

## Products of Direct Hydroalkoxylation of Norbornene with Alcohols over H-Beta Zeolite Catalyst

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**Abstract**—The reaction of direct hydroalkoxylation of norbornene in the presence of H-beta zeolite catalyst has been studied. It has been found that the selectivity for *exo*-alkoxynorbornanes of the reaction of norbornene with monohydric alcohols (saturated, unsaturated, or aromatic) reaches 98% at a conversion of 78–98% of the unsaturated compound. The reaction of norbornene with diols (ethylene glycol and 2-butene-1,4-diol) in the presence of H-beta zeolite affords mono- and diethers, whose yield and ratio can be controlled by varying reaction parameters.

**Keywords:** hydroalkoxylation with alcohols, norbornene, zeolite catalyst

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Norbornene derivatives are used in organic synthesis and medicinal chemistry [1, 2] and in the perfume industry [3, 4]. In addition to the first methods for the synthesis of alkoxynorbornenes described in [5–9], the direct addition of alcohols to the double bond of norbornene in the presence of sulfuric acid [10] or the cation-exchange resin KU-2-8 [11] was proposed.

New catalytic systems that can mediate the norbornene hydroalkoxylation reaction have been reported recently. Most of them are based on trifluoromethanesulfonic acid (TfOH) [12, 13] and its salts, such as Cu(OTf)<sub>2</sub> [14, 15], AuClPPh<sub>3</sub>–AgOTf [16], Cp\*RuCl<sub>2</sub>(PPh<sub>3</sub>)–AgOTf [17], and AgOTf [18]. High yields (90–98%) of alkoxynorbornanes over these catalytic systems are obtained only in the reaction of norbornene with alcohols containing functional groups, for example, Cl or OR. The addition of unsubstituted aliphatic alcohols occurs less effectively: the yield of alkoxynorbornanes is 25–75% in this case [14]. The *exo*-isomers dominate (>95%) in the product [14, 15].

The use of other heterogeneous catalysts, besides the aforementioned sulfonated cation-exchange resin KU-2-8 [11], for the preparation of alkoxynorbornanes has not been described. At the same time, there are examples of the use of zeolite Beta in the hydroalkoxylation of limonene and  $\alpha$ -pinene [19], as well as hexene [20]. It has been shown that alkoxynorbornanes can be obtained through the addition of simple alcohols **2–12** (see below) to norbornene on H-Beta zeolite [21, 22].

These results have stimulated the development and continuation of the study of the reaction of alcohols

and diols with norbornene in the presence of a commercially available H-Beta zeolite catalyst.

### EXPERIMENTAL

Chromatographic analysis of the products was performed on a Carlo Erba HRGS 5300 Mega Series chromatograph with a flame-ionization detector using helium as the carrier gas at a flow rate of 30 mL/min, a SE-30-coated column of a 25 m length, and the column temperature programmed from 50 to 280°C at a rate of 8°C/min. Mass chromatograms were recorded on Fisons (50-m fused-silica capillary column DB 560) and Focus instruments with a Finigan DSQ II mass spectrometric detector (ion source temperature, 200°C; on-column injection temperature, 50–270°C; heating rate, 10°C/min; Thermo TR-5MS column, 50 × 2.5 × 10<sup>−4</sup> m; helium flow rate, 0.7 mL/min). The mass spectra of the compounds were obtained in the electron ionization mode. NMR spectra were recorded on a Bruker AVANCE-400 (<sup>1</sup>H 400.13 MHz) spectrometer in CDCl<sub>3</sub>, using benzene-d<sub>6</sub> and toluene-d<sub>8</sub> as an internal standard. One- and two-dimensional NMR spectra were recorded using standard pulse sequences. 2D homonuclear (COSY HH, NOESY) and heteronuclear (HSQC, HMBS) correlation experiments were carried out using pulsed field gradient techniques.

The H-Beta zeolite catalyst was prepared by high-temperature treatment at 540°C of NH<sub>4</sub>-Beta zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 18.0 for 4 h in an air atmosphere.

*Procedure for Norbornene Reaction  
with Alcohols (2–10) and Diols (11, 12)*

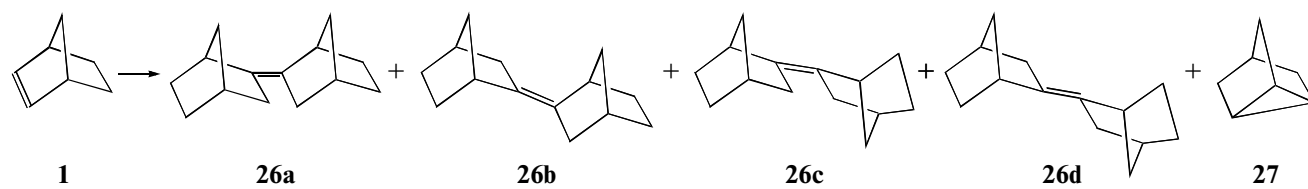
A mixture of alcohol and norbornene **1**, taken in a molar ratio of 1 : (1–3), and the H-Beta catalyst taken in an amount of 20 wt % (based on a mixture of norbornene : alcohol = 1 : 1 mol/mol) was heated at 50–80°C with vigorous stirring for 5 h. After completion of the reaction, the catalyst was filtered off. To isolate the products from the reaction mixture, the unreacted alcohol was distilled off and ethers **13–21** and **22–25** were isolated by distillation under reduced pressure.

The reaction of norbornene with methanol or ethanol at 80°C was carried out in a continuously rotating thermostated autoclave. The norbornene conversion was determined chromatographically.

The structural characteristics of the synthesized compounds are shown in Table 1.

## RESULTS AND DISCUSSION

The H-Beta zeolite-catalyzed reaction of norbornene with various monohydric alcohols (aliphatic

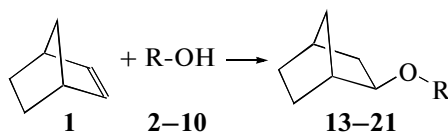


Using the reaction of norbornene with butanol as an example, we studied the influence of the temperature and the molar ratio of reactants on the norbornene conversion and alkoxy norbornane selectivity (runs 4–6, Table 2). It was shown that the conversion of norbornene increases as the temperature increases from 50 to 80°C, with the selectivity for butoxy norbornane slightly (by 5%) decreasing as a result of an increase in the amount of nortricyclane **27**.

The reactant molar ratio has the most significant effect on the ether selectivity. For example, a reduction in the norbornene : butanol molar ratio from 1 : 3 to 1 : 1 leads to a significant decrease (by 21%) in the selectivity for butoxy norbornane, although the conversion of the cycloalkene remains almost unchanged. In this case (norbornene : butanol = 1 : 1), the contribution of both the cyclization reaction of norbornene and its dimerization increases.

The H-Beta zeolite catalyst exhibits a high efficiency not only in the norbornene reaction with aliphatic alcohols. Benzyloxy norbornane is produced with a selectivity of 95% and an almost complete conversion of the olefin. Note that these results are similar to those obtained by Taylor et al. [14], who prepared benzyloxy norbornane in the presence of the homoge-

$C_1$ – $C_7$ , allyl, and benzyl alcohols) gives corresponding alkoxy norbornanes **13–21**:



R = Me (**2**, **13**); Et (**3**, **14**); n-Pr (**4**, **15**); n-Bu (**5**, **16**); Am (**6**, **17**); n-Hex (**7**, **18**); n-Hept (**8**, **19**); Bn (**9**, **20**); All (**10**, **21**).

The data presented in Table 2 show that at 80°C, 20 wt % catalyst, and a norbornene : alcohol molar ratio of 1 : 3, the norbornene conversion reaches 98–99% and the selectivity for alkoxy norbornanes is 84–98%.

Along with alkoxy norbornanes, the reaction mixture contained the following products of side reactions: nortricyclane (NTC), formed via the intramolecular cyclization of the reactant olefin, and norbornene dimers:

neous catalyst  $Cu(OTf)_2$ , with the reaction being carried out in a dioxane medium for 18 h.

Norbornene reacts with allyl alcohol with a high selectivity (90%) only at 50°C. As the temperature is elevated to 80°C, oligomeric and polymeric compounds become the main reaction products.

As can be seen from the data in Table 2, by reacting norbornene with aliphatic  $C_1$ – $C_4$  alcohols and allyl or benzyl alcohol, the ethers are formed in the *exo*-configuration. The analysis by  $^1H$  and  $^{13}C$  NMR techniques of alkoxy norbornanes **17–19** obtained by reacting norbornene with amyl, hexyl, and heptyl alcohol, respectively, showed that two diastereomeric products (*exo*- and *endo*-isomers) were formed in all cases. The  $^{13}C$  NMR technique proved to be most informative for the rigorous quantitative determination of the isomeric ratio. According to our data, the *exo* : *endo* ratios for ethers **17–19** are 8.5, 4.1, and 2.3, respectively.

The structure of all alkoxy norbornanes synthesized in this study was proved by one-dimensional and two-dimensional homonuclear (SOSY, NOESY) and heteronuclear (HSQC, HMBC)  $^1H$ ,  $^{13}C$  NMR spectroscopy. In the  $^{13}C$  NMR spectrum, signals of the C-7 atom of alkoxy norbornenes **13–21** appear in the region of 34.7–35.1 ppm, suggesting the *exo*-configu-

**Table 1.** Spectral and physicochemical characteristics of the synthesized compounds [21]

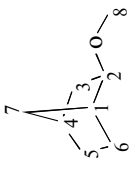
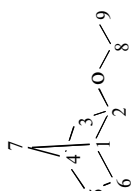
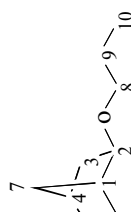
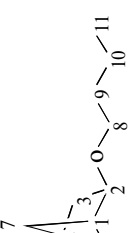
| Compound, $T_{bp}$ , °C ( $p$ , mm Hg)   | NMR (CDCl <sub>3</sub> , $\delta$ , ppm)   | Mass spectrum, $m/z$ ( $I_{rel.}$ , %)   |
|--|--|--|
| <p><i>exo</i>-2-Methoxybicyclo[2.2.1]heptane (<b>13</b>)</p>  <p><math>T_{bp}</math> 54–55°C (310 mm Hg); <math>n_D^{20}</math> = 1.453</p>   | <p><sup>1</sup>H NMR: 0.93–1.06 (m, 1H, C<sup>6</sup>H<sub>a</sub>), 0.93–1.06 (m, 1H, C<sup>5</sup>H<sub>a</sub>), 0.93–1.06 (m, 1H, C<sup>7</sup>H<sub>a</sub>), 1.24–1.37 (m, 1H, C<sup>5</sup>H<sub>b</sub>), 1.24–1.37 (m, 1H, C<sup>3</sup>H<sub>a</sub>), 1.51–1.58 (m, 1H, C<sup>6</sup>H<sub>b</sub>), 1.51–1.58 (m, 1H, C<sup>7</sup>H<sub>b</sub>), 2.19 (s, 1H, C<sup>4</sup>H), 2.28 (s, 1H, C<sup>1</sup>H), 3.20–3.78 (m, 1H, C<sup>2</sup>H), 3.20–3.78 (m, 3H, C<sup>8</sup>H<sub>3</sub>).</p> <p><sup>13</sup>C NMR: 24.57 C<sup>6</sup>, 28.49 C<sup>5</sup>, 34.69 C<sup>4</sup>, 35.11 C<sup>7</sup>, 39.29 C<sup>3</sup>, 39.86 C<sup>1</sup>, 55.77 C<sup>8</sup>, 84.18 C<sup>2</sup>.</p>  | <p>126 M<sup>+</sup> (1), 97 [M–CHO]<sup>+</sup> (20.0), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (13), 94[C<sub>7</sub>H<sub>10</sub>]<sup>+</sup> (100), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (98.0), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (10.0), 71 [C<sub>5</sub>H<sub>11</sub>]<sup>+</sup> (23.0), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (48.0), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup> (81.0), 58 [C<sub>4</sub>H<sub>10</sub>]<sup>+</sup> (26.0), 55 [C<sub>4</sub>H<sub>7</sub>]<sup>+</sup> (18.0), 41[C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (42.0). Kovats index <math>I_K</math> = 952.</p>   |
| <p><i>exo</i>-2-Ethoxybicyclo[2.2.1]heptane (<b>14</b>)</p>  <p><math>T_{bp}</math> 52–53°C (80 mm Hg), (publ. 95–97°C/740 mm Hg [21]); <math>n_D^{20}</math> = 1.455</p>                     | <p><sup>1</sup>H NMR: 0.96–1.03 (m, 1H, C<sup>6</sup>H<sub>a</sub>), 1.06–1.08 (m, 2H, C<sup>3</sup>H<sub>a</sub>, C<sup>3</sup>H<sub>b</sub>), 1.16 (t, 3H, C<sup>9</sup>H<sub>3</sub>), 1.33–1.37 (m, 2H, C<sup>7</sup>H<sub>a</sub>, C<sup>6</sup>H<sub>b</sub>), 1.42–1.45 (m, 1H, C<sup>5</sup>H<sub>a</sub>), 1.50–1.56 (m, 2H, C<sup>5</sup>H<sub>b</sub>, C<sup>7</sup>H<sub>b</sub>), 2.21 (s, 1H, C<sup>4</sup>H), 2.29–2.99 (m, 1H, C<sup>1</sup>H), 3.31–3.33 (m, 1H, C<sup>2</sup>H), 3.35–3.46 (m, 1H, C<sup>4</sup>H).</p> <p><sup>13</sup>C NMR: 15.53 C<sup>9</sup>, 24.69 C<sup>6</sup>, 28.55 C<sup>5</sup>, 34.79 C<sup>7</sup>, 35.12 C<sup>4</sup>, 39.66 C<sup>3</sup>, 40.34 C<sup>1</sup>, 63.55 C<sup>8</sup>, 82.33 C<sup>2</sup>.</p>  | <p>140 M<sup>+</sup> (1), 112 [M–C<sub>2</sub>H<sub>4</sub>]<sup>+</sup> (8.0), 95[C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (44.0), 94[C<sub>7</sub>H<sub>10</sub>]<sup>+</sup> (100), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (72.0), 71 [C<sub>5</sub>H<sub>11</sub>]<sup>+</sup> (26), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (79.0), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup> (80.0), 58 [C<sub>4</sub>H<sub>10</sub>]<sup>+</sup> (21.0), 55 [C<sub>4</sub>H<sub>7</sub>]<sup>+</sup> (19.0), 45 [C<sub>2</sub>H<sub>5</sub>O]<sup>+</sup> (12), 41[C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (41.0).</p>   |
| <p><i>exo</i>-2-Propoxybicyclo[2.2.1]heptane (<b>15</b>)</p>  <p><math>T_{bp}</math> 64–66°C (41 mm Hg); <math>n_D^{20}</math> = 1.455</p>  | <p><sup>1</sup>H NMR: 0.82–0.89 (m, 3H, C<sup>10</sup>H<sub>3</sub>), 0.99–1.06 (m, 1H, C<sup>6</sup>H<sub>a</sub>), 0.99–1.06 (m, 1H, C<sup>5</sup>H<sub>a</sub>), 0.99–1.06 (m, 1H, C<sup>7</sup>H<sub>a</sub>), 1.27–1.42 (m, 1H, C<sup>5</sup>H<sub>b</sub>), 1.27–1.42 (m, 1H, C<sup>3</sup>H<sub>a</sub>), 1.50–1.58 (m, 1H, C<sup>6</sup>H<sub>b</sub>), 1.50–1.58 (m, 1H, C<sup>7</sup>H<sub>b</sub>), 1.50–1.58 (m, 2H, C<sup>9</sup>H<sub>2</sub>), 2.18 (s, 1H, C<sup>4</sup>H), 2.28 (s, 1H, C<sup>1</sup>H), 3.19–3.33 (m, 1H, C<sup>2</sup>H), 3.19–3.33 (m, 2H, C<sup>8</sup>H<sub>2</sub>). <sup>13</sup>C NMR: 10.65 C<sup>10</sup>, 23.19 C<sup>9</sup>, 28.58 C<sup>5</sup>, 34.72 C<sup>7</sup>, 35.07 C<sup>4</sup>, 39.58 C<sup>3</sup>, 40.32 C<sup>1</sup>, 69.84 C<sup>8</sup>, 82.33 C<sup>2</sup>.</p>  | <p>154 M<sup>+</sup> (2), 112 [M–C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> (12.0), 95[C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (35.0), 94[C<sub>7</sub>H<sub>10</sub>]<sup>+</sup> (100), 83[M–C<sub>3</sub>H<sub>6</sub>–CHO]<sup>+</sup> (24.0), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (82.0), 68 [C<sub>5</sub>H<sub>8</sub>]<sup>+</sup> (17.0), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (62.0), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup> (82.0), 57 [C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> (16.0), 55 [C<sub>4</sub>H<sub>7</sub>]<sup>+</sup> (20.0), 44 [C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> (11), 43 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (38), 41[C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (51.0). <math>I_K</math> = 1093.</p> |
| <p><i>exo</i>-2-Butoxybicyclo[2.2.1]heptane (<b>16</b>)</p>  <p><math>T_{bp}</math> 89–90°C (18 mm Hg), (publ. 59–60°C/2 mm Hg [5]; 120°C/25 mm Hg [14]); <math>n_D^{20}</math> = 1.456</p> | <p><sup>1</sup>H NMR: 0.91 (m, 3H, C<sup>11</sup>H<sub>3</sub>), 0.96–1.07 (m, 1H, C<sup>6</sup>H<sub>a</sub>), 0.96–1.07 (m, 1H, C<sup>5</sup>H<sub>a</sub>), 0.96–1.07 (m, 1H, C<sup>7</sup>H<sub>a</sub>), 1.32–1.41 (m, 1H, C<sup>5</sup>H<sub>b</sub>), 1.32–1.41 (m, 1H, C<sup>3</sup>H<sub>a</sub>), 1.32–1.41 (m, 2H, C<sup>10</sup>H<sub>2</sub>), 1.46–1.55 (m, 1H, C<sup>6</sup>H<sub>b</sub>), 1.46–1.55 (m, 1H, C<sup>7</sup>H<sub>b</sub>), 1.46–1.55 (m, 1H, C<sup>4</sup>H), 1.46–1.55 (m, 2H, C<sup>9</sup>H<sub>2</sub>), 2.20 (s, 1H, C<sup>4</sup>H), 2.29 (s, 1H, C<sup>1</sup>H), 3.24–3.40 (m, 1H, C<sup>2</sup>H), 3.24–3.40 (m, 2H, C<sup>8</sup>H<sub>2</sub>). <sup>13</sup>C NMR: 13.87 C<sup>11</sup>, 19.47 C<sup>10</sup>, 24.64 C<sup>6</sup>, 28.59 C<sup>5</sup>, 32.15 C<sup>9</sup>, 34.75 C<sup>7</sup>, 35.10 C<sup>4</sup>, 39.61 C<sup>3</sup>, 40.33 C<sup>1</sup>, 67.92 C<sup>8</sup>, 82.38 C<sup>2</sup>.</p> | <p>168 M<sup>+</sup> (≤1), 112 [M–C<sub>4</sub>H<sub>8</sub>]<sup>+</sup> (12.0), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (39.0), 94 [C<sub>7</sub>H<sub>10</sub>]<sup>+</sup> (100), 83 [M–C<sub>4</sub>H<sub>8</sub>–CHO]<sup>+</sup> (19.0), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (65.0), 68 [C<sub>5</sub>H<sub>8</sub>]<sup>+</sup> (16.0), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (56.0), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup> (74.0), 57 [C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> (28.0), 56 [C<sub>4</sub>H<sub>8</sub>]<sup>+</sup> (13.0), 55 [C<sub>4</sub>H<sub>7</sub>]<sup>+</sup> (17.0), 41 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (49.0). <math>I_K</math> = 1190.</p>  |

Table 1. (Contd.)

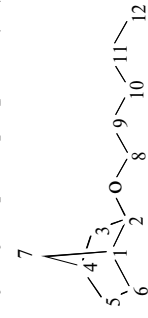
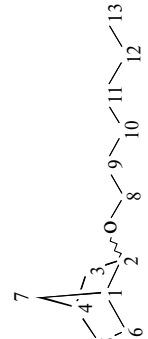
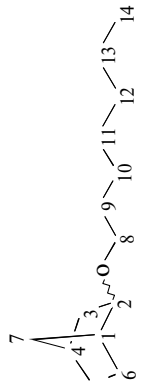
| Compound, $T_{bp}$ , °C (p, mm Hg)   | NMR (CDCl <sub>3</sub> , δ, ppm)   | Mass spectrum, $m/z$ ( $I_{rel.}$ , %)   |
|--|--|--|
| 2-Amyloxybicyclo[2.2.1]heptane (17)<br><br>$T_{bp}$ 91–92°C (10 mm Hg); $n_D^{20}$ = 1.457      | <sup>1</sup> H NMR: 0.87–0.93 (m, 3H, C <sup>12</sup> H <sub>3</sub> ), 0.95–1.08 (m, 1H, C <sup>6</sup> H <sub>a</sub> ), 0.95–1.08 (m, 1H, C <sup>5</sup> H <sub>a</sub> ), 0.95–1.08 (m, 1H, C <sup>7</sup> H <sub>a</sub> ), 1.25–1.33 (m, 1H, C <sup>5</sup> H <sub>b</sub> ), 1.25–1.33 (m, 1H, C <sup>3</sup> H <sub>a</sub> ), 1.25–1.33 (m, 2H, C <sup>9</sup> H <sub>2</sub> ), 1.25–1.33 (m, 2H, C <sup>10</sup> H <sub>2</sub> ), 1.25–1.33 (m, 2H, C <sup>11</sup> H <sub>2</sub> ), 1.48–1.57 (m, 1H, C <sup>6</sup> H <sub>b</sub> ), 1.48–1.57 (m, 1H, C <sup>3</sup> H <sub>b</sub> ), 1.48–1.57 (m, 1H, C <sup>7</sup> H <sub>b</sub> ), 2.20 (c, 1H, C <sup>4</sup> H), 2.29 (s, 1H, C <sup>1</sup> H), 3.73–3.77 (m, 1H, C <sup>1</sup> H), 3.73–3.77 (m, 2H, C <sup>8</sup> H <sub>2</sub> ). <sup>13</sup> C NMR: <i>exo</i> -13.99 C <sup>12</sup> , 20.13 C <sup>11</sup> , 22.56 C <sup>6</sup> , 28.52 C <sup>10</sup> , 28.59 C <sup>5</sup> , 29.76 C <sup>9</sup> , 34.75 C <sup>7</sup> , 35.10 C <sup>4</sup> , 37.10 C <sup>3</sup> , 39.61 C <sup>1</sup> , 68.26 C <sup>8</sup> , 82.38 C <sup>2</sup> ; <i>endo</i> -13.99 C <sup>12</sup> , 20.13 C <sup>11</sup> , 24.64 C <sup>6</sup> , 28.52 C <sup>10</sup> , 28.59 C <sup>5</sup> , 29.71 C <sup>9</sup> , 34.75 C <sup>7</sup> , 35.10 C <sup>4</sup> , 37.03 C <sup>3</sup> , 40.32 C <sup>1</sup> , 69.12 C <sup>8</sup> , 80.24 C <sup>2</sup> .   | 182 M <sup>+</sup> (≤1), 112 [M – C <sub>5</sub> H <sub>10</sub> ] <sup>+</sup> (15.0), 95 [C <sub>7</sub> H <sub>11</sub> ] <sup>+</sup> (51.0), 94 [C <sub>7</sub> H <sub>10</sub> ] <sup>+</sup> (100), 83[M – C <sub>5</sub> H <sub>10</sub> – CHO] <sup>+</sup> (18.0), 79 [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> (57.0), 71 [C <sub>5</sub> H <sub>11</sub> ] <sup>+</sup> (15), 70 [C <sub>5</sub> H <sub>10</sub> ] <sup>+</sup> (16), 68 [C <sub>5</sub> H <sub>8</sub> ] <sup>+</sup> (17.0), 67 [C <sub>5</sub> H <sub>7</sub> ] <sup>+</sup> (56.0), 66 [C <sub>5</sub> H <sub>6</sub> ] <sup>+</sup> (72.0), 55 [C <sub>4</sub> H <sub>7</sub> ] <sup>+</sup> (26.0), 43 [C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup> (59), 42 [C <sub>3</sub> H <sub>4</sub> ] <sup>+</sup> (11), 41 [C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup> (42.0). $I_K$ = 1291. |
| 2-Hexyloxybicyclo[2.2.1]heptane (18)<br><br>$T_{bp}$ 106–107°C (10 mm Hg); $n_D^{20}$ = 1.453   | <sup>1</sup> H NMR: 0.88 (m, 3H, C <sup>13</sup> H <sub>3</sub> ), 0.98–1.11 (m, 1H, C <sup>6</sup> H <sub>a</sub> ), 0.98–1.11 (m, 1H, C <sup>5</sup> H <sub>a</sub> ), 0.98–1.11 (m, 1H, C <sup>7</sup> H <sub>a</sub> ), 1.28 (m, 1H, C <sup>5</sup> H <sub>b</sub> ), 1.28 (m, 1H, C <sup>3</sup> H <sub>a</sub> ), 1.28 (m, 2H, C <sup>9</sup> H <sub>2</sub> ), 1.28 (m, 2H, C <sup>10</sup> H <sub>2</sub> ), 1.28 (m, 2H, C <sup>11</sup> H <sub>2</sub> ), 1.28 (m, 2H, C <sup>12</sup> H <sub>2</sub> ), 1.50–1.54 (m, 1H, C <sup>6</sup> H <sub>b</sub> ), 1.50–1.54 (m, 1H, C <sup>3</sup> H <sub>b</sub> ), 1.50–1.54 (m, 1H, C <sup>7</sup> H <sub>b</sub> ), 2.21 (c, 1H, C <sup>4</sup> H), 2.29 (s, 1H, C <sup>1</sup> H), 3.25–3.40 (m, 1H, C <sup>2</sup> H), 3.25–3.40 (m, 2H, C <sup>8</sup> H <sub>2</sub> ). <sup>13</sup> C NMR: <i>exo</i> -14.06 C <sup>13</sup> , 22.64 C <sup>12</sup> , 24.68 C <sup>6</sup> , 26.00 C <sup>10</sup> , 28.60 C <sup>5</sup> , 30.04 C <sup>9</sup> , 31.74 C <sup>11</sup> , 34.80 C <sup>7</sup> , 35.13 C <sup>4</sup> , 39.64 C <sup>3</sup> , 40.34 C <sup>1</sup> , 68.29 C <sup>8</sup> , 82.41 C <sup>2</sup> ; <i>endo</i> -14.06 C <sup>13</sup> , 22.64 C <sup>12</sup> , 24.68 C <sup>6</sup> , 26.00 C <sup>10</sup> , 28.60 C <sup>5</sup> , 29.86 C <sup>9</sup> , 31.74 C <sup>11</sup> , 34.80 C <sup>7</sup> , 35.13 C <sup>4</sup> , 36.51 C <sup>3</sup> , 37.12 C <sup>1</sup> , 68.32 C <sup>8</sup> , 82.38 C <sup>2</sup> .  | 196 M <sup>+</sup> (≤1), 112 [M – C <sub>6</sub> H <sub>12</sub> ] <sup>+</sup> (14.0), 95 [C <sub>7</sub> H <sub>11</sub> ] <sup>+</sup> (55.0), 94 [C <sub>7</sub> H <sub>10</sub> ] <sup>+</sup> (100), 83[M – C <sub>6</sub> H <sub>12</sub> – CHO] <sup>+</sup> (17.0), 79 [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> (51.0), 68 [C <sub>5</sub> H <sub>8</sub> ] <sup>+</sup> (13.0), 67 [C <sub>5</sub> H <sub>7</sub> ] <sup>+</sup> (51.0), 66 [C <sub>5</sub> H <sub>6</sub> ] <sup>+</sup> (65.0), 57 [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> (12.0), 55 [C <sub>4</sub> H <sub>7</sub> ] <sup>+</sup> (21.0), 43 [C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup> (69), 41 [C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup> (44.0). $I_K$ = 1393, 1397.   |
| 2-Heptyloxybicyclo[2.2.1]heptane (19)<br><br>$T_{bp}$ 104–105°C (8 mm Hg); $n_D^{20}$ = 1.453 | <sup>1</sup> H NMR: 0.88 (m, 3H, C <sup>14</sup> H <sub>3</sub> ), 0.95–1.11 (m, 1H, C <sup>6</sup> H <sub>a</sub> ), 0.95–1.11 (m, 1H, C <sup>5</sup> H <sub>a</sub> ), 0.95–1.11 (m, 1H, C <sup>7</sup> H <sub>a</sub> ), 1.26 (m, 1H, C <sup>5</sup> H <sub>b</sub> ), 1.26 (m, 1H, C <sup>3</sup> H <sub>a</sub> ), 1.26 (m, 2H, C <sup>9</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>10</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>11</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>12</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>13</sup> H <sub>2</sub> ), 1.49–1.55 (m, 1H, C <sup>6</sup> H <sub>b</sub> ), 1.49–1.55 (m, 1H, C <sup>3</sup> H <sub>b</sub> ), 1.49–1.55 (m, 1H, C <sup>7</sup> H <sub>b</sub> ), 2.21 (s, 1H, C <sup>4</sup> H), 2.29 (s, 1H, C <sup>1</sup> H), 3.24–3.40 (m, 1H, C <sup>2</sup> H), 3.24–3.40 (m, 2H, C <sup>8</sup> H <sub>2</sub> ). <sup>13</sup> C NMR: <i>exo</i> -14.02 C <sup>14</sup> , 22.60 C <sup>13</sup> , 24.64 C <sup>6</sup> , 26.31 C <sup>11</sup> , 28.60 C <sup>5</sup> , 29.17 C <sup>12</sup> , 29.83 C <sup>9</sup> , 30.07 C <sup>10</sup> , 34.76 C <sup>7</sup> , 35.10 C <sup>4</sup> , 39.55 C <sup>3</sup> , 40.32 C <sup>1</sup> , 68.27 C <sup>8</sup> , 82.39 C <sup>2</sup> ; <i>endo</i> -14.02 C <sup>14</sup> , 22.60 C <sup>13</sup> , 24.64 C <sup>6</sup> , 26.31 C <sup>11</sup> , 28.60 C <sup>5</sup> , 29.17 C <sup>12</sup> , 30.02 C <sup>9</sup> , 30.07 C <sup>10</sup> , 34.76 C <sup>7</sup> , 35.10 C <sup>4</sup> , 36.51 C <sup>3</sup> , 37.10 C <sup>1</sup> , 69.14 C <sup>8</sup> , 80.24 C <sup>2</sup> . | 210 M <sup>+</sup> (≤1), 112 [M – C <sub>7</sub> H <sub>14</sub> ] <sup>+</sup> (15.0), 95 [C <sub>7</sub> H <sub>11</sub> ] <sup>+</sup> (60.0), 94 [C <sub>7</sub> H <sub>10</sub> ] <sup>+</sup> (100), 83 [M – C <sub>7</sub> H <sub>14</sub> – CHO] <sup>+</sup> (14.0), 79 [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> (44.0), 68 [C <sub>5</sub> H <sub>8</sub> ] <sup>+</sup> (11.0), 67 [C <sub>5</sub> H <sub>7</sub> ] <sup>+</sup> (40.0), 66 [C <sub>5</sub> H <sub>6</sub> ] <sup>+</sup> (54.0), 57 [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> (48.0), 55 [C <sub>4</sub> H <sub>7</sub> ] <sup>+</sup> (18.0), 43 [C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup> (26), 41 [C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup> (39.0). $I_K$ = 1496.  |

Table 1. (Contd.)

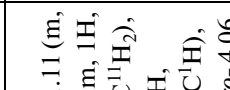
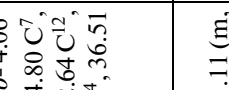
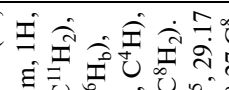
| Compound, $T_{bp}$ , °C (p, mm Hg)  | NMR (CDCl <sub>3</sub> , δ, ppm)   | Mass spectrum, $m/z$ ( $I_{rel.}$ , %)   |
|---|--|--|
| 2-Hexyloxybicyclo[2.2.1]heptane ( <b>18</b> )<br><br>$T_{bp}$ 106–107°C (10 mm Hg); $n_D^{20} = 1.457$                                   | <sup>1</sup> H NMR: 0.88 (m, 3H, C <sup>13</sup> H <sub>3</sub> ), 0.98–1.11 (m, 1H, C <sup>6</sup> H <sub>a</sub> ), 0.98–1.11 (m, 1H, C <sup>5</sup> H <sub>a</sub> ), 0.98–1.11 (m, 1H, C <sup>7</sup> H <sub>a</sub> ), 1.28 (m, 1H, C <sup>5</sup> H <sub>b</sub> ), 1.28 (m, 1H, C <sup>3</sup> H <sub>a</sub> ), 1.28 (m, 2H, C <sup>9</sup> H <sub>2</sub> ), 1.28 (m, 2H, C <sup>10</sup> H <sub>2</sub> ), 1.28 (m, 2H, C <sup>11</sup> H <sub>2</sub> ), 1.28 (m, 2H, C <sup>12</sup> H <sub>2</sub> ), 1.50–1.54 (m, 1H, C <sup>6</sup> H <sub>b</sub> ), 1.50–1.54 (m, 1H, C <sup>3</sup> H <sub>b</sub> ), 1.50–1.54 (m, 1H, C <sup>7</sup> H <sub>b</sub> ), 2.21 (c, 1H, C <sup>4</sup> H), 2.29 (s, 1H, C <sup>1</sup> H), 3.25–3.40 (m, 1H, C <sup>2</sup> H), 3.25–3.40 (m, 2H, C <sup>8</sup> H <sub>2</sub> ). <sup>13</sup> C NMR: <i>exo</i> -4.06 C <sup>13</sup> , 22.64 C <sup>12</sup> , 24.68 C <sup>6</sup> , 26.00 C <sup>10</sup> , 28.60 C <sup>5</sup> , 30.04 C <sup>9</sup> , 31.74 C <sup>11</sup> , 34.80 C <sup>7</sup> , 35.13 C <sup>4</sup> , 39.64 C <sup>3</sup> , 40.34 C <sup>1</sup> , 68.29 C <sup>8</sup> , 82.41 C <sup>2</sup> ; <i>endo</i> -14.06 C <sup>13</sup> , 22.64 C <sup>12</sup> , 24.68 C <sup>6</sup> , 26.00 C <sup>10</sup> , 28.60 C <sup>5</sup> , 29.86 C <sup>9</sup> , 31.74 C <sup>11</sup> , 34.80 C <sup>7</sup> , 35.13 C <sup>4</sup> , 36.51 C <sup>3</sup> , 37.12 C <sup>1</sup> , 68.32 C <sup>8</sup> , 82.38 C <sup>2</sup> .   | 196 M <sup>+</sup> (≤1), 112 [M–C <sub>6</sub> H <sub>12</sub> ] <sup>+</sup> (14.0), 95 [C <sub>7</sub> H <sub>11</sub> ] <sup>+</sup> (55.0), 94 [C <sub>7</sub> H <sub>10</sub> ] <sup>+</sup> (100), 83[M–C <sub>6</sub> H <sub>12</sub> –CHO] <sup>+</sup> (17.0), 79 [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> (51.0), 68 [C <sub>5</sub> H <sub>8</sub> ] <sup>+</sup> (13.0), 67 [C <sub>5</sub> H <sub>7</sub> ] <sup>+</sup> (51.0), 66 [C <sub>5</sub> H <sub>6</sub> ] <sup>+</sup> (65.0), 57 [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> (12.0), 55 [C <sub>4</sub> H <sub>7</sub> ] <sup>+</sup> (21.0), 43 [C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup> (69), 41 [C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup> (44.0). $I_K = 1393, 1397$ . |
| 2-Heptyloxybicyclo[2.2.1]heptane ( <b>19</b> )<br><br>$T_{bp}$ 104–105°C (8 mm Hg); $n_D^{20} = 1.453$                                   | <sup>1</sup> H NMR: 0.88 (m, 3H, C <sup>14</sup> H <sub>3</sub> ), 0.95–1.11 (m, 1H, C <sup>6</sup> H <sub>a</sub> ), 0.95–1.11 (m, 1H, C <sup>5</sup> H <sub>a</sub> ), 0.95–1.11 (m, 1H, C <sup>7</sup> H <sub>a</sub> ), 1.26 (m, 1H, C <sup>5</sup> H <sub>b</sub> ), 1.26 (m, 1H, C <sup>3</sup> H <sub>a</sub> ), 1.26 (m, 2H, C <sup>9</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>10</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>11</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>12</sup> H <sub>2</sub> ), 1.26 (m, 2H, C <sup>13</sup> H <sub>2</sub> ), 1.49–1.55 (m, 1H, C <sup>6</sup> H <sub>b</sub> ), 1.49–1.55 (m, 1H, C <sup>3</sup> H <sub>b</sub> ), 1.49–1.55 (m, 1H, C <sup>7</sup> H <sub>b</sub> ), 2.21 (c, 1H, C <sup>4</sup> H), 2.29 (s, 1H, C <sup>1</sup> H), 3.24–3.40 (m, 1H, C <sup>2</sup> H), 3.24–3.40 (m, 2H, C <sup>8</sup> H <sub>2</sub> ). <sup>13</sup> C NMR: <i>exo</i> -14.02 C <sup>14</sup> , 22.60 C <sup>13</sup> , 24.64 C <sup>6</sup> , 26.31 C <sup>11</sup> , 28.60 C <sup>5</sup> , 29.17 C <sup>12</sup> , 29.83 C <sup>9</sup> , 30.07 C <sup>10</sup> , 34.76 C <sup>7</sup> , 35.10 C <sup>4</sup> , 39.55 C <sup>3</sup> , 40.32 C <sup>1</sup> , 68.27 C <sup>8</sup> , 82.39 C <sup>2</sup> ; <i>endo</i> -14.02 C <sup>14</sup> , 22.60 C <sup>13</sup> , 24.64 C <sup>6</sup> , 26.31 C <sup>11</sup> , 28.60 C <sup>5</sup> , 29.17 C <sup>12</sup> , 30.02 C <sup>9</sup> , 30.07 C <sup>10</sup> , 34.76 C <sup>7</sup> , 35.10 C <sup>4</sup> , 36.51 C <sup>3</sup> , 37.10 C <sup>1</sup> , 69.14 C <sup>8</sup> , 80.24 C <sup>2</sup> . | 210 M <sup>+</sup> (≤1), 112 [M–C <sub>7</sub> H <sub>14</sub> ] <sup>+</sup> (15.0), 95 [C <sub>7</sub> H <sub>11</sub> ] <sup>+</sup> (60.0), 94 [C <sub>7</sub> H <sub>10</sub> ] <sup>+</sup> (100), 83 [M–C <sub>7</sub> H <sub>14</sub> –CHO] <sup>+</sup> (14.0), 79 [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> (44.0), 68 [C <sub>5</sub> H <sub>8</sub> ] <sup>+</sup> (11.0), 67 [C <sub>5</sub> H <sub>7</sub> ] <sup>+</sup> (40.0), 66 [C <sub>5</sub> H <sub>6</sub> ] <sup>+</sup> (54.0), 57 [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> (48.0), 55 [C <sub>4</sub> H <sub>7</sub> ] <sup>+</sup> (18.0), 43 [C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup> (26), 41 [C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup> (39.0). $I_K = 1496$ .      |
| $exo$ -2-Benzyloxybicyclo[2.2.1]heptane ( <b>20</b> )<br><br>$T_{bp}$ 102–103°C (3 mm Hg); (publ. 80°C/1 mm Hg [14]); $n_D^{20} = 1.542$ | <sup>1</sup> H NMR: 0.92–1.05 (m, 1H, C <sup>6</sup> H <sub>a</sub> ), 0.92–1.05 (m, 1H, C <sup>5</sup> H <sub>a</sub> ), 0.92–1.05 (m, 1H, C <sup>7</sup> H <sub>a</sub> ), 1.25–1.40 (m, 1H, C <sup>5</sup> H <sub>b</sub> ), 1.25–1.40 (m, 1H, C <sup>3</sup> H <sub>a</sub> ), 1.51–1.56 (m, 1H, C <sup>6</sup> H <sub>b</sub> ), 1.51–1.56 (m, 1H, C <sup>3</sup> H <sub>b</sub> ), 1.51–1.56 (m, 1H, C <sup>7</sup> H <sub>b</sub> ), 2.19 (s, 1H, C <sup>4</sup> H), 2.28 (s, 1H, C <sup>1</sup> H), 3.64–4.51 (m, 1H, C <sup>2</sup> H), 3.64–4.51 m, 2H, C <sup>8</sup> H <sub>2</sub> ), 7.00–7.05 (m, 5H, Ar). <sup>13</sup> C NMR: 24.73 C <sup>6</sup> , 28.70 C <sup>5</sup> , 35.05 C <sup>7</sup> , 35.33 C <sup>4</sup> , 39.72 C <sup>3</sup> , 40.52 C <sup>1</sup> , 70.25 C <sup>8</sup> , 72.20 C <sup>2</sup> , 127.58–128.50 (Ar), 139.20 C <sup>9</sup> .   | 202 M <sup>+</sup> (1), 95 [C <sub>7</sub> H <sub>11</sub> ] <sup>+</sup> (42.0), 94 [C <sub>7</sub> H <sub>10</sub> ] <sup>+</sup> (58), 93 [C <sub>7</sub> H <sub>9</sub> ] <sup>+</sup> (18), 91 [C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup> (72), 79 [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> (27.0), 77 [C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> (98), 67 [C <sub>5</sub> H <sub>7</sub> ] <sup>+</sup> (63.0), 66 [C <sub>5</sub> H <sub>6</sub> ] <sup>+</sup> (41.0), 41 [C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup> (21.0).   |

Table 1. (Contd.)

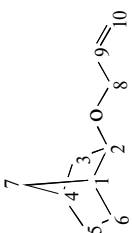
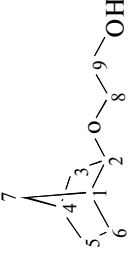
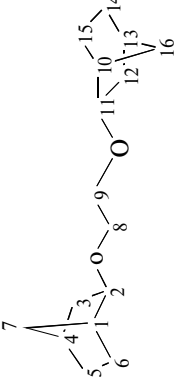
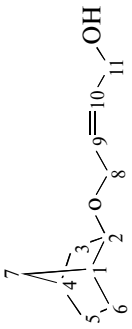
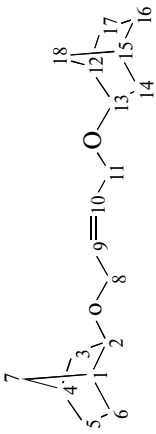
| Compound, $T_{bp}$ , °C (P, mm Hg)  | NMR (CDCl <sub>3</sub> , δ, ppm)  | Mass spectrum, $m/z$ ( $I_{rel.}$ , %)   |
|---|---|--|
| <p><i>exo</i>-2-Aallyloxybicyclo[2.2.1]heptane (<b>21</b>)</p>  <p><math>T_{bp}</math> 78°C (10 mm Hg); <math>n_D^{20} = 1.472</math></p>    | <p><sup>1</sup>H NMR: 0.95–1.12 (m, 3H, C<sup>6</sup>H<sub>a</sub>, C<sup>6</sup>H<sub>b</sub>, C<sup>3</sup>H<sub>a</sub>), 1.37–1.60 (m, 5H, C<sup>3</sup>H<sub>b</sub>, C<sup>7</sup>H<sub>a</sub>, C<sup>7</sup>H<sub>b</sub>, C<sup>4</sup>H<sub>a</sub>, C<sup>4</sup>H<sub>b</sub>), 2.25 (s, 1H, C<sup>2</sup>H), 2.30 (m, 1H, C<sup>1</sup>H), 2.33 (d, 1H, C<sup>5</sup>H), 3.89–4.00 (m, 2H, C<sup>8</sup>H<sub>a</sub>, C<sup>8</sup>H<sub>b</sub>), 5.10–5.18 (d, 1H, C<sup>10</sup>H<sub>a</sub>, <sup>2</sup>J = 1.6, <sup>3</sup>J = 10.4), 5.22–5.32 (d, 1H, C<sup>10</sup>H<sub>b</sub>, <sup>2</sup>J = 1.6, <sup>3</sup>J = 17.2).<br/> <sup>13</sup>C NMR: 24.40 C<sup>6</sup>, 28.10 C<sup>5</sup>, 35.16 C<sup>7</sup>, 35.41 C<sup>4</sup>, 40.38 C<sup>3</sup>, 42.36 C<sup>1</sup>, 69.20 C<sup>8</sup>, 82.14 C<sup>2</sup>, 116.27 C<sup>10</sup>, 135.47 C<sup>9</sup>.</p>  | <p>152 M<sup>+</sup>• (1), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (41.0), 94 [C<sub>7</sub>H<sub>10</sub>]<sup>+</sup>• (51), 93 [C<sub>7</sub>H<sub>9</sub>]<sup>+</sup> (23), 91 [C<sub>7</sub>H<sub>7</sub>]<sup>+</sup> (11), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (29.0), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (11), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (100.0), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup>• (34.0), 55 [C<sub>3</sub>H<sub>3</sub>O]<sup>+</sup> (27.0), 41 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (56.0).<br/> <math>I_K = 1101</math>.</p>   |
| <p><i>exo</i>-2-Bicyclo[2.2.1]heptyl-2-oxyethanol (<b>22</b>)</p>  <p><math>T_{bp}</math> 130°C (4 mm Hg); <math>n_D^{20} = 1.416</math></p> | <p><sup>1</sup>H NMR: 0.95–1.10 (m, 3H, C<sup>3</sup>H<sub>a</sub>, C<sup>3</sup>H<sub>b</sub>, C<sup>6</sup>H<sub>a</sub>), 1.38–1.59 (m, 5H, C<sup>6</sup>H<sub>b</sub>, C<sup>5</sup>H<sub>a</sub>, C<sup>5</sup>H<sub>b</sub>, C<sup>7</sup>H<sub>a</sub>, C<sup>7</sup>H<sub>b</sub>), 2.23 (m, 1H, C<sup>1</sup>H), 2.33 (m, 1H, C<sup>4</sup>H), 2.55 (1H, OH), 3.39 (d, 1H, C<sup>2</sup>H), 3.49–3.57 (m, 2H, C<sup>9</sup>H<sub>a</sub>, C<sup>9</sup>H<sub>b</sub>), 3.70–3.77 (m, 2H, C<sup>8</sup>H<sub>a</sub>, C<sup>8</sup>H<sub>b</sub>). <sup>13</sup>C NMR: 24.61 C<sup>6</sup>, 28.55 C<sup>5</sup>, 34.77 C<sup>7</sup>, 35.17 C<sup>4</sup>, 39.56 C<sup>3</sup>, 40.36 C<sup>1</sup>, 63.71 C<sup>9</sup>, 67.66 C<sup>8</sup>, 83.0 C<sup>2</sup>.</p>  | <p>156 M<sup>+</sup>• (2), 155 [M–H]<sup>+</sup> (19), 111 [C<sub>7</sub>H<sub>11</sub>O]<sup>+</sup> (18), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (100), 94 [C<sub>7</sub>H<sub>10</sub>]<sup>+</sup>• (16), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (49), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup>• (15), 41 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (15).<br/> <math>I_K = 1834</math>.</p>   |
| <p><i>exo</i>-2,2'-[Ethane-1,2-diyilbis(oxy)]bicyclo[2.2.1]heptane (<b>23</b>)</p>  <p><math>T_{bp}</math> 158°C (2 mm Hg)</p>             | <p><sup>1</sup>H NMR: 0.86–1.26 (m, 8H, C<sup>3</sup>H<sub>a</sub>, C<sup>3</sup>H<sub>b</sub>, C<sup>12</sup>H<sub>a</sub>, C<sup>12</sup>H<sub>b</sub>, C<sup>6</sup>H<sub>a</sub>, C<sup>6</sup>H<sub>b</sub>, C<sup>15</sup>H<sub>a</sub>, C<sup>15</sup>H<sub>b</sub>), 1.32–1.40 (m, 8H, C<sup>5</sup>H<sub>b</sub>, C<sup>14</sup>H<sub>b</sub>, C<sup>7</sup>H<sub>b</sub>, C<sup>16</sup>H<sub>b</sub>), 1.55–1.58 (m, 2H, C<sup>7</sup>H<sub>a</sub>, C<sup>16</sup>H<sub>a</sub>), 1.63 (m, 1H, C<sup>1</sup>H), 1.73 (m, 2H, C<sup>3</sup>H<sub>a</sub>, C<sup>14</sup>H<sub>a</sub>), 2.04 (m, 2H, C<sup>4</sup>H, C<sup>13</sup>H), 3.20 (m, 2H, C<sup>10</sup>H<sub>a</sub>, C<sup>10</sup>H<sub>b</sub>), 3.42 (m, 2H, C<sup>11</sup>H<sub>a</sub>, C<sup>11</sup>H<sub>b</sub>), 3.57 (d, 1H, C<sup>2</sup>H). <sup>13</sup>C NMR: 24.60 C<sup>6,15</sup>, 28.52 C<sup>5,14</sup>, 34.71 C<sup>7,16</sup>, 35.18 C<sup>4,13</sup>, 39.54 C<sup>3,12</sup>, 40.32 C<sup>1,10</sup>, 63.72 C<sup>8,9</sup>, 83.5 C<sup>2,11</sup>.</p> | <p>250 M<sup>+</sup>• (1), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (100), 94 [C<sub>7</sub>H<sub>10</sub>]<sup>+</sup>• (95), 83 [C<sub>6</sub>H<sub>11</sub>]<sup>+</sup> (17), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (77), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (13), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (52), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup>• (87), 65 [C<sub>5</sub>H<sub>5</sub>]<sup>+</sup> (13), 57 [C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> (18.0), 55 [C<sub>4</sub>H<sub>7</sub>]<sup>+</sup> (19.0), 45 [C<sub>3</sub>H<sub>5</sub>O]<sup>+</sup> (47), 44 [C<sub>2</sub>H<sub>4</sub>O]<sup>+</sup>• (16), 43 [C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> (14), 41 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (33). <math>I_K = 1229</math>.</p> |

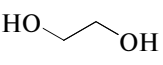
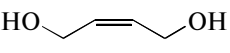
Table 1. (Contd.)

| Compound, $T_{bp}$ , °C (p, mm Hg)   | NMR (CDCl <sub>3</sub> , δ, ppm)   | Mass spectrum, $m/z$ ( $I_{rel}$ , %)  |
|--|--|--|
| <p><i>exo</i>-4-Bicyclo[2.2.1]hept-2-yloxybut-2-en-1-ol (<b>24</b>)</p>  <p><math>T_{bp}</math> 141 °C (2 mm Hg); <math>n_D^{20}</math> = 1.492</p> | <p><sup>1</sup>H NMR: 0.95–1.03 (m, 2H, C<sup>6</sup>H<sub>b</sub>, C<sup>3</sup>H<sub>a</sub>), 1.03–1.14 (m, 2H, C<sup>6</sup>H<sub>a</sub>, C<sup>3</sup>H<sub>b</sub>), 1.37–1.48 (m, 1H, C<sup>5</sup>H<sub>b</sub>), 1.50–1.60 (m, 1H, C<sup>5</sup>H<sub>a</sub>), 2.17 (s, 1H, C<sup>1</sup>H), 2.25 (s, 1H, -OH), 2.34 (d, 1H, C<sup>4</sup>H), 3.40 (d, 1H, C<sup>2</sup>H), 3.95–4.09 (m, 1H, C<sup>8</sup>H<sub>a</sub>), 4.19 (m, 1H, C<sup>8</sup>H<sub>b</sub>), <math>^2J</math> = 6.4, <math>^3J</math> = 18.8), 4.22 (d, 2H, C<sup>11</sup>H<sub>a</sub>, C<sup>11</sup>H<sub>b</sub>), <math>^2J</math> = 4.4–<math>^3J</math> = 16.8), 5.67–5.75 (m, 1H, C<sup>9</sup>H), 5.76–5.85 (m, 1H, C<sup>10</sup>H). <sup>13</sup>C NMR: 24.58 C<sup>6</sup>, 28.40 C<sup>5</sup>, 35.14 C<sup>4</sup>, 39.51 C<sup>3</sup>, 40.28 C<sup>1</sup>, 58.53 C<sup>11</sup>, 64.03 C<sup>8</sup>, 82.67 C<sup>2</sup>, 128.82 C<sup>10</sup>, 131.82 C<sup>9</sup>.</p>  | <p>182 M<sup>+</sup> (2), 164 [M–H<sub>2</sub>O]<sup>+</sup> (7), 138 [M–H<sub>2</sub>O–C<sub>2</sub>H<sub>2</sub>]<sup>+</sup> (12), 109 [C<sub>7</sub>H<sub>9</sub>O]<sup>+</sup> (12), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (100), 94 [C<sub>7</sub>H<sub>10</sub>]<sup>+</sup> (22), 79 [C<sub>6</sub>H<sub>7</sub>]<sup>+</sup> (46), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (10), 71 [C<sub>5</sub>H<sub>11</sub>]<sup>+</sup> (17), 70 [C<sub>5</sub>H<sub>10</sub>]<sup>+</sup> (27), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (90), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup> (40), 57 [C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> (10), 55 [C<sub>4</sub>H<sub>7</sub>]<sup>+</sup> (27), 53 [C<sub>4</sub>H<sub>5</sub>]<sup>+</sup> (18), 43 [C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> (40).</p> |
| <p><i>exo,exo</i>-[(2<i>Z</i>)-but-2-ene-1,4-diy]bis(oxy)]bicyclo[2.2.1]heptane (<b>25</b>)</p>  <p><math>T_{bp}</math> 183 °C (2 mm Hg)</p>      | <p><sup>1</sup>H NMR: 0.97–1.12 (m, 6H, C<sup>6</sup>H<sub>a</sub>, C<sup>14</sup>H<sub>a</sub>, C<sup>5</sup>H<sub>a</sub>, C<sup>17</sup>H<sub>a</sub>, C<sup>7</sup>H<sub>a</sub>, C<sup>18</sup>H<sub>a</sub>), 1.34–1.48 (m, 6H, C<sup>3</sup>H<sub>a</sub>, C<sup>14</sup>H<sub>b</sub>, C<sup>5</sup>H<sub>b</sub>, C<sup>16</sup>H<sub>b</sub>, C<sup>6</sup>H<sub>b</sub>, C<sup>17</sup>H<sub>b</sub>), 1.49–1.58 (m, 4H, C<sup>7</sup>H<sub>b</sub>, C<sup>18</sup>H<sub>b</sub>, C<sup>3</sup>H<sub>b</sub>, C<sup>14</sup>H<sub>b</sub>), 2.23 (c, 2H, C<sup>4</sup>H, C<sup>15</sup>H), 2.30–2.34 (d, 2H, C<sup>1</sup>H, C<sup>12</sup>H), 3.35–3.40 (d, 2H, C<sup>2</sup>H, C<sup>13</sup>H), 3.95–4.05 (m, 2H, C<sup>8</sup>H<sub>a</sub>, C<sup>8</sup>H<sub>b</sub>), 4.09 (d, 1H, C<sup>11</sup>H<sub>a</sub>), 4.19 (d, 1H, C<sup>11</sup>H<sub>b</sub>), 5.63–5.74 (m, 1H, C<sup>10</sup>H), 5.75–5.88 (m, 1H, C<sup>9</sup>H). <sup>13</sup>C NMR: 23.75 C<sup>6</sup>, 27.62 C<sup>5</sup>, 33.93 C<sup>7</sup>, 34.27 C<sup>4</sup>, 38.71 C<sup>3</sup>, 39.42 C<sup>1</sup>, 57.54 C<sup>11</sup>, 63.04 C<sup>8</sup>, 81.25 C<sup>2</sup>, 129.41 C<sup>10</sup>, 131.96 C<sup>9</sup>.</p> | <p>276 M<sup>+</sup> (1), 164 [M–C<sub>7</sub>H<sub>11</sub>–H<sub>2</sub>O]<sup>+</sup> (6), 95 [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> (100), 93 [C<sub>7</sub>H<sub>9</sub>]<sup>+</sup> (6), 79 (6), 7yc0 [C<sub>5</sub>H<sub>10</sub>]<sup>+</sup> (10), 67 [C<sub>5</sub>H<sub>7</sub>]<sup>+</sup> (42), 66 [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup> (82.0), 41 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (13).</p>  |

**Table 2.** Reaction of norbornene **1** with monohydric alcohols **2–10** in the presence of H-Beta zeolite (20 wt % H-Beta catalyst, 5 h)

| Run no. | ROH            | T, °C | 1 : ROH molar ratio | Conversion of 1, % | Selectivity, % |               |     |                 |
|---------|----------------|-------|---------------------|--------------------|----------------|---------------|-----|-----------------|
|         |                |       |                     |                    | ether          |               | NTC | dimers <b>1</b> |
|         |                |       |                     |                    | <i>exo</i> -   | <i>endo</i> - |     |                 |
| 1       | MeOH           | 80    | 1 : 3               | 96                 | 84             | —             | 12  | 4               |
| 2       | EtOH           | 80    | 1 : 3               | 93                 | 92             | —             | 8   | —               |
| 3       | <i>n</i> -PrOH | 80    | 1 : 3               | 88                 | 87             | —             | 13  | —               |
| 4       | <i>n</i> -BuOH | 50    | 1 : 3               | 70                 | 98             | —             | 2   | —               |
| 5       | <i>n</i> -BuOH | 80    | 1 : 3               | 96                 | 93             | —             | 7   | —               |
| 6       | <i>n</i> -BuOH | 80    | 1 : 3               | 98                 | 77             | —             | 17  | 6               |
| 7       | <i>n</i> -AmOH | 80    | 1 : 3               | 93                 | 77             | 9             | 14  | —               |
| 8       | <i>n</i> -HeOH | 80    | 1 : 3               | 95                 | 74             | 18            | 8   | —               |
| 9       | <i>n</i> -HpOH | 80    | 1 : 3               | 99                 | 63             | 27            | 10  | —               |
| 10      | <i>n</i> -BnOH | 80    | 1 : 3               | 99                 | 95             | —             | 5   | —               |
| 11      | AlOH           | 50    | 1 : 3               | 78                 | 90             | —             | 8   | 2               |

**Table 3.** Reaction of norbornene with diols in the presence of H-Beta zeolite (of norbornene : diol molar ratio = A : B, 20 wt % catalyst, 5 h)

| Diol   | A : B | T, °C | Conversion of 1, % | Selectivity, % |         |     |        |
|--|-------|-------|--------------------|----------------|---------|-----|--------|
|  |       |       |                    | monoether      | diether | NTC | dimers |
| <br><b>11</b>  | 1 : 3 | 50    | 80                 | 92             | 4       | 2   | 2      |
|  |       | 60    | 88                 | 84             | 12      | 1   | 3      |
|  |       | 80    | 92                 | 58             | 32      | 3   | 7      |
| <br><b>12</b> | 3 : 1 | 80    | 78*                | 25             | 68      | 2   | 5      |
|  |       | 1 : 1 | 90                 | 46             | 41      | 5   | 8      |
|  |       | 1 : 3 | 91                 | 60             | 30      | 2.5 | 7.5    |

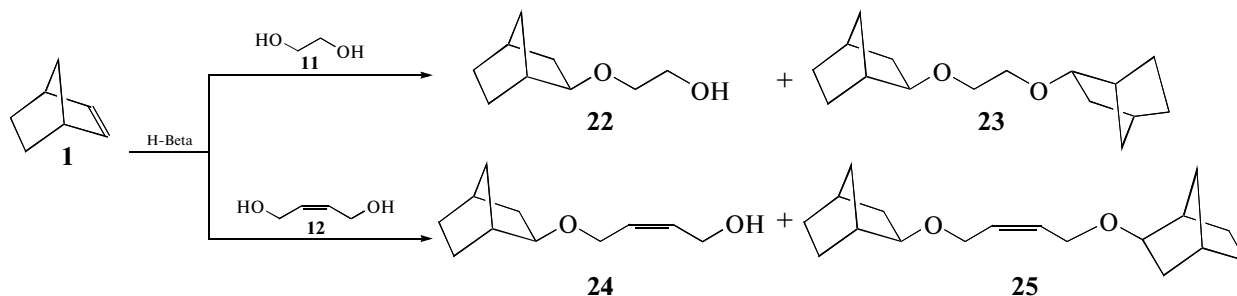
\* Diol conversion.

ration of the ethers, since the signals of the *endo*-isomers are in a weaker field (~40 ppm) [23].

As direct evidence for the stereo configuration of alkoxy-norbornanes, we used NOESY data. For example, the NOESY spectrum of *exo*-methoxynorbornane **13** exhibits cross peaks between the protons of the C-6 and C-2 atoms. These protons cannot approach each other in space unless the substituent is in the *exo*-position on the norbornene cage. The NOESY spectra of

amiloxy-, hexoxy-, and heptoxynorbornanes, which are mixtures of the *exo*- and *endo*-isomers, display proton coupling of the C-2 and C-7 atoms in addition to these cross peaks for the *exo*-isomers.

The reaction of norbornene with diol (ethylene glycol **11** or 2-butene-1,4-diol **12**) mediated by the H-Beta zeolite catalyst sequentially gives monoether **22** or **24** and diether **23** or **25**, respectively:





The reactions proceed to a high conversion of norbornene and quite selectively (Table 3).

The reaction of norbornene with ethylene glycol as an example in the presence of H-Beta zeolite showed that the yield of the diether increases with the increasing temperature. Thus, the amount of diether **23** in the products of the reaction at 50°C is about 5% (Table 3), whereas it is formed in an amount comparable to that of monoether **22** at 80°C. The total selectivity for ethers **23** and **25** decreases with the increasing temperature, since the amount of the byproducts nortricyclane (NTC) and norbornene dimers grows.

Variation of the norbornene : diol molar ratio from 1 : 3 to 3 : 1 in the reaction of norbornene with 2-butene-1,4-diol results in an increase in the proportion of diether **25** in the products (Table 3).

In summary, the data obtained in the study show a high efficiency of the H-Beta zeolite catalyst in reactions of the direct hydroalkoxylation of norbornene.

In the reaction of norbornene with monohydric alcohols, H-Beta zeolite does not rank below homogeneous catalytic systems based on trifluoromethanesulfonic acid in activity and selectivity and is even superior to them in the case of saturated aliphatic alcohols. The conversion of norbornene in the reaction with saturated and unsaturated aliphatic and aromatic monohydric alcohols is 78–98%, and the selectivity for alkoxynorbornanes reaches 98%.

The products of the norbornene reactions with diols in the presence of H-Beta zeolite are mono- and diethers, whose yield and ratio can be controlled by varying the reaction parameters.

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