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BRIEF COMMUNICATIONS

Synthesis of Bicyclo[2.2.1]heptyl Monoethers of Aliphatic Diols

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Abstract—An effective procedure for the synthesis of bicyclic monoethers by etherification of bicyclo[2.2.1] heptane-exo-2-ol and its exo-5-methyl-substituted derivative by aliphatic diols in the presence of naphthalene-1,5-disulfonic acid as a catatlyst was developed.

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Monoalkyl ethers of ethylene glycol are known to be successfully applied as effective solvents of varnishes, resins, and plasticizers of polymeric materials [1–3]. Mono- and bicyclic ethers of ethylene glycol not only have plasticizing properties, but also are initial compounds for the synthesis of mixed esters, which can be used as components of synthetic fragrant materials [4, 5].

In view of the important practical value of monoethers for organic synthesis more effective procedure of their synthesis via etherification of bicyclic alcohols by aliphatic diols was developed (Scheme 1).

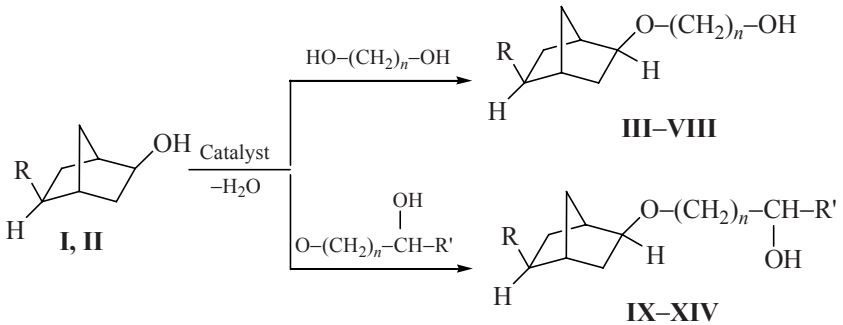
To select the effective catalyst for this reaction, various sulfo compounds were applied: sulfuric acid, *p*-toluenesulfonic acid (TSA), ion-exchange resins KU-2, KU-2×8, naphthalene-1,5-disulfonic acid (NDSA), and naphthalene-2-sulfonic acid (NSA). The results obtained are shown in Table 1.

It is seen from Table 1 that NDSA has proved to be the most successful among the tested catalysts of bicyclo[2.2.1]heptane-*exo*-2-ol (BHO) etherification by ethylene glycol (EG). The use of the other proton catalysts promotes passing not only the main reaction, but also the concurrent reaction of etherification of the initial alcohols with the formation of by-products.

In further studies of the BHO and *exo*-5-methyl-BHO etherification by aliphatic diols we used NDSK as catalyst.

We have found optimal conditions for the synthesis of bicyclic monoethers of aliphatic diols: the ratio

Scheme 1.



R = H, n = 2 (**I**, **III**); R = H, n = 3 (**I**, **IV**); R = H, n = 4 (**I**, **V**); R = CH_3, n = 2 (**II, VI**); R = CH_3, n = 3 (**II, VII**); R = CH_3, n = 4 (**II, VIII**); R = H, R' = CH_3, n = 1 (**I, IX**); R = H, R' = C_2H_5, n = 1 (**I, X**); R = H, R' = CH_3, n = 2 (**I, XI**); R = R' = CH_3, n = 1 (**II, XII**); R = CH_3, R' = C_2H_5, n = 1 (**II, XIII**); R = R' = CH_3, n = 2 (**II, XIV**).

BHO:*exo*-5-methyl-BHO/diol 1:1, the amount of the NDSK catalyst 10% of the weight of initial components, temperature 80°C, and duration 3 h. In this case the yield of monoethers is 86.4–8.9%.

The yield and physicochemical properties of bicyclic monoethers of aliphatic diols are given in Table 2. These data show that the yield of bicyclic monoethers of diols decreases from 98.9 to 88.9% as the molecular weight of aliphatic diols increases. It was found that the primary hydroxyl group of diols, which is more reactive than the secondary group, participates in the formation of the monoethers.

The yield of bicyclic monoethers also depends on the structure of aliphatic diols. Thus, as the chain of diols is elongated the yield of monoethers in the case of the etherification of *exo*-5-methyl-BHO decreases from 96.4 for ethanediol-1,2 to 86.4% for butanediol-1,4.

The synthesized monoethers are viscous light liquids. The physicochemical constants of the synthesized bicyclic compounds, except for ethylene glycol monoethers, were measured for the first time. The bicyclic monoethers can be used for the synthesis of numerous organic compounds, including fragrant materials and reactive monomers [6], some of them being of interest as plasticizers [7].

According to the gas-liquid chromatographic analysis, the purity of the synthesized monoethers is 99.6–99.8%. Their structure was proved by the IR and ^{1}H and ^{13}C NMR spectral methods.

Table 1. Effect of catalysts on the yield of monoether **III** in the etherification of BHO by ethylene glycol. Mole ratio BHO:EG = 1:1, temperature 80°C, amount of the catalyst 10% of the weight of reacting substances

Catalyst	Reaction duration, h	Yield, %
p-TSA	6	52.5
H_2SO_4	2	63.0
KU-2	5	72.5
KU-2×8	4.5	80.0
KU-2×2	6.5	6.5
NDSA	3	98.9
NSA	3	68.9

The following absorption bands are observed in the IR spectra of bicyclic monoethers of diols (cm^{-1}): 1100-1000 (C–O–C), 1800–1400 (CH_2), 2840 (CH), 1380 (CH_3), 2962 (–CH_2– in the cycle), and 3360 (OH).

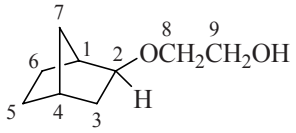
In the ^{1}H NMR spectra of *exo*-bicyclic monoethers shifts of *exo*-C^2 protons are observed in the region of 4.8, OH-group protons at 3.6, and –CH_2–CH_2– protons at 2.2 ppm.

Table 2. Yield and physicochemical properties of synthesized bicyclic monoethers of aliphatic diols

Monoether	Yield, %	bp, °C (3 mm Hg)	d_4^{20}, g cm^{-3}	n_D^{20}	Found, %		Formula	Calculated, %		Molecular weight
					C	H		C	H	
III	98.9	59–60	1.0159	1.4721	69.11	10.00	$C_9H_{16}O_2$	69.19	10.25	156.2
IX	94.5	58–59	1.0239	1.4659	70.23	10.42	$C_{10}H_{18}O_2$	70.55	10.66	170.2
IV	92.6	67–68	1.0105	1.4685	70.33	10.38	$C_{10}H_{18}O_2$	70.55	10.66	170.2
X	91.6	78–79	1.0001	1.4679	71.20	10.65	$C_{11}H_{20}O_2$	71.70	10.94	184.3
XI	90.6	80–81	1.0013	1.4695	71.19	10.68	$C_{11}H_{20}O_2$	71.70	10.94	184.3
V	88.9	90–91	1.0109	1.4701	71.01	10.58	$C_{11}H_{20}O_2$	71.70	10.94	184.3
VI	96.4	79–80	1.0031	1.4730	70.33	10.51	$C_{10}H_{18}O_2$	70.55	10.66	170.2
XII	93.8	82–83	0.9997	1.4692	71.27	10.59	$C_{11}H_{20}O_2$	71.70	10.94	184.3
VII	91.3	101–102	1.0021	1.4730	71.38	10.61	$C_{11}H_{20}O_2$	71.70	10.94	184.3
XIII	92.9	87–88	0.9961	1.4719	72.34	11.00	$C_{12}H_{22}O_2$	72.68	11.18	190.3
XIV	89.4	90–91	1.0029	1.4752	72.29	11.01	$C_{12}H_{22}O_2$	72.68	11.18	190.3
VIII	86.4	120–121	1.0048	1.4762	72.40	11.08	$C_{12}H_{22}O_2$	72.68	11.18	190.3

The IR and ^1H and ^{13}C NMR spectra of synthesized 2-(*exo*-2-bicyclo[2.2.1] heptoxy)ethanol are given in Scheme 2:

Scheme 2.



IR spectrum, ν, cm^{-1}: 1000–1200 (C–O–C), 1400–1800 (CH_2), 2840 (CH), 2960 (CH_2), 3350 (OH).

^1H NMR spectrum, δ, ppm: 1.3 d (2H, CH_2), 1.4 d (2H, CH_2), 1.7 d (4H, $2CH_2$), 1.8 s (2H, 2CH), 2.2 d (4H, $2CH_2$), 3.6 s (H, OH), 4.8 s (*exo*-H).

^{13}C NMR spectrum, δ, ppm: 85.6 (C^2), 70.6 (C^9), 70.1 (C^8), 41.1 (C^1), 39.9 (C^4), 36.9 (C^3), 28.7 (C^6), 25.9 (C^7), 24.0 (C^5).

EXPERIMENTAL

The initial bicyclic alcohols were obtained by the hydrolysis of bicyclo[2.2.1]hept-*exo*-2-ylformiate and *exo*-5-methylbicyclo[2.2.1]hept-*exo*-2-ylacetate synthesized by the procedure described in [8, 9]; bicyclo-[2.2.1]heptane-*exo*-2-ol (bp 127°C); *5-exo*-methylbicyclo[2.2.1]heptane-*exo*-2-ol [bp 73–74°C (30 mm Hg), $d_4^{20} = 0.9988$, $n_D^{20} = 1.4826$].

The aliphatic diols used had the following physicochemical constants which coincided with the published data [10]: 1,2-ethanediol (bp 188–189°C, $d_4^{20} = 1.1150$); 1,2-propanediol (bp 188°C, $d_4^{20} = 1.0356$); 1,3-propanediol (bp 213°C, $d_4^{20} = 1.0521$); 1,2-butane-diol (bp 192°C, $d_4^{20} = 1.0205$); 1,3-butanediol (bp 204°C, $d_4^{20} = 1.0051$); 1,4-butanediol (bp 230°C, $d_4^{20} = 1.0202$).

NDSK used as a catalyst is a crystalline product, mp 240–245°C.

The composition and purity of the initial and synthesized compounds were determined by chromatography on an LKhM-8MD instrument, the length of a column 1.5 m, stationary phase 10 wt % of ethylene glycol succinate on spherochromium; the temperature of the evaporator and columns 250 and 120°C, respectively; the gas-carrier rate 45 ml min^{-1}.

The IR spectra of the synthesized compounds were taken on a UR-20 instrument, the ^1H and ^{13}C NMR spectra on a BS-487 spectrometer at the frequency of 80 MHz. The internal reference was HMDS and the solvent, CCl_4.

Etherification of bicyclic alcohols by aliphatic diols in the presence of naphthalene-1,5-disulfonic acid was carried out in a Dyne-Stark apparatus with benzene as a solvent. Optimal conditions for the reaction are: the mole ratio of reacting components bicyclic alcohol: glycol = 1:1, the catalyst–NDSA, 2.0% to the weight of initial components, temperature 80°C, and duration 3 h. After separation of a calculated amount of formed water the reaction was stopped, then the etherate was separated by filtration and distilled.

CONCLUSIONS

(1) Naphthalene-1,5-disulphonic acid is the most effective catalyst for obtaining bicyclic monoether of ethylene glycol by etherification of bicycloheptanol with ethylene glycol.

(2) Naphthalene-1,5-disulphonic acid for the first time was applied to the etherification of bicycle-heptanols by C_3–C_4 aliphatic glycols with the formation of the corresponding monoethers which might used as components of synthetic fragrant substances and plasticizers of polymeric materials.

REFERENCES

1. Mamedov, M.K., *Prostye efiry glikolei* (Ethers of Glycols), Baku: Akademiay Nauk Azerbaizhanskoi SSR, 1961.
2. Zeinalov, S.B., *Efiry alitsiklicheskogo ryada* (Eether of Alicyclic Series), Baku: Elm, 1996.
3. Mikhant'ev, V.B. and Mikhant'eva, O.N., *Efiry glikolei* (Ethers of Glycols), Voronezh. universitet, 1984.
4. Gasanov, A.G. and Nagiev, A.V., *Zh. Org. Khim*., 1994, vol. 30, no. 5, p. 707.
5. Gasanov, A.G. and Nagiev, A.V., *Zh. Org. Khim*., 2005, vol. 41, no. 12, p. 1793.
6. Mamedov, M.K., Piraliev, A.G., and Rasulova, R.A., *Zh. Prikl. Khim*., 2007, vol. 80, no. 12, p. 2007.
7. Sadieva, N.F., Iskenderova, S.A., and Zeinalov, E.B., *Plast. Massy*, 2007, vol. 11, p. 29.
8. Mamedov, M.K., *Zh. Org. Khim*., 1997, vol. 33, no. 2, p. 192.
9. Mamedov, M.K., Nabieva, E.K., and Rasulova, R.A., *Zh. Org. Khim*., 2005, vol. 41, no. 7, p. 995.
10. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1964, vol. 2.