

# Reactions of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane with Aliphatic Alcohols under the Action of Ionic Liquids <sup>†</sup>

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**Abstract:** It has been established for the first time that ionic liquids catalyze the alcoholysis of a hydrogenated norbornadiene dimer—*exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane with aliphatic C<sub>1</sub>–C<sub>4</sub> alcohols. The reaction proceeds along the hydrocarbon cyclopropane ring by regioselective C<sup>4</sup>–C<sup>5</sup> bond cleavage to form previously undescribed 4-*exo*-alkoxy-pentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecanes in high yields, promising as precursors for the synthesis of drugs, as well as in the role of transmission media.

**Keywords:** alcoholysis; norbornadiene dimer; alcohols; ionic liquids

## 1. Introduction

Despite the existence of a wide range of known catalysts, chemical engineering and organic synthesis is constantly in need of new, more efficient and environmentally acceptable catalysts and reaction media. Ionic liquids (ILs) meet these requirements. For example, ILs based on aluminum, iron, and other metal halides are an alternative to traditional catalysts, in particular, they catalyze Friedel-Crafts alkylation and acylation reactions, hydrogenation, and isomerization of alkanes and polycyclic hydrocarbons [1–16].

On the other hand, the chemistry of small cycles is an intensively developing branch of organic chemistry. Three-carbon rings are unique fragments that, due to their significant stress, are capable of unusual structural transformations with expansion and rearrangement of the small ring.

The reactions of cyclopropane compounds have been actively studied for more than three decades. In the world literature, there are very few examples of works on the functionalization of highly stressed cyclopropane-containing polycyclic hydrocarbons, the reaction products of which can be widely used as precursors for the synthesis of drugs and also as transmission media and working fluids. In addition, the analysis of literature data showed that ring-opening reactions of cyclopropanes are catalyzed mainly by transition metal complexes and there are no examples of the use of ILs as catalysts or their transformations.

In this work, we have developed new methods for the synthesis of previously undescribed 4-*exo*-alkoxy-pentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecanes **1–4** by the reaction of a saturated dimer of norbornadiene—*exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5** with aliphatic alcohols C<sub>1</sub>–C<sub>4</sub> under the action of ILs.

## 2. Experimental Section

### 2.1. General Procedures and Materials

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-II 400 Ascend instrument (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C in CDCl<sub>3</sub>) and Bruker Avance-III HD 500 Ascend instrument (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C in CDCl<sub>3</sub>). Mass spectra were run on a

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Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m × 0.25 mm, helium as the carrier gas, temperature programming from 40 to 300 °C at 8 °C/min, evaporation temperature of 280 °C, ion source temperature of 200 °C, and ionization energy of 70 eV). The elemental composition of the samples was determined on a Carlo Erba 1106 elemental analyzer. The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a Shimadzu GC-9A, GC-2014 instrument [2 m × 3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270 °C at 8 °C/min, helium as the carrier gas (47 mL/min)].

Norbornadiene dimer (*exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradec-12-ene) was prepared as described in ref. [17], then hydrogenated with hydrogen (1 atm) in the presence of a Pd-C catalyst (10%) to obtain *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5**. Aliphatic alcohols (methanol, ethanol, *n*-propanol, *n*-butanol), AlCl<sub>3</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, SnCl<sub>2</sub>, CuCl<sub>2</sub> (Acros), Me<sub>3</sub>N-HCl, Et<sub>3</sub>N-HCl, EMIM-Cl и BMIM-Cl (Aldrich) were commercial reagents.

## 2.2. Preparation of Ionic Liquids

The ionic liquids were prepared by the reaction of AlCl<sub>3</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, or SnCl<sub>2</sub> with Me<sub>3</sub>N-HCl, Et<sub>3</sub>N-HCl, EMIM-Cl, or BMIM-Cl. Me<sub>3</sub>N-HCl, Et<sub>3</sub>N-HCl, EMIM-Cl, or BMIM-Cl (10 mmol) and a metal (Al (III), Fe (III), Zn (II), Sn (II)) chloride (10–30 mmol) were charged into a glass reactor (V = 50 mL) under argon. The reaction was conducted with continuous stirring at 70–80 °C for 3 h.

## 2.3. General Procedure for the Preparation of 4-*exo*-alkoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecanes

1 mmol of IL, 10 mmol of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane, 30 mmol of aliphatic alcohol ROH (where, R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>) were loaded into an ampoule under argon. The reaction was carried out with stirring at 120 °C for 8 h. After the completion of the reaction, the autoclave was cooled to room temperature, the ampoule was opened, the reaction mixture was filtered through a layer of aluminum oxide (eluent – petroleum ether). The solvent was distilled off on a rotary evaporator. The products were isolated by column chromatography (silica gel from Acros (0.060–0.200 mm), eluent – petroleum ether: ethyl acetate = 10:1).

*4-exo-Methoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 1*. Colorless oil, yield 88%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.21–1.25 (m, 1H), 1.26–1.28 (m, 1H), 1.35–1.39 (m, 2H), 1.40–1.43 (m, 4H), 1.48–1.53 (m, 4H), 1.71–1.76 (m, 1H), 1.86–1.90 (m, 2H), 2.09–2.15 (m, 2H), 2.82 (d, 1H, *J* = 4.4 Hz), 3.30 (s, 3H), 3.69–3.71 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.42, 25.52, 25.57, 25.93, 36.14, 39.85, 40.81, 41.13, 41.81, 43.62, 46.52, 49.37, 52.73, 57.72, 85.03. EIMS (70 eV, *m/z*): 218 [M]<sup>+</sup>. Anal. calcd. for C<sub>15</sub>H<sub>22</sub>O: C, 83.52; H, 10.16; found: C, 83.59; H, 10.24.

*4-exo-Ethoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 2*. Colorless oil, yield 89%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.09–1.13 (m, 1H), 1.23–1.25 (m, 1H), 1.26–1.29 (m, 2H) 1.33–1.38 (m, 2H), 1.40–1.43 (m, 4H), 1.46–1.51 (m, 6H), 1.69–1.73 (m, 1H), 1.87–1.91 (m, 2H), 2.10–2.17 (m, 1H), 2.82 (d, 1H, *J* = 12 Hz), 3.35–3.39 (m, 2H), 3.85–3.88 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 15.51, 24.52, 25.62, 25.67, 29.12, 34.82, 36.14, 39.85, 40.81, 41.13, 41.81, 43.62, 46.52, 49.37, 66.72, 82.91. EIMS (70 eV, *m/z*): 232 [M]<sup>+</sup>. Anal. calcd. for C<sub>16</sub>H<sub>24</sub>O: C, 82.70; H, 10.41; found: C, 82.79; H, 10.47.

*4-exo-Propoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 3*. Colorless oil, yield 88%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.90–1.11 (m, 1H), 1.21–1.26 (m, 2H), 1.25–1.29 (m, 2H) 1.32–1.37 (m, 2H), 1.40–1.45 (m, 4H), 1.46–1.51 (m, 6H), 1.67–1.71 (m, 2H), 1.87–1.91 (m, 2H), 2.11–2.15 (m, 1H), 2.82 (d, 1H, *J* = 12 Hz), 3.17–3.37 (m, 2H), 3.78–3.81 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 10.42, 23.32, 24.53, 25.62, 25.69, 25.93, 29.01, 39.85, 40.83, 41.15, 41.78, 43.64,

46.55, 49.31, 52.71, 74.63, 82.98. EIMS (70 eV,  $m/z$ ): 247  $[M]^+$ . Anal. calcd. for  $C_{17}H_{26}O$ : C, 83.27; H, 11.18; found: C, 83.32; H, 11.23.

*4-exo-Butoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 4*. Colorless oil, yield 87%;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.87–0.94 (m, 1H), 1.21–1.24 (m, 2H), 1.25–1.29 (m, 4H) 1.34–1.37 (m, 2H), 1.39–1.43 (m, 4H), 1.44–1.51 (m, 5H), 1.72–1.76 (m, 2H), 1.86–1.91 (m, 2H), 2.10–2.14 (m, 2H), 2.85 (d, 1H,  $J = 8.8$  Hz), 3.56–3.66 (m, 2H), 3.79–3.80 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  14.12, 19.20, 24.53, 25.62, 25.69, 29.01, 31.64, 32.53, 34.86, 36.37, 39.85, 42.08, 43.64, 46.55, 49.31, 52.71, 70.23, 89.98. EIMS (70 eV,  $m/z$ ): 260  $[M]^+$ . Anal. calcd. for  $C_{18}H_{28}O$ : C, 83.38; H, 11.33; found: C, 83.42; H, 11.39.

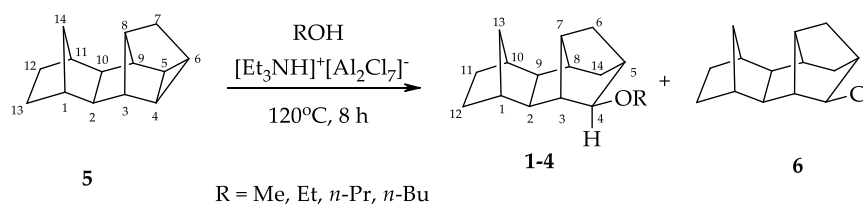
*4-exo-Chloropentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 6*. Colorless oil, yield 44%;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.73–0.08 (m, 2H), 1.09–1.13 (m, 2H), 1.24–1.37 (m, 4H) 1.47–1.61 (m, 4H), 1.83–1.87 (m, 2H), 1.94–2.02 (m, 2H), 2.08–2.14 (m, 2H), 3.94 (s, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  23.15, 25.66, 33.95, 37.85, 38.26, 38.61, 38.80, 39.83, 41.57, 43.45, 43.88, 45.81, 46.78, 65.22. EIMS (70 eV,  $m/z$ ): 222  $[M]^+$ . Anal. calcd. for  $C_{14}H_{19}Cl$ : C, 75.49; H, 8.60; found: C, 76.01; H, 7.88.

### 3. Results and Discussion

Previously, we found that inorganic ionic liquids actively catalyze reactions from the heptacyclic dimer of norbornadiene (NBD), *endo-endo*-heptacyclo[8.4.0.0<sup>2,12</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>.0<sup>11,13</sup>]tetradecane (binor-S), with primary and secondary alcohols and  $\alpha,\omega$ -diols with the formation of 10-*exo*-alkoxyhexacyclo[9.2.1.0<sup>2,7</sup>.0<sup>3,5</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tetradecanes in 85–90% yields [18,19].

Continuing research in this direction, in this work we studied the reaction of another saturated cyclopropane-containing NBD dimer—*exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane with alcohols (methanol, ethanol, *n*-propanol and *n*-butanol) under the action of ionic liquids containing Al (III), Fe (III), Ni (II), Zn (II), Mn (II), Sn (II) and Cu (II) chlorides. Based on a series of experiments, it was established that the best catalyst for the alcoholysis of a hydrocarbon **5** with alcohols is aluminate IL— $[Et_3NH]^+[Al_2Cl_7]^-$ .

It has been experimentally established that the reaction of hydrocarbon **5** with alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol) under the action of the ionic liquid  $[Et_3NH]^+[Al_2Cl_7]^-$  leads to the formation of 4-*exo*-alkoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecanes **1-4** in 87–89% yields.



**Figure 1.** Reactions of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5** with aliphatic alcohols under the action of ionic liquids.

Under the developed conditions: 120 °C, 8 h, at a molar ratio of  $[5]:[ROH]:[IL]=[1\div 30]:[3\div 90]:[1]$ , alcoholysis proceeds by opening the C<sup>4</sup>-C<sup>5</sup> bond of the cyclopropane ring of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5**. In all experiments, the formation of 4-*exo*-chloropentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecanes **6**, the product of the reaction of hydrocarbon **5** with HCl, which is part of the catalyst, was observed.

**Table 1.** Alcoholysis of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5** with alcohols under the action of ionic liquid [Et<sub>3</sub>NH]<sup>+</sup>[Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup>.

ROH	Ratio 5:IL	Yield, %	
		1–4	6
MeOH	1:1	33	44
EtOH	1:1	36	42
<i>n</i> -PrOH	1:1	32	39
<i>n</i> -BuOH	1:1	29	38
MeOH	5:1	49	31
EtOH	5:1	51	27
<i>n</i> -PrOH	5:1	50	26
<i>n</i> -BuOH	5:1	49	23
MeOH	10:1	88	12
EtOH	10:1	89	11
<i>n</i> -PrOH	10:1	88	12
<i>n</i> -BuOH	10:1	87	13
MeOH	30:1	36	10
EtOH	30:1	39	12
<i>n</i> -PrOH	30:1	33	9
<i>n</i> -BuOH	30:1	31	7

<sup>1</sup> Reaction conditions: 120 °C, 8 h.

It should be noted that the maximum conversion of hydrocarbon **5** was observed at the ratio [5]:[IL] = 10:1. With an increase in the concentration of the ionic liquid (1÷5:1), the yield of chlorine derivative **6** increases, and with a decrease in the concentration of IL (30:1), the conversion of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5** decreases to 38–46%.

Compounds **1-4** were isolated individually by column chromatography on SiO<sub>2</sub> (eluent—petroleum ether: ethyl acetate = 10:1), the structure of esters **1-4** was proved on the basis of <sup>1</sup>H and <sup>13</sup>C NMR spectra. Thus, in the <sup>1</sup>H NMR spectra of esters **2-4** there are characteristic signals at 3.17–3.66 ppm, belonging to the –O–CH<sub>2</sub>– group protons. And the protons of the –CH–O– group resonate at 3.79–3.88 ppm. Signals at 3.30 ppm and 3.69–3.71 ppm belongs to the –OCH<sub>3</sub> and –CH–O– groups, respectively, of compound **1**.

In the <sup>13</sup>C NMR spectra of compounds **1-4**, there are characteristic signals of the C<sup>4</sup>-carbon atom at 82.91–89.98 ppm, as well as signals of carbon atoms –O–C<sub>H</sub>– (57.72 ppm) and –O–C<sub>H</sub>– (66.72–74.63 ppm).

Considering the formation of chlorine derivative **6**, it can be assumed that esters **1-4** are secondary products, i.e., at first stage, hydrocarbon **5** reacts with HCl to give chloride **6**, which undergoes alcoholysis. To verify this assumption, experiments were carried out with known 4-*exo*-chloropentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane **6** with alcohols in the presence and absence of IL. The attempts were unsuccessful: the alcohols and the chlorine derivative **6** returned unchanged from the reaction.

#### 4. Conclusions

Thus, it was found that the ionic liquid [Et<sub>3</sub>NH]<sup>+</sup>[Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> is an effective catalyst for the reaction of *exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5** with aliphatic alcohols. The reaction proceeds with selective cleavage of the cyclopropane ring at the C<sup>4</sup>-C<sup>5</sup> bond in the molecule of the hydrogenated *exo-exo*-dimer of norbornadiene **5** with the formation of 4-*exo*-alkoxy-pentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecanes **1-4** in 80–89% yields.

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