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The Use of Glycerol in the Synthesis of Polycyclic Glycerides

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Abstract

Systematic studies in the field of the synthesis of ethers based on glycerol and polycyclic unsaturated hydrocarbons have been carried out. The reactions of glycerol addition to cyclohexene, bicyclo[2.2.1]hept-2-ene, tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, tetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene and their alkyl-substituted derivatives were carried out in the presence of a homogeneous catalyst – boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$). It was revealed that the $\text{BF}_3 \cdot \text{OEt}_2$ catalyst promotes the successful transformation of the above-indicated polycyclic olefins and their alkyl-substituted derivatives into glycerol monoethers in the yields of 70–87, 81 and 64–74 %, respectively. The effects of temperature, reaction duration, the molar ratio of initial components and the amount of the catalyst on ether yields were studied, and the optimal conditions for the synthesis of bi-, tri- and tetracyclic glycerides were determined. The synthesized ethers may be used as additives to synthetic oils.

Keywords: glycerol, cycloolefin, glycerides, addition reaction, boron trifluoride etherate

INTRODUCTION

During recent years, the production of biodiesel is scaling up. A side product of the production of biofuel is glycerol, with its mass ratio to the target product equal to 10 : 1 [1, 2]. Glycerol is also formed during soap production as a product of fat saponification. In connection with a sharp increase in the production of glycerol, search for new methods of its purification and the methods of its transformation into useful products is carried out.

At present, many methods of glycerol application in different areas are known. Nevertheless, attention to the studies of the new directions of its processing is permanently increasing because of the availability of this product. During the recent decade, a number of reviews dealing with this subject were published [3, 4].

The synthetic potential of glycerol and its derivatives is almost inexhaustible, and the use of

these products leads to obtaining the substances with valuable properties. Ethers and esters of glycerol find application as the major components of antimicrobial preparations, surfactants, emulsifiers in food industry, pharmaceuticals and cosmetics, etc. [5–7].

The synthesis glycerides having cyclic structure and investigation of their properties are of great interest. The main method of obtaining glycerol ethers and esters is etherification or esterification [8–10]. However, in the case of obtaining the ethers and esters with cyclic structure, this method encounters difficulties because of the poor availability of the corresponding alcohols. Moreover, the reactions of glycerol with alcohols in the presence of acid or alkaline catalysts exhibit some disadvantages, in particular, the formation of side products. They get mixed with the target product and colour it; besides, they cause a sharp smell. Difficulties in the isolation of the major product in the pure form cause an in-

crease in its prime cost, which makes its application in cosmetics and pharmaceuticals unprofitable [11–13].

It is known from the published data that glycerol catalytically adds to isobutene and isomylene. However, substantial excess of isobutene is required for this process. The process is characterized by insufficient selectivity because the major products are triglycerides [14–16].

Previously we studied the addition of glycerol to tricyclodecadiene in the presence of various catalysts. Results showed that the most efficient catalyst was the etherate of boron trifluoride ($\text{BF}_3 \cdot \text{OEt}_2$) [17]. On the basis of glycerol, we obtained various organic structural compounds using a simplified method, in a single stage without any use of solvents. It is remarkable that this provides the possibility to transform glycerol into useful chemical substances with a broad application range using an ecologically friendly and simple way.

In the present work, we demonstrate the possibility to synthesize glycerides through the catalytic addition of glycerol to cycloolefin hydrocarbons.

EXPERIMENTAL

Experiments on the synthesis of polycyclic ethers based on glycerol were carried out in an alkylating set-up equipped with a thermometer and a magnetic mixer. The catalyst was introduced into the reaction mixture drop by drop under intense mixing. After the experiment, the catalyst was removed by washing the reaction mixture with distilled water, then the mixture was dried above MgSO_4 . The target product was then isolated by means of vacuum distillation.

The composition and purity of the obtained glycerides were determined with the help of gas-liquid chromatography (GLC) using a Tsvet-100 chromatograph (Russia). Conditions: liquid phase (polyethylene glycol succinate) supported on spherochrom (10 mass %); column length 2 m; evaporator temperature 230–260 °C; column temperature 140–150 °C; detector temperature 200–220 °C; current 100 mA; carrier gas (helium) flow rate 60 mL/min.

IR spectra were recorded with the help of a Fourier transform spectrometer ALPHA (Bruker, Germany), NMR ^1H and ^{13}C spectra were recorded with the help of an AV-300 instrument (Bruker, Germany) at the frequency of 300 MHz. Acetone- d_6 was used as a solvent.

Initial components used in the syntheses were of Ch. reagent grade (pure). The physicochemical constants of some of them are listed below: glycerol (G1) – boiling point 290 °C, d_4^{20} 1.261, n_D^{20} 1.4790; $\text{BF}_3 \cdot \text{OEt}_2$ – boiling point 126 °C, d_4^{20} 1.154; cyclohexene (CH) (**1**) – boiling point 83 °C, d_4^{20} 0.810, n_D^{20} 1.446; bicyclo[2.2.1]hept-2-ene (**3**) – melting point 96 °C; tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**17**) – melting point 19.5 °C, d_4^{20} 0.9760, n_D^{20} 1.5051; tetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene (**19**) – boiling point 95–96 °C/11 mm Hg, d_4^{20} 1.0044, n_D^{20} 1.5180.

Initial tetracyclic hydrocarbons (**19–24**) were obtained by means of the condensation of norbornene and its alkyl-substituted derivatives with cyclopentadiene; the dimer of the latter compound was used as the initial component in the presence of nano- TiO_2 (20 nm according to the procedure described in [18]).

Below we present the spectral data of some glycerol ethers synthesized herein.

Compound (2). IR spectrum, ν , cm^{-1} : 1248 (C–O–C), 1453 (CH_2), 2857–2925 (CH), 3388 (OH). NMR ^1H spectrum, δ , ppm: 1.30–1.70 (m, 10H, 5 CH_2), 2.90 (m, H, CH–O), 3.60 (d, 4H, 2 CH_2 , $J = 10.9$ Hz), 3.64 (m, H, CH), 3.55–3.60 (s, 2H, 2OH). NMR ^{13}C spectrum, δ , ppm: 32.23 ($\text{C}^{1,3}$), 82.1 (C^2), 24.2 ($\text{C}^{4,6}$), 25.88 (C^5), 71.59 (C^7), 69.0 (C^8), 62.7 (C^9).

Compound (10). IR spectrum, ν , cm^{-1} : 1199 (C–O–C), 1450 (CH_2), 2875–2943 (CH), 3327 (OH). NMR ^1H spectrum, δ , ppm: 1.3 (d, 2H, CH_2), 1.4 (d, 2H, CH_2), 1.6–1.7 (d, 4H, 2 CH_2), 3.6–3.9 (m, 4H, 2 CH_2), 3.9 (s, 1H, CHO–), 4.0 (m, 2H, CH_2 –O–), 3.57–3.78 (s, 2H, 2OH). NMR ^{13}C spectrum, δ , ppm: 85.6 (C^2), 73.5 (C^9), 70.5 (C^{10}), 70.1 (C^8), 41.1 (C^1), 39.9 (C^4), 36.9 (C^3), 30.4 (C^6), 32.9 (C^7), 38.3 (C^5).

Compound (16). IR spectrum, ν , cm^{-1} : 1356 (CH_3), 1182 (C–O–C), 1453 (CH_2), 2877–2931 (CH), 3378 (OH). NMR ^1H spectrum, δ , ppm: 1.3 (d, 2H, CH_2), 1.4 (d, 2H, CH_2), 1.6–1.7 (d, 4H, 2 CH_2), 3.6–3.9 (m, 4H, 2 CH_2), 3.9 (s, 1H, CHO–), 4.0 (m, 2H, CH_2 –O–), 3.57–3.78 (s, 2H, 2OH), 1.23–1.25 (t, 6H, 3 CH_2), 1.28–1.32 (m, 4H, 2 CH_2), 0.86 (t, 3H, CH_3). NMR ^{13}C spectrum, δ , ppm: 85.6 (C^2), 73.5 (C^9), 70.5 (C^{10}), 70.1 (C^8), 41.1 (C^1), 39.9 (C^4), 36.9 (C^3), 28.6 (C^6), 25.9 (C^7), 24.0 (C^5), 29.1 (C^{11}), 27.3 (C^{12}), 28.5 (C^{13}), 32.1 (C^{14}), 23.2 (C^{15}), 13.9 (C^{16}).

Compound (18). IR spectrum, ν , cm^{-1} : 1620 (CH=CH), 1206 (C–O–C), 1352 (CH_2), 2884–2946 (CH), 3396 (OH). NMR ^1H spectrum, δ , ppm: 1.30–1.70 (m, 3H, 3CH), 2.10 (m, H, CH), 2.76 (m, H, CH–O), 3.45–3.55 (m, 4H, 2 CH_2), 3.60–3.65 (m, 2H, 2OH), 1.85–2.30 (m, 6H, 3 CH_2), 5.54 (m, H, CH=), 6.20 (m, H, CH=). NMR ^{13}C spectrum, δ , ppm: 44.9

(C¹), 51.2 (C²), 132 (C³), 132.4 (C⁴), 39.3 (C⁵), 43.2 (C⁶), 41.7 (C⁷), 39.6 (C⁸), 83 (C⁹), 28.4 (C¹⁰), 70.8 (C¹¹), 70.1 (C¹²), 61.9 (C¹³).

Compound (25). IR spectrum, ν , cm⁻¹: 1210 (C–O–C), 1417 (CH₂), 2881–2933 (CH), 3266 (OH). NMR ¹H spectrum, δ , ppm: 1.41 (m, 6H, 6CH), 1.76 (s, H, CH), 2.80 (d, H, CH–O), 1.25–1.82 (m, 4H, 2CH₂), 1.78–2.10 (m, 4H, 2CH₂), 3.34–3.57 (m, H, CH; 2H, CH₂), 3.53–3.62 (m, 2H, 2OH), 1.25–1.31 (m, 6H, 3CH₂). NMR ¹³C spectrum, δ , ppm: 45.5 (C^{1,10}), 42.7 (C²), 86.6 (C³), 40.5 (C⁴), 41.8 (C⁵), 54.3 (C⁶), 39.8 (C⁷), 33.8 (C^{8,9}), 28.2 (C¹¹), 37.0 (C¹²), 72.1 (C^{13,14}), 65.4 (C¹⁵).

Compound (27). IR spectrum, ν , cm⁻¹: 1327 (CH₃), 1225 (C–O–C), 1420 (CH₂), 2875–2921 (CH), 3278 (OH). NMR ¹H spectrum, δ , ppm: 1.40 (m, 6H, 6CH), 1.70 (s, H, CH), 2.75 (d, H, CH–O), 1.25–1.80 (m, 4H, 2CH₂), 1.78–2.10 (m, 4H, 2CH₂), 3.45–3.55 (m, H, CH; 4H, 2CH₂), 3.60–3.65 (m, 2H, 2OH), 1.26–1.32 (m, 6H, 3CH₂), 0.93 (t, 3H, CH₃). NMR ¹³C spectrum, δ , ppm: 46.0 (C^{1,10}), 44.9 (C²), 86.1 (C³), 40.5 (C⁴), 42.1 (C⁵), 54.8 (C⁶), 40.1 (C⁷), 34.8 (C^{8,9}), 28.9 (C^{11,17}), 38.0 (C¹²), 72.2 (C^{13,14}), 65.0 (C¹⁵), 27.4 (C¹⁶).

RESULTS AND DISCUSSION

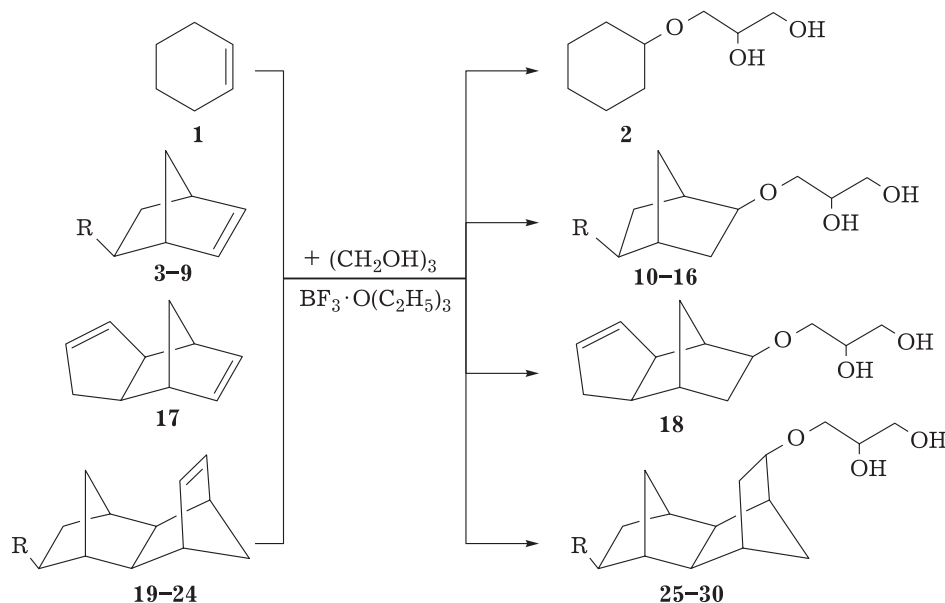
The addition of Gl to the series of polycyclic unsaturated hydrocarbons – CH (1), bicyclo[2.2.1]hept-2-ene (3), tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (17),

tetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene (19) and their alkyl substituted derivatives (20–24) was carried out in the presence of a homogeneous catalyst BF₃ · OEt₂ (Scheme 1).

The effect of various factors on ether yield was studied: temperature, reaction time (τ), the molar ratio of initial components, and the amount of the catalyst. It was revealed in the studies of the effect of temperature on the yield of cyclohexyl-2-glyceride (2) that an increase in reaction temperature from 80 to 90 °C (τ = 2 h, BF₃ · OEt₂ content 0.5 %) causes an increase in the yield of ether 2 from 42 to 47 %, with further temperature rise to 100 °C no increase in the yield of ether is observed (Table 1). At 90 °C, the effect of the molar ratio of reacting components Gl/CH within the limits (1 : 1)–(1 : 1.4) was studied; it was established that at the ratio of 1 : 1.2 the highest ether yield is 51 % (see Table 1).

The effect of the amount of the catalyst on the formation of compound 2 was studied with the catalyst/initial raw material ratio equal to 0.5–2 mass %. The largest relative yield of ether 2 (55 %) was observed with catalyst content 1.3 mass % (τ = 2 h). At τ = 4 h, ether yield reached 70 %. With an increase in τ to 5 h, the yield of the target product varied only slightly (see Table 1).

The catalyst BF₃ · OEt₂ promoted the successful transformation of norbornene (3), dicyclopentadiene (17), tetracyclododecene (19) and their alkyl-



Scheme 1.

TABLE 1
Effect of different factors on the formation of cyclohexyl-2-glyceride

Influencing factors				Yield of cyclohexyl-2-glyceride, %
Amount of catalyst, %	Molar ratio Gl/CH	Temperature, °C	τ , ч	
0.5	1 : 1	80	2	42
0.5	1 : 1	90	2	47
0.5	1 : 1	100	2	47
0.5	1 : 1.1	90	2	49
0.5	1 : 1.2	90	2	51
0.5	1 : 1.3	90	2	52
0.5	1 : 1.4	90	2	52
1.0	1 : 1.2	90	2	53
1.2	1 : 1.2	90	2	54
1.3	1 : 1.2	90	2	55
1.5	1 : 1.2	90	2	56
1.3	1 : 1.2	90	3	67
1.3	1 : 1.2	90	4	70
1.3	1 : 1.2	90	5	71

Note. Here and in Table 2: catalyst is $\text{BF}_3 \cdot \text{OEt}_2$, τ is the duration of the reaction.

TABLE 2
Optimal conditions for the synthesis of glycerides

Glyceride	Temperature, °C	τ , h	Molar ratio of components (Gl/Cycloolefin)	Catalyst content, %
Monocyclic	90	4	1 : 1.2	1.3
Bicyclic	80	4	1 : 1.25	1.25
Tricyclic	100	4	1 : 1.4	1.4
Tetracyclic	100	5	1 : 2.0	1.5

substituted derivatives into monoethers of glycerol with the yield of 70–87, 81 and 64–74 %, respectively. In the case of dicyclopentadiene, nucleophilic addition of Gl was observed exclusively at the 8,9-double bond. This is explained by the higher activity of the double bond in the norbornene fragment of dicyclopentadiene in comparison with cyclopentene fragment.

Hydroquinone in the amount of 0.1 mass % with respect to the cycloolefin was used as an inhibitor to prevent polymerization in the reactions under investigation.

So, optimal conditions for the synthesis of bi-, tri- and tetracyclic glycerides were determined as a result of investigation (Table 2).

According to the data of GLC analysis, the purity of the synthesized ethers was 98–99 %. Yields, physicochemical properties and elemental analysis data for the synthesized compounds are presented in Table 3.

It was established that the addition of polycyclic olefins to Gl proceeds mainly at the primary

hydroxyl group and in an insignificant amount at the secondary hydroxyl group at a ratio of (85–89) : (15–11).

Analysis of the data showed that an increase in the length of the alkyl radical in bicycloheptene and tetracyclododecene from C_1 to C_6 causes a substantial decrease in the yield of bicyclic glycerides **11–16** (from 85 to 70 %) and tetracyclic glycerides **26–30** (from 84 to 64 %). This fact is explained by the spatial conformation, or, to be more precise, by the negative effect of electron donor alkyl radicals on the reactivity of π -bonds of bicycloheptene ring.

The structure of the synthesized ethers was confirmed by the data of IR and BNR spectroscopy. For example, the IR spectra of the synthesized ethers contain the following absorption bands: 3350–3400 cm^{-1} , related to the primary and secondary hydroxyl groups; 1190–1200 cm^{-1} , providing evidence of the presence of an ether fragment (C–O–C group) in the molecule. Absorption bands in the regions of 2857–2932, 1460,

TABLE 3

Physicochemical properties of the synthesized ethers of glycerol

Compound No.	Yield, %	Boiling point, °C/mm Hg	d_4^{20}	n_D^{20}	Found, %		Formula	Calculated, %	
					C	H		C	H
2	70	180/45	1.100	1.4870	61.97	10.35	C ₉ H ₁₈ O ₃	62.04	10.41
10	87	110–111/1	1.2556	1.4730	64.49	9.61	C ₁₀ H ₁₈ O ₃	64.54	9.67
11	85	122–123/1	1.1816	1.4800	65.91	9.81	C ₁₁ H ₂₀ O ₃	66.02	10.00
12	84	131–133/1	1.1309	1.4818	67.26	10.21	C ₁₂ H ₂₂ O ₃	67.31	10.28
13	80	146–148/1	1.1209	1.4820	68.35	10.42	C ₁₃ H ₂₄ O ₃	68.45	10.52
14	78	151–155/1	1.1190	1.4844	69.25	10.54	C ₁₄ H ₂₆ O ₃	69.45	10.74
15	75	160–161/1	1.1065	1.4900	70.12	10.73	C ₁₅ H ₂₈ O ₃	70.32	10.93
16	70	169–170/1	1.1021	1.5051	70.92	10.91	C ₁₆ H ₃₀ O ₃	71.12	11.10
18	81	165–166/2	1.1429	1.5138	69.57	8.97	C ₁₃ H ₂₀ O ₃	69.61	8.99
25	74	155–156/1	1.1358	1.5235	72.22	8.46	C ₁₅ H ₂₁ O ₃	72.26	8.49
26	70	165–166/1	1.1337	1.5248	72.93	8.77	C ₁₆ H ₂₃ O ₃	72.97	8.80
27	69	172–173/1	1.1311	1.5259	73.58	9.05	C ₁₇ H ₂₅ O ₃	73.61	9.08
28	67	190–191/1	1.1286	1.5267	74.15	9.31	C ₁₈ H ₂₇ O ₃	74.19	9.34
29	66	196–197/1	1.1264	1.5274	74.68	9.53	C ₁₉ H ₂₉ O ₃	74.72	9.57
30	64	210–211/1	1.1242	1.5283	75.15	9.74	C ₂₀ H ₃₁ O ₃	75.20	9.78

1367 cm⁻¹ relate to CH, CH₂, CH₃ groups, respectively.

The synthesized ethers are transparent liquids with typical odour, which may be used as additives to synthetic oil.

CONCLUSION

Optimal conditions for the synthesis of cyclohexylglyceride in the presence of homogeneous catalyst (BF₃ · OEt₂) with the yield of 70 % were determined as a result of investigations. Under similar conditions, the synthesis of a series of representatives of polycyclic ethers of glycerol was carried out through the addition of glycerol to bi-, tri-, tetracyclic hydrocarbons and to their alkyl-substituted derivatives, with the yield of 64–87 %.

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