

Synthesis of Monoethers by Addition of Aliphatic Diols to Bicyclo[2.2.1]hept-2-enes

M. K. Mamedov and A. G. Piraliev

Institute of Petrochemical Processes, National Academy of Azerbaijan, pr. Khodzhalı 30, Baku, Az 1025 Azerbaijan

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Abstract—Addition of aliphatic diols to bicyclo[2.2.1]hept-2-ene and its 5-alkyl-substituted derivatives in the presence of naphthalene-1,5-disulfonic acid leads to the formation of the corresponding bicyclo[2.2.1]hept-2-yl monoethers in high yields.

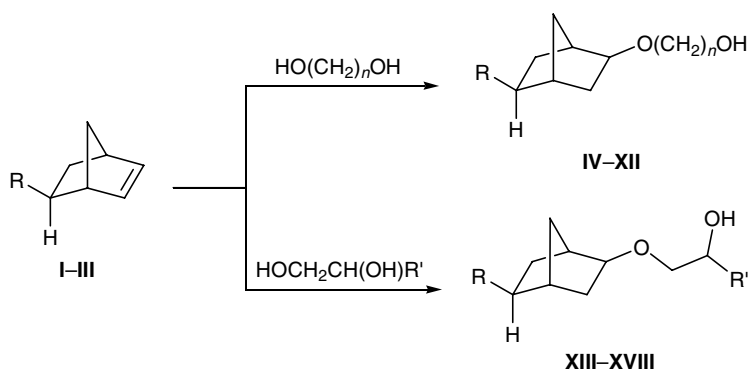
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Additions of alcohols and diols to cyclic olefins in the presence of various acid catalysts, including boron trifluoride–ether complex [1], heteropolyacids [2], Lewis acids [3], and KU-2-8 ion exchanger (H-form) [4], were reported to give the corresponding ethers and hydroxy ethers. In the present work we used a new catalyst, naphthalene-1,5-disulfonic acid, to effect the addition of aliphatic diols to bicyclo[2.2.1]hept-2-enes **I–III** and obtained the corresponding monoethers (Scheme 1). We also examined the effect of various parameters on the reaction course and found optimal conditions for the process: temperature 100°C, amount of the catalyst 2.5 wt % relative to the initial bicyclic olefin, molar reactant ratio 2:1, reaction time 3 h. Under these conditions, the yields of monoethers **IV–XVIII** attained 83–98%. The physical constants and spectral data for compounds **IV** and **VII** coincided with those reported in [4], and the data for the newly synthesized compounds are given in Experimental.

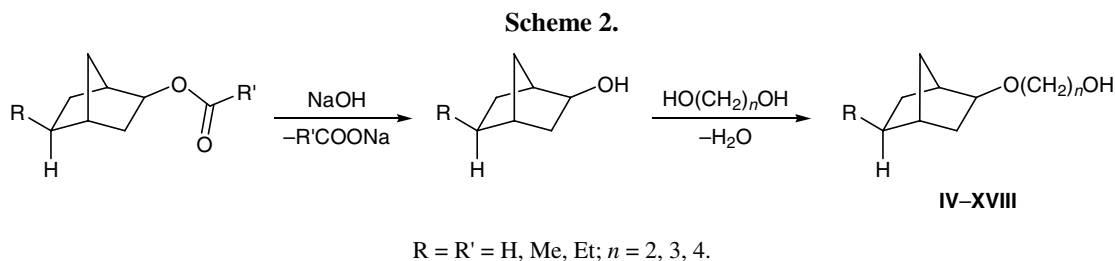
The yield of monoethers decreases as the molecular weight of the diol rises and in going from α,ω -diols to 1,2-diols; the primary hydroxy group in diol molecule was more active than the secondary one, and only the former was involved in the ether formation. The addition of diols to bicyclo[2.2.1]hept-2-ene (**I**) was stereoselective, and only bicyclo[2.2.1]hept-*exo*-2-yl ethers were obtained. In the reactions with 5-alkylbicyclo[2.2.1]hept-2-enes **II** and **III** regioisomeric 5- and 6-alkylbicyclo[2.2.1]hept-2-yl ethers were formed at a ratio of 49:1.

The structure of hydroxy ethers **IV–XVIII** was confirmed by the GLC data and IR and ^1H and ^{13}C NMR spectra. The IR spectra of **IV–XVIII** contained a strong absorption band at 880 and 920 cm^{-1} , typical of *exo*-2 isomers; the hydroxy group and ether bond gave rise to absorption bands at 3350 and 1200–1000 cm^{-1} , respectively. Compounds **IV–XVIII** were also obtained by independent synthesis, i.e., by hydrol-

Scheme 1.



IV–VI, VIII, R = H; VII, VIII, X, XV, R = Me; X–XII, XVIII, R = Et; XIII, XV, XVII, R' = Me; XIV, XVI, XVIII, R' = Et;
 $n = 2, 3, 4.$



ysis of bicyclo[2.2.1]hept-2-yl esters [5] and subsequent etherification of bicyclic alcohols with the corresponding diols in the presence of naphthalene-1,5-disulfonic acid in a flask equipped with a Dean-Stark trap (Scheme 2).

All the obtained monoethers are colorless liquids, some of which possess a pleasant odor and are promising as components of synthetic fragrant substances, as well as for esterification of saturated and unsaturated acids.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. The ^1H and ^{13}C NMR spectra were measured from solutions in CCl_4 on a Varian FT-80 instrument (80 MHz) using HMDS as internal reference. The purity of the products was checked by GLC on an LKhM-8MD chromatograph equipped with a 2-m column packed with 10% of poly(ethylene glycol) succinate on Sferokhrom; oven temperature 140°C , detector temperature 200°C , injector temperature 250°C ; detector current 120 mA; carrier gas helium, flow rate 45 ml/min; the purity was 99.2–99.7%.

The addition of diols to bicyclo[2.2.1]hept-2-enes **I–III** was carried out in a high-pressure reactor. Initial compounds **I–III** were synthesized by condensation of the corresponding olefins with cyclopentadiene [6, 7]. 5-Methyl- and 5-ethylbicyclo[2.2.1]hept-2-enes were isolated as mixtures of *endo* and *exo* isomers, which were converted into the *exo* isomers in the presence of AlCl_3 [8]; Bicyclo[2.2.1]hept-2-ene (**I**), mp 46°C ; *exo*-5-methylbicyclo[2.2.1]hept-2-ene (**II**), bp 115.5°C , $d_4^{20} = 0.8605$, $n_D^{20} = 1.4600$; *exo*-5-ethylbicyclo[2.2.1]hept-2-ene (**III**), bp 130°C , $d_4^{20} = 0.8551$, $n_D^{20} = 1.4609$. The properties of the diols used were consistent with reference data [9]. Naphthalene-1,5-disulfonic acid had mp $240\text{--}245^\circ\text{C}$.

2-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)ethanol (**IV**).

a. A mixture of 47.0 g of compound **I**, 62.0 g of ethylene glycol, and 1.17 g of naphthalene-1,5-disul-

fonic acid was heated for 3 h at 100°C . Fractional distillation under reduced pressure gave 76.4 g (98%) of hydroxy ether **IV**, bp $71\text{--}71.5^\circ\text{C}$ (5 mm), $d_4^{20} = 1.0152$, $n_D^{20} = 1.4718$. ^1H NMR spectrum, δ , ppm: 1.3 d (2H, CH_2), 1.4 d (2H, CH_2), 1.7 d (4H, CH_2), 2.5 m (2H, CH_2), 3.7 q (4H, OCH_2), 3.9 m (1H, CHO), 4.8 s (1H, OH). ^{13}C NMR spectrum, δ_{C} , 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). Found, %: C 69.11; H 10.10. $\text{C}_9\text{H}_{16}\text{O}_2$. Calculated, %: C 69.19; H 10.25.

Compounds **V–XVIII** were synthesized in a similar way.

b. A mixture of 56.0 g of bicyclo[2.2.1]heptan-*exo*-2-ol, 31.0 g of ethylene glycol, 100 g of benzene, and 2.17 g of naphthalene-1,5-disulfonic acid was heated for 3 h at 80°C . Yield 74.0 g (95%), bp $71\text{--}71.5^\circ\text{C}$ (5 mm), $d_4^{20} = 1.0150$, $n_D^{20} = 1.4715$.

3-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)propan-1-ol (V**)** was obtained from 47.0 g of compound **I** and 76.0 g of propane-1,3-diol. Yield 80.7 g (95%), bp $80\text{--}82^\circ\text{C}$ (5 mm), $d_4^{20} = 1.0165$, $n_D^{20} = 1.4690$. ^1H NMR spectrum, δ , ppm: 1.3 d (2H, CH_2), 1.4 d (2H, CH_2), 1.8 d (4H, CH_2), 2.5 m (2H, CH), 3.8 q (6H, CH_2), 3.9 m (1H, CHO), 4.8 s (1H, OH). ^{13}C NMR spectrum, δ_{C} , ppm: 85.6 (C^2), 70.5 (C^9), 70.3 (C^{10}), 70.1 (C^8), 40.1 (C^1), 39.9 (C^4), 36.8 (C^3), 30.4 (C^5), 28.7 (C^6), 25.9 (C^7). Found, %: C 70.41; H 10.55. $\text{C}_{10}\text{H}_{18}\text{O}_2$. Calculated, %: C 70.55; H 10.66.

4-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)butan-1-ol (VI**)** was obtained from 47.0 g of compound **I** and 90.0 g of butane-1,4-diol. Yield 85.1 g (93%), bp $102\text{--}103^\circ\text{C}$ (5 mm), $d_4^{20} = 1.0100$, $n_D^{20} = 1.4699$. ^1H NMR spectrum, δ , ppm: 1.3 d (2H, CH_2), 1.4 d (2H, CH_2), 1.8 d (4H, CH_2), 2.5 m (2H, CH), 3.5–3.8 q (8H, CH_2), 3.9 m (1H, CHO), 4.7 s (1H, OH). ^{13}C NMR spectrum, δ_{C} , ppm: 85.6 (C^2), 70.6 (C^8), 70.1 (C^9), 69.8 (C^{10}), 68.1 (C^{11}), 40.1 (C^1), 39.9 (C^4), 36.8 (C^3), 28.7 (C^6), 25.9 (C^7). Found, %: C 71.21; H 10.71. $\text{C}_{11}\text{H}_{20}\text{O}_2$. Calculated, %: C 71.70; H 10.94.

2-(*exo*-5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)-ethanol (VII**)** was obtained from 54.0 g of compound

II and 62.0 g of ethylene glycol in the presence of 1.35 g of the catalyst. Yield 79.4 g (93%), bp 95–96°C (5 mm), $d_4^{20} = 1.0040$, $n_D^{20} = 1.4726$. ^1H NMR spectrum, δ , ppm: 0.9 d (3H, CH₃), 1.3 d (2H, CH₂), 1.4 d (2H, CH₂), 1.7 d (2H, CH₂), 2.1 d (1H, CH), 2.5 m (2H, CH), 3.8 q (4H, CH₂), 3.9 m (1H, CHO), 4.8 s (1H, OH). ^{13}C NMR spectrum, δ_C , ppm: 85.4 (C²), 70.5 (C⁹), 70.2 (C¹⁰), 42.0 (C¹), 39.4 (C⁴), 36.2 (C³), 35.1 (C⁷), 30.8 (C⁵), 28.8 (C⁶), 28.5 (C⁸). Found, %: C 70.50; H 10.62. C₁₀H₁₈O₂. Calculated, %: C 70.55; H 10.66.

3-(*exo*-5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)propan-1-ol (VIII) was obtained from 54.0 g of compound **II** and 76.0 g of propane-1,3-diol in the presence of 1.35 g of the catalyst. Yield 84.9 g (92%), bp 107–108°C (5 mm), $d_4^{20} = 1.0012$, $n_D^{20} = 1.4735$. ^1H NMR spectrum, δ , ppm: 0.9 d (3H, CH₃), 1.3 d (2H, CH₂), 1.4 d (2H, CH₂), 1.7 d (2H, CH₂), 2.1 d (1H, CH), 2.5 m (2H, CH), 3.6–3.8 q (6H, CH₂), 3.9 m (1H, CHO), 4.7 s (1H, OH). ^{13}C NMR spectrum, δ_C , ppm: 85.4 (C²), 70.5 (C⁹), 70.2 (C¹⁰), 69.8 (C¹¹), 42.0 (C¹), 39.4 (C⁴), 36.2 (C³), 35.0 (C⁷), 30.8 (C⁵), 28.7 (C⁶), 28.4 (C⁸). Found, %: C 71.49; H 10.71. C₁₁H₂₀O₂. Calculated, %: C 71.70; H 10.94.

4-(*exo*-5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)butan-1-ol (IX) was obtained from 54.0 g of compound **II** and 90.0 g of butane-1,4-diol in the presence of 1.35 g of the catalyst. Yield 86.1 g (87%), bp 120–121°C (5 mm), $d_4^{20} = 0.9978$, $n_D^{20} = 1.4749$. Found, %: C 72.42; H 11.0. C₁₂H₂₂O₂. Calculated, %: C 72.68; H 11.18.

2-(*exo*-5-Ethylbicyclo[2.2.1]hept-*exo*-2-yloxy)ethanol (X) was obtained from 61.0 g of compound **III** and 62.0 g of ethylene glycol in the presence of 1.52 g of the catalyst. Yield 81.2 g (88%), bp 108–109°C (5 mm), $d_4^{20} = 1.0000$, $n_D^{20} = 1.4738$. Found, %: C 71.68; H 10.90. C₁₁H₂₀O₂. Calculated, %: C 71.70; H 10.94.

3-(*exo*-5-Ethylbicyclo[2.2.1]hept-*exo*-2-yloxy)propan-1-ol (XI) was obtained from 61.0 g of compound **III** and 76.0 g of propane-1,3-diol in the presence of 1.52 g of the catalyst. Yield 86.0 g (87%), bp 112–113°C (5 mm), $d_4^{20} = 0.9905$, $n_D^{20} = 1.4749$. Found, %: C 72.48; H 11.01. C₁₂H₂₂O₂. Calculated, %: C 72.68; H 11.18.

4-(*exo*-5-Ethylbicyclo[2.2.1]hept-*exo*-2-yloxy)butan-1-ol (XII) was obtained from 61.0 g of compound **III** and 90.0 g of butane-1,4-diol in the presence of 1.52 g of the catalyst. Yield 87.5 g (83%), bp 130–

131°C (5 mm), $d_4^{20} = 0.9815$, $n_D^{20} = 1.4769$. Found, %: C 73.29; H 11.21. C₁₃H₂₄O₂. Calculated, %: C 73.54; H 11.39.

1-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)propan-2-ol (XIII) was obtained from 47.0 g of compound **I** and 76.0 g of propane-1,2-diol in the presence of 1.17 g of the catalyst. Yield 81.6 g (96%), bp 68–69°C (5 mm), $d_4^{20} = 1.0255$, $n_D^{20} = 1.4652$. ^1H NMR spectrum, δ , ppm: 1.0 d (3H, CH₃), 1.3 d (2H, CH₂), 1.4 d (2H, CH₂), 1.7 d (2H, CH₂), 2.1 d (1H, CH), 2.5 m (2H, CH), 3.8 q (4H, OCH₂), 3.9 m (1H, CHO), 4.8 s (1H, OH). ^{13}C NMR spectrum, δ_C , ppm: 85.6 (C²), 70.5 (C⁸), 70.1 (C⁹), 41.1 (C¹), 39.9 (C⁴), 36.9 (C³), 30.4 (C⁵), 28.7 (C⁶), 25.9 (C⁷), 28.4 (C¹⁰). Found, %: C 70.33; H 10.41. C₁₀H₁₈O₂. Calculated, %: C 70.55; H 10.66.

1-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)butan-2-ol (XIV) was obtained from 47.0 g of compound **I** and 90.0 g of butane-1,2-diol in the presence of 1.17 g of the catalyst. Yield 83.6 g (91%), bp 91–92°C (5 mm), $d_4^{20} = 1.0011$, $n_D^{20} = 1.4669$. ^1H NMR spectrum, δ , ppm: 1.0 d (3H, CH₃), 1.3 d (2H, CH₂), 1.4 d (2H, CH₂), 1.7 d (2H, CH₂), 2.1 d (1H, CH), 2.5 m (2H, CH₂), 2.5 m (2H, CH), 3.8 q (4H, OCH₂), 3.9 m (1H, CHO), 4.8 s (1H, OH). ^{13}C NMR spectrum, δ , ppm: 85.6 (C²), 70.6 (C⁹), 70.1 (C⁸), 69.8 (C¹⁰), 40.1 (C¹), 39.9 (C⁴), 36.8 (C³), 28.7 (C⁶), 28.4 (C¹¹), 25.9 (C⁷). Found, %: C 71.29; H 10.74. C₁₁H₂₀O₂. Calculated, %: C 71.70; H 10.94.

1-(*exo*-5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)propan-2-ol (XV) was obtained from 54.0 g of compound **II** and 76.0 g of propane-1,2-diol in the presence of 1.35 g of the catalyst. Yield 84.1 g (91.4%), bp 96–97°C (5 mm), $d_4^{20} = 0.9988$, $n_D^{20} = 1.4690$. Found, %: C 71.38; H 10.70. C₁₁H₂₀O₂. Calculated, %: C 71.70; H 10.94.

1-(*exo*-5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)butan-2-ol (XVI) was obtained from 54.0 g of compound **II** and 90.0 g of butane-1,2-diol in the presence of 1.35 g of the catalyst. Yield 87.7 g (88.6%), bp 98–99°C (5 mm), $d_4^{20} = 0.9967$, $n_D^{20} = 1.4708$. Found, %: C 72.48; H 11.02. C₁₂H₂₂O₂. Calculated, %: C 72.68; H 11.18.

1-(*exo*-5-Ethylbicyclo[2.2.1]hept-*exo*-2-yloxy)propan-2-ol (XVII) was obtained from 61.0 g of compound **III** and 76.0 g of propane-1,2-diol in the presence of 1.52 g of the catalyst. Yield 87.1 g (88%), bp 105–106°C (5 mm), $d_4^{20} = 0.9890$, $n_D^{20} = 1.4701$. Found, %: C 72.28; H 11.08. C₁₂H₂₂O₂. Calculated, %: C 72.68; H 11.18.

1-(exo-5-Ethylbicyclo[2.2.1]hept-exo-2-yloxy)-butan-2-ol (XVIII) was obtained from 61.0 g of compound **III** and 90.0 g of butane-1,2-diol in the presence of 1.52 g of the catalyst. Yield 90.6 g (86%), bp 116–118°C (5 mm), $d_4^{20} = 0.9806$, $n_D^{20} = 1.4700$. Found, %: C 73.32; H 11.22. $C_{13}H_{24}O_2$. Calculated, %: C 73.54; H 11.39.

REFERENCES

1. Yashna, O.G., Gavrilova, L.D., Rudnov, S.A., and Vereshchagin, L.I., *Zh. Org. Khim.*, 1970, vol. 6, p. 971.
2. JPN Patent Appl. no. 55-76832; *Ref. Zh., Khim.*, 1982, no. 2N35P.
3. Bogatskii, A.V., Kotlyar, S.A., and Klimova, E.I., *Ukr. Khim. Zh.*, 1985, vol. 51, p. 1206.
4. Gasanov, A.G. and Nagiev, A.V., *Zh. Org. Khim.*, 1994, vol. 30, p. 707.
5. Mamedov, M.K., Nabieva, E.K., and Rasulova, R.A., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 974.
6. Gasanov, A.G., Mekhtiev, S.D., and Suleimanova, E.T., *Azerb. Neft. Khoz.*, 1985, no. 7, p. 36.
7. Mamedov, M.K. and Suleimanova, E.T., *Neftekhimiya*, 1991, vol. 31, p. 350.
8. US Patent no. 4107223, 1978; *Ref. Zh., Khim.*, 1980, no. 10N108P.
9. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1964, vol. 2.