stage of the studies, the reaction of esterification of obtained cyclohexyl glyceride with carboxylic acids in the presence of a heterogeneous catalyst KU-2-8 (H-form) was carried out and 1,3-glycerol mixed diesters obtained.

To find the optimal conditions for the synthesis of cyclohexyl-2-glyceride-3-formate, the influence of the molar ratio of reacting components **3: 4** (1: 1-1: 2) and the amount of

catalyst KU-2-8 (1-3%) influence on the yield of ether **9** was studied.

Studies revealed that a high yield of ester **9** was achieved with a **3: 4** molar ratio of 1: 1 to make up 65%, because with an excess of carboxylic acid, the number of by-products - triesters of glycerol increases resulting from the addition of a secondary hydroxyl group. The optimal amount of catalyst was considered to be 2.5 wt. %, with a further increase in its amount, the yield of ether does not increase significantly.

The reaction was carried out in benzene at a temperature of 80 °C with duration of the reaction which was determined through the termination of water release which is about 3 hours. The yield of ether **9** reaches 91%.

Under similar conditions, a catalytic addition of acetic **5**, propionic **6**, butyric **7**, valeric **8** acids to **3** was carried and appropriate diesters synthesized.

In the course of esterification of saturated acids with cyclohexyl-2-glyceride, along with basic product in the amount of 7-9%, mixed triesters of glycerol were obtained.

The purity of isomeric composition and the structure of the synthesized esters were studied and proved using GLC, IR, and ^1H , ^{13}C NMR spectra. The purity of the esters, according to GLC analysis, is 98-99%.

In the IR spectra of the synthesized esters of cyclohexyl glyceride, along with intense absorption bands in the 2857-2932 ($-\text{CH}$), 1450 ($-\text{CH}_2$), there were intense absorption bands in the 1740 cm^{-1} ($\text{C}=\text{O}$) and 1229 cm^{-1} ($-\text{COO}-$) characterizing the presence of an ester group. Intense absorption bands in the 3380–3420 cm^{-1} correspond to stretching vibrations of the OH group at the secondary carbon atom which are absent in the IR spectra of mixed triglycerides as by-products of the reaction.

^{13}C NMR chemical shifts of carbon atoms of the carboxyl group are apparent in

the 160.87-165.24 ppm.

Experimental

IR spectra of the synthesized compounds were recorded on an "ALPHA IQ-FURYE" spectrophotometer by Bruker (Germany) while ^1H and ^{13}C NMR spectra were recorded on the "Bruker AV-300" with a frequency of 300 MHz (300 MHz) in acetone d_6 .

The composition and purity of the synthesized ethers, as well as the starting compounds, were determined by means of GLC analysis. The analysis was carried on a LKhM-8 MD chromatograph, column length 1.5 m, liquid phase 10 wt. % polyethylene glycol succinate on spherochrome, evaporator temperature 200-250 °C, columns 120-150 °C, detector current 100 mA, carrier gas helium, speed 45 ml / min.

Formic acid – b.p. 100.5 °C, d_4^{20} 1.220, n_D^{20} 1.3714; acetic acid – b.p. 118.1 °C, d_4^{20} 1.049, n_D^{20} 1.3698; propionic acid – b.p. 141.4 °C, d_4^{20} 0.992, n_D^{20} 1.3874; butyric acid – b.p. 163.5 °C, d_4^{20} 0.959, n_D^{20} 1.3991; valerianic acid – b.p. 186.4 °C, d_4^{20} 0.939, n_D^{20} 1.4086; $\text{BF}_3 \cdot \text{OEt}_2$ - b.p. 126 °C, d_4^{20} 1.239, n_D^{20} 1.308.

The physicochemical constants of the saturated acids coincided with published data [12].

Cyclohexyl-2-glyceride (3). A mixture of 82 g (1 mol) of reagent **1**, 110.4 g (1.2 mol) of glycerol and 1.3 g (0.01 mol) of $\text{BF}_3 \cdot \text{OEt}_2$ catalyst was stirred for 4 hours at 80 °C. The reaction mixture was washed with water, dried with magnesium sulfate and subjected to vacuum fractionation. Yield 128.8 (70%), b.p. 180 °C (45 mm Hg), d_4^{20} 1.100, n_D^{20} 1.4870. IR spectrum, ν , cm^{-1} : 1740 (C = O), 1229 (C-O-C), 1367 (CH₃), 1450 (CH₂), 2857-2932 (CH), 3412 (OH). ^1H NMR spectrum, δ , ppm: 1.30-1.70 m (10H, 5CH₂), 2.90 m (H, CH-O), 3.60 d (4H, 2CH₂, J 10.9 Hz), 3.64 m (H, CH), 3.55-3.60 s (2H, 2OH). ^{13}C NMR spectrum, δC , ppm: 32.23 (C^{1,3}), 82.1 (C²), 24.2 (C^{4,6}), 25.88 (C⁵), 71.59 (C⁷), 69.0 (C⁸), 62.7 (C⁹).

Founded, %: C 61.97; H, 10.35. C₉H₁₈O₃. Calculated, %: C 62.04; H 10.41.

Cyclohexyl-2-glyceride-3-formate

(9). A mixture of 87 g (0.5 mol) of reagent **3**, 23 g (0.5 mol) of formic acid, 50 ml of benzene and 4.4 g of KU-2-8 catalyst was heated at 80 °C for 3 h. 91.7 g (91%) compound **9** was isolated by vacuum distillation. B.p. 145-146 °C (8 mm Hg), d_4^{20} 1.1733, n_D^{20} 1.4685. IR spectrum, ν , cm^{-1} : 1738 (C = O), 1225 (C-O-C), 1364 (CH₃), 1448 (CH₂), 2856-2931 (CH), 3414 (OH). ^1H NMR spectrum, δ , ppm: 1.31-1.73 m (10H, 5CH₂), 2.88 m (H, CH-O), 3.59-4.15 d (4H, 2CH₂, J 10.9 Hz), 4.02 m (H, CH), 3.55 s (H, OH), 7.85 d (H, HCOO, J 8.3 Hz). ^{13}C NMR spectrum, δC , ppm: 31.88 (C^{1,3}), 82.08 (C²), 23.7 (C^{4,6}), 23.97 (C⁵), 72.0 (C⁷), 68.40 (C⁸), 67.91 (C⁹). 159.7 (C¹⁰). Founded, %: C 59.31; H, 8.91. C₁₀H₁₈O₄. Calculated, %: C 59.39; H, 8.97.

Cyclohexyl-2-glyceride-3-acetate

(10). A mixture of 87 g (0.5 mol) of reagent **3**, 30 g (0.5 mol) of acetic acid, 50 ml of benzene and 4.4 g of KU-2-8 was heated at 80 °C for 3 h. 92 g (85%) of the compound **10** were isolated by vacuum distillation. B.p. 150-152 °C (8 mm Hg), d_4^{20} 1.1356, n_D^{20} 1.4686. IR spectrum, ν , cm^{-1} : 1742 (C = O), 1230 (C-O-C), 1362 (CH₃), 1452 (CH₂), 2848-2929 (CH), 3410 (OH). ^1H NMR spectrum, δ , ppm: 1.29-1.70 m (10H, 5CH₂), 2.83 m (H, CH-O), 3.48-4.21 d (4H, 2CH₂, J 10.9 Hz), 4.18 m (H, CH), 3.49 s (H, OH), 2.19 m (3H, CH₃). ^{13}C NMR spectrum, δC , ppm: 31.92 (C^{1,3}), 79.00 (C²), 23.66 (C^{4,6}), 25.69 (C⁵), 72.6 (C⁷), 68.4 (C⁸), 64.7 (C⁹). 169.3 (C¹⁰), 20.1 (C¹¹). Founded, %: C 61.13; H, 9.25. C₁₁H₂₀O₄. Calculated, %: C 61.09; H, 9.32.

Cyclohexyl-2-glyceride-3-propionate

(11). A mixture of 87 g (0.5 mol) of reagent **3**, 37 g (0.5 mol) of propionic acid, 50 ml of benzene and 4.4 g of KU-2-8 was heated at 80 °C for 3 h. 73.4 g (64%) of the compound **11** was isolated by vacuum distillation. B.p. 159-161 °C (8 mm Hg), d_4^{20} 1.0961, n_D^{20} 1.4687. IR

spectrum, ν , cm^{-1} : 1730 (C = O), 1212 (C-O-C), 1358 (CH_3), 1433 (CH_2), 2860-2932 (CH), 3380 (OH). ^1H NMR spectrum, δ , ppm: 1.36-1.69 m (10 H, 5 CH_2), 2.79 m (H, CH-O), 3.39-4.08 d (4H, 2 CH_2 , J 10.9 Hz), 4.10 m (H, CH), 3.50 s (H, OH), 2.29 s (2H, CH_2), 1.04 t (3H, CH_3 , J 7.1 Hz). ^{13}C NMR spectrum, δC , ppm: 31.8 ($\text{C}^{1,3}$), 80.2 (C^2), 24.1 ($\text{C}^{4,6}$), 25.73 (C^5), 72.48 (C^7), 69.2 (C^8), 64.6 (C^9), 169.9 (C^{10}), 26.3 (C^{11}), 8.2 (C^{12}). Founded, %: C 62.61; H, 9.57. $\text{C}_{12}\text{H}_{22}\text{O}_4$. Calculated, %: C 62.58; H, 9.62.

Cyclohexyl-2-glyceride of butyric acid (12). A mixture of 87 g (0.5 mol) of cyclohexyl-2-glyceride, 44 g (0.5 mol) of butyric acid, 50 ml of benzene and 4.4 g of KU-2-8 was heated at 80 ° C for 4 h. 88 g (72 %) of compound **12** were isolated by vacuum distillation. B.p. 169-170 ° C (8 mm Hg), d_4^{20} 1.0735, n_D^{20} 1.4696. IR spectrum, ν , cm^{-1} : 1732 (C = O), 1217 (C-O-C), 1363 (CH_3), 1456 (CH_2), 2863-2935 (CH), 3420 (OH). ^1H NMR spectrum, δ , ppm: 1.38-1.63 m (10H, 5 CH_2), 2.85 m (H, CH-O), 3.40-4.11 d (4H, 2 CH_2 , J 10.9 Hz), 4.15 m (H, CH), 3.53 s (H, OH), 2.32 s (2H, CH_2), 0.85 t (3H, CH_3 , J 7.1 Hz), 1.79 m (2H, CH_2). ^{13}C NMR spectrum, δC ,

ppm: 31.92 ($\text{C}^{1,3}$), 79.53 (C^2), 23.91 ($\text{C}^{4,6}$), 26.5 (C^5), 72.2 (C^7), 68.3 (C^8), 63.98 (C^9), 172.3 (C^{10}), 35.60 (C^{11}), 17.5 (C^{12}), 12.8 (C^{13}). Founded, %: C 63.83; H, 9.85. $\text{C}_{13}\text{H}_{24}\text{O}_4$. Calculated, %: C 63.90; H, 9.90.

Cyclohexyl-2-glyceride of valerianic acid (13). A mixture of 87 g (0.5 mol) of cyclohexyl-2-glyceride, 51 g (0.5 mol) of n-valerianic acid, 50 ml of benzene and 4.4 g of KU-2-8 was heated at 80 ° C for 4 h. 91 g (71%) of compound **13** was isolated by vacuum distillation. B.p. 178-179 ° C (8 mm Hg), d_4^{20} 1.0586, n_D^{20} 1.4709. IR spectrum, ν , cm^{-1} : 1735 (C = O), 1223 (C-O-C), 1360 (CH_3), 1448 (CH_2), 2849-2930 (CH), 3380 (OH). ^1H NMR spectrum, δ , ppm: 1.30-1.71 m (10H, 5 CH_2), 2.80 m (H, CH-O), 3.50-4.03 d (4H, 2 CH_2 , J 10.9 Hz), 4.13 m (H, CH), 3.55 s (H, OH), 2.30 s (2H, CH_2), 0.80 t (3H, CH_3 , J 7.1 Hz), 1.65-2.13 m (4H, 2 CH_2). ^{13}C NMR spectrum, δC , ppm: 32.88 ($\text{C}^{1,3}$), 81.3 (C^2), 24.18 ($\text{C}^{4,6}$), 25.6 (C^5), 71.9 (C^7), 69.4 (C^8), 64.18 (C^9), 171.8 (C^{10}), 32.52 (C^{11}), 26.3 (C^{12}), 20.8 (C^{13}), 12.9 (C^{14}). Founded, %: C 65.12; H 10.08. $\text{C}_{14}\text{H}_{26}\text{O}_4$. Calculated, %: C 65.08; H 10.14.

Conclusion

By using the reaction of esterification in the presence of a heterogeneous catalyst KU-2-8 (H-form) monocyclic glycerol ether-cyclohexyl-2-glyceride was synthesized. Mixed diesters of glycerol based on

cyclohexyl-2-glyceride, formic, acetic, propionic, butyric and valerianic acids were also obtained, which are transparent viscous liquids and that can be used as additives to synthetic oils.

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QLİSERİNİN MONOTSİKLİK QURULUŞLU DİEFİRLƏRİNİN SİNTEZİ

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*BF₃·O(C₂H₅)₂ katalizatorunun iştirakında qliserinin tsikloheksenə birləşmə reaksiyası tədqiq olunmuş, nəticədə tsikloheksil-2-qliserid sadə efiri sintez edilmişdir. Sintez olunmuş tsikloheksil-2-qliseridin C₁-C₅ birəsaslı karbon turşuları ilə heterogen KÜ-2-8 (H formada) katalizatorunun iştirakında efirləşmə reaksiyası da öyrənilmişdir. Tsikloheksil-2-qliseridin və qliserinin diefirlərinin çıxımına müxtəlif faktorların təsiri tədqiq olunmuş və reaksiyanın optimal şəraiti tapılmışdır. Nəticədə 71-91% çıxımla diefirlər sintez olunmuş, fiziki-kimyəvi xassələri təyin olunaraq, quruluşları təsəiç edilmişdir.
Açar sözlər: qliserin, tsikloheksen, tsikloheksilqliserid, monotsiklik diefirlər, efirləşmə, formiat.*

ПОЛУЧЕНИЕ МОНОЦИКЛИЧЕСКИХ ДИЭФИРОВ ГЛИЦЕРИНА

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Проведено присоединение глицерина к циклогексену в присутствии эфира трифтористого бора BF₃·O(C₂H₅)₂ с получением простого эфира циклогексил-2-глицерида. Изучена также реакция этерификации полученного циклогексил-2-глицерида C₁-C₅ одноосновными насыщенными карбоновыми кислотами в присутствии гетерогенного катализатора КУ-2-8 (H-форма). Для получения целевого продукта с максимальным выходом изучено влияние различных факторов на выход циклогексил-2-глицерида и сложного эфира – формиата, полученного на его основе, и найдены оптимальные условия реакции. В результате были получены соответствующие эфиры с выходами 71%-91%. Определены физико-химические свойства синтезированных эфиров и доказано их строение.

Ключевые слова: глицерин, циклогексен, циклогексилглицерид, этерификация, моноциклические диэфиры, формиат