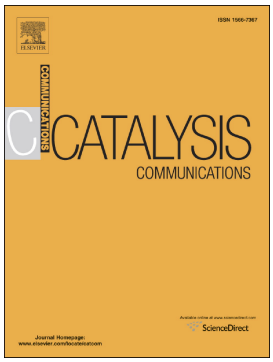

Hydroisomerization of hexacyclo[9.2.1.02,10.03,8.04,6.05,9]tetradecanes to diamantane induced by ionic liquids

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Hydroisomerization of hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecanes to diamantane induced by ionic liquids

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A B S T R A C T

Hydroisomerization of endo-endo-, exo-exo-, exo-endo-, and endo-exo-, hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecanes to diamantane was performed for the first time in 80-96% yields under the action of ionic liquids (ILs), $[Et_3NH]^+[Al_2Cl_7]^-$ and $[BMIM]^+[Fe_2Cl_7]^-$. Ionic liquids have multiple functions, promoting the following reactions of hexacyclotetradecanes: hydrogenation, dehydrogenation, and skeletal rearrangement; simultaneously, they serve as HCl donors.

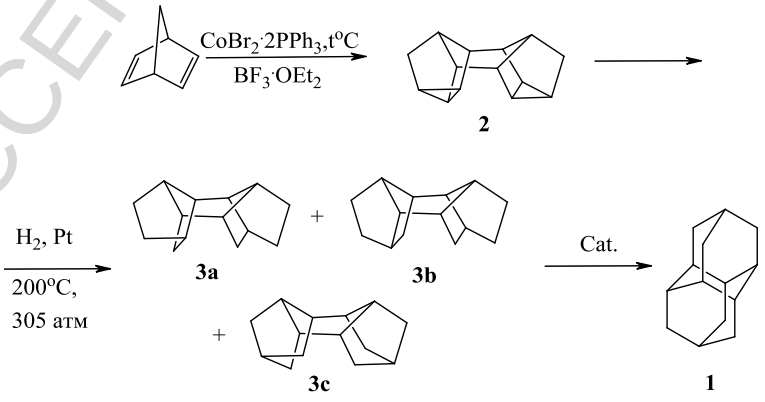
Keywords: diamantane, ionic liquid, hydroisomerization [4+4]-dimers of norbornadiene

1. Introduction

Diamondoids (adamantane, diamantane, triamantane) represent a separate class of hydrocarbons possessing a unique structure and unusual properties. Adamantane derivatives have found application as antiviral and anti-Parkinson drugs [1-5] and in the manufacture of light- and heat-resistant polymers [6-8].

The second representative of the diamondoid homologous series, diamantane (pentacyclo[7.3.1.$1^{4,12}$.$0^{2,7}$.$0^{6,11}$]tetradecane) **1**, is the raw material for the synthesis of heat-resistant synthetic lubricating oils and transmission fluids. It is promising for the preparation of pharmaceuticals and solvent-resistant polymeric materials and rubbers [9-13].

The known synthetic routes to diamantane **1** are based on the skeletal rearrangement of strained, thermodynamically less stable polycyclic hydrocarbons $C_{14}H_{20}$ [14-18]. In particular, the [4+4]-dimer of norbornadiene (NBD), heptacyclo[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecane **2** (binor-S), is the most convenient starting compound for the preparative synthesis of diamantane **1**. Hydrocarbon **2**, which has the composition $C_{14}H_{16}$, is converted to the precursor of diamantane **1** by hydrogenation under drastic conditions (200°C and 305 atm of H_2) in the presence of a platinum catalyst (H_2PtCl_6 or PtO_2) in glacial acetic acid. The hydrogenation of **2** is accompanied by cyclopropane ring opening giving rise to a mixture of three $C_{14}H_{20}$ hydrocarbons **3a-c** [19, 20]. According to published data, $C_{14}H_{20}$ hydrocarbons **3a-c** isomerize in the presence of superacid catalysts such as $B(OSO_2CF_3)_3$, CF3SO_3H-SbF_5 (1:1), CF_3SO_3H-$B(OSO_2CF_3)_3$ (1:1) [21], $NaBH_4$/CF_3SO_3H [22], or zeolite Y in the NaH form [23] to give diamantane in a yield of up to 99% (Scheme 1).



Scheme 1. Isomerization of **3a-c** to diamantane.

At the end of the 20th century, inorganic ionic liquids (ILs) started to be used in the synthetic practice. Ionic liquids are unique objects for chemical research; they are widely employed in catalysis and organic synthesis. Inorganic ionic liquids are known to possess Brønsted or Lewis acidity or superacidity. In

particular, superacid properties are inherent in melts containing $AlCl_3$, which makes them attractive for catalysis [24-27]. According to the works [28–30], the ionic liquid $[Et_3NH]^+[Al_2Cl_7]^-$ is characterized by high catalytic activity in the skeletal isomerization of cyclohexane to methylcyclopentane and polycyclic hydrocarbons of composition $C_{12\text{-}15}H_{18\text{-}22}$ to derivatives of adamantane and diamantane.

2. Experimental

2.1. General procedures and materials

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-III 400 Ascend instrument (400 MHz for ^1H and 100 MHz for ^{13}C in $CDCl_3$). Mass spectra were run on a 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)].

*2.2. General procedure for the preparation of saturated polycyclic hydrocarbons **4-7**.*

A glass reactor was charged with the Pd/C catalyst (0.5 g) and hydrocarbon (5 g) dissolved in hexane (15 mL). Hydrogenation of norbornadiene dimers was carried out at room temperature (1 atm H_2). After completion of the reaction, the reaction mixture was filtered through a silica gel layer (elution with hexane).

2.3. Preparation of the ionic liquids

The ionic liquids were prepared by direct reactions of metal halides with $[Et_3NH]^+Cl^-$, $[Et_3DH]^+Cl^-$, EMIM-Cl, or $BMIM^-Cl$.

A glass reactor (V=50 mL) was charged under argon with $[Et_3NH]^+Cl^-$ ($[Et_3DH]^+Cl^-$, EMIM-Cl, or $BMIM^-Cl$) (10 mmol) and metal chloride (Al (III), Fe (III), Zn (II), Sn (II), Cu (II)) (10–20 mmol). The reaction was carried out with continuous stirring at 70°C for 3 h. In the case of reactions involving copper (II)

sulfate, $CuSO_4$ (0.05 mmol) was added to the prepared ionic liquid, and the mixture was stirred for additional 1 h at room temperature.

2.4. Preparation of diamantane.

A glass reactor (V=50 mL) was charged under argon with hydrogenated norbornadiene dimer (**4-7**) (1 mmol) and the ionic liquid prepared in advance (3 mmol). The reaction was carried out with continuous stirring at 50°C for 6 h. Then the reactor was cooled down to room temperature, and the reaction mixture was extracted with petroleum ether and filtered through a silica gel layer (elution with petroleum ether).

The products were separated by column chromatography: hydrocarbon **9** and diamantane **1** were eluted with hexane, while chlorinated derivatives **8** and **10** were eluted with a hexane–ethyl acetate mixture (10:1).

Diamantane 1. White crystals; mp 244–245°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72–1.80 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.95 (C^4, C^9), 37.64 (C^3, C^5, C^8, C^{10}, C^{13}, C^{14}), 38.37 (C^1, C^2, C^6, C^7, C^{11}, C^{12}). MS (EI, 70 eV): m/z (%) = 188 $[M]^+$ (100), 189 (15), 187 (18), 159 (10), 145 (8), 131 (23), 130 (18), 117 (12), 105 (13), 93 (12), 92 (11), 91 (28), 77 (15), 67 (8). Calcd for $C_{14}H_{20}$: C, 88.29; H, 11.71; found C, 88.75; H, 11.25.

***endo-exo*-4-Chloropentacyclo[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]tetradecane 8.** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 10.4 Hz, 1H), 1.33 (s, 3H), 1.42–1.45 (m, 3H), 1.54 (d, *J* = 10.4 Hz, 1H), 1.93–2.03 (m, 2H), 2.11 (d, *J* = 9.6 Hz, 2H), 2.17 (s, 2H), 2.24 (s, 3H), 2.58 (s, 1H), 3.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.95 (C^{12}), 24.05 (C^{11}), 37.12 (C^{14}), 38.77 (C^{10}), 38.80 (C^1), 41.82 (C^6), 41.86 (C^5), 42.35 (C^3), 44.92 (C^9), 47.78 (C^2), 52.12 (C^{13}), 54.22 (C^{10}), 54.38 (C^7), 72.25 (C^4). MS (EI, 70 eV): m/z (%) = 222[M]+ (100). Calcd for $C_{14}H_{19}Cl$: C, 75.48; H, 8.60; Cl, 15.92; found C, 75.38; H, 8.54; Cl, 16.08.

Heptacyclo[6.6.0.0^{2,12}.0^{3,7}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane 9. White crystals; mp 164–165°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.28 (m, 6H), 1.48–1.53 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.69 (C^6), 50.99 (C^5, C^7, C^{12}, C^{14}), 53.19 (C^1, C^2, C^3, C^4, C^8, C^9, C^{10}). MS (EI, 70 eV): m/z (%) = 184 (100) $[M]^+$, 142 (5), 129 (6), 118 (13), 117 (29), 116 (8),115 (10), 106 (16), 105 (15), 104 (18). Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75; found C, 91.36; H, 8.64.

***exo-exo*-4-Chloropentacyclo[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]tetradecane 10.** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 10 Hz 1H), 1.04–1.12 (m, 2H), 1.35–1.44 (m, 3H), 1.53 (d, *J* = 10 Hz, 1H), 1.73 (d, *J* = 6.8 Hz, 1H), 1.92–2.03 (m, 4H), 2.10 (s, 1H), 2.17 (s, 2H), 2.18 (s, 1H), 2.59 (s, 1H), 3.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.14 (C^{12}), 29.36 (C^{11}), 34.81 (C^{14}), 37.13 (C^{10}), 38.46

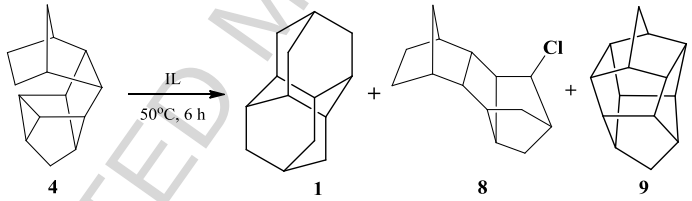
(C^1), 41.64 (C^6), 41.84 (C^5), 43.40 (C^3), 43.84 (C^9), 47.75 (C^2), 55.42 (C^{13}), 57.35 (C^{10}), 58.83 (C^7), 71.95 (C^4). MS (EI, 70 eV): m/z (%) = 222 [M]+ (100). Calcd for $C_{14}H_{19}Cl$: C, 75.48; H, 8.60; Cl, 15.92; found: C, 75.56; H, 8.51; Cl, 15.93.

3. Result and Discussion

This communication describes the first synthesis of diamantane by hydroisomerization of $C_{14}H_{18}$ hydrocarbons containing two hydrogen atoms less than diamantane, namely, *endo-endo*- **4**, *endo-exo*- ***5***, *exo-exo*- **6**, and *exo-endo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecanes **7** (hydrogenated [4+2] norbornadiene dimers). The reaction is induced by inorganic ionic liquids containing Al (III), Fe (III), Zn (II), Sn (II), and Cu (II) chlorides.

In the presence of ILs, hydrocarbon **4** is converted to a mixture of three products: diamantane **1**, *endo-exo*-chloropentacyclo[8.2.1.1^{5,8}.$0^{2,9}$.$0^{3,7}$]tetradecane **8**, and [4π+4π] NBD dimer, heptacyclo[6.6.0.$0^{2,12}$.$0^{3,7}$.$0^{4,11}$.$0^{5,9}$.$0^{10,14}$]tetradecane **9** (Table 1).

Table 1 Hydroisomerization of *endo-endo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **4** in the presence of ionic liquids.[a]



Entry	ILs	Ratio **4** : IL	Yield (%)[b]		
			1	**8**	**9**
1	$[Et_3NH]^+[AlCl_4]^-$	1:3	-	100	-
2	$[Et_3NH]^+[AlCl_4]^-$	1:1	4	50	7
3	$[Et_3NH]^+[AlCl_4]^-$	3:1	-	31	5
4	$[EMIM]^+[Al_2Cl_7]^-$	1:3	28	-	45
5	$[EMIM]^+[Al_2Cl_7]^-$	1:1	22	-	23
6	$[EMIM]^+[Al_2Cl_7]^-$	3:1	11	35	49
7	$[Et_3NH]^+[Al_2Cl_7]^-$	1:3	64	32	-
8	$[Et_3NH]^+[Al_2Cl_7]^-$	1:1	25	61	14
9	$[Et_3NH]^+[Al_2Cl_7]^-$	3:1	21	-	10
10	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:3	80	20	-
11	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:2	68	24	5
12	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:1	32	54	14
13	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	3:1	44	-	8
14	$[BMIM]^+[FeCl_4]^-$	1:3	8	79	-

15	$[BMIM]^+[FeCl_4]^-$	1:1	3	42	12
16	$[BMIM]^+[FeCl_4]^-$	3:1	12	-	18
17	$[BMIM]^+[Fe_2Cl_7]^-$	1:3	82	18	-
18	$[BMIM]^+[Fe_2Cl_7]^-$	1:1	35	50	15
19	$[BMIM]^+[Fe_2Cl_7]^-$	3:1	6	51	12
20	$[EMIM]^+[Fe_2Cl_7]^-$	1:3	54	26	20
21	$[EMIM]^+[Fe_2Cl_7]^-$	1:1	26	64	10
22	$[EMIM]^+[Fe_2Cl_7]^-$	3:1	3	58	10
23	$[Et_3NH]^+[Fe_2Cl_7]^-$	1:3	6	90	2
24	$[Et_3NH]^+[Fe_2Cl_7]^-$	1:1	11	86	3
25	$[Et_3NH]^+[Fe_2Cl_7]^-$	3:1	11	6	55
26	$[Et_3NH]^+[Zn_2Cl_5]^-$	1:3	5	56	4
27	$[Et_3NH]^+[Zn_2Cl_5]^-$	1:1	3	-	2
28	$[Et_3NH]^+[Sn_2Cl_5]^-$	1:3	1	16	7
29	$[Et_3NH]^+[Sn_2Cl_5]^-$	1:1	2	-	8
30	$[Et_3NH]^+[Cu_2Cl_5]^-$	1:3	2	5	7
31	$[Et_3NH]^+[Cu_2Cl_5]^-$	1:1	<1	-	8

[a]Reaction conditions: 50°C, 6 h.

[b]Determined by GC using $C_{12}H_{26}$ as the internal standard.

It was shown experimentally that the highest yield of diamantane **1** attained with ionic liquids based on $SnCl_2$, $ZnCl_2$, and $CuCl_2$ does not exceed 5%, which might be attributable to the decrease in the Lewis acidity in the series $AlCl_3$>$FeCl_3$>$ZnCl_2$>$SnCl_2$>$CuCl_2$. Compound **8** results from the addition of hydrogen chloride present in the ionic liquid to compound **4**.

The formation of hydrocarbon **9**, $C_{14}H_{16}$, which is [4+4] norbornadiene dimer, heptacyclo[6.6.0.$0^{2,12}$.$0^{3,7}$.$0^{4,11}$.$0^{5,9}$.$0^{10,14}$]tetradecane, is more unusual [31, 32]. The pathway to **9** obviously includes dehydrogenation and skeletal isomerization.

As can be seen in Table 1 (entry 10, 17), the highest yield of diamantane **1** (80-82%) is attained under conditions that include 50°C, 6 h, and the presence of $[Et_3NH]^+[Al_2Cl_7]^-$ and copper(II) sulfate or the ionic liquid based on 1-butyl-3-methylimidazolium chloride (BMIM-Cl) and iron(III) chloride ($[BMIM]^+[Fe_2Cl_7]^-$). A high yield of diamantane is observed when IL is present in a threefold excess over hydrocarbon **4**. Note that this is the first example of using iron compounds in diamantane synthesis.

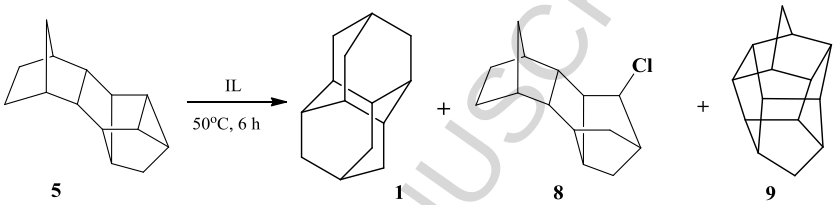
Considering the presence of $CuSO_4$, it was found [33, 34] that $AlCl_3$-$CuSO_4$ mixtures show higher catalytic activity towards *n*-pentane isomerization than $AlCl_3$ alone. Thus, copper(II) sulfate being added to an ionic liquid gives rise to a more efficient catalytic system. It is known that ionic liquids, which are polar, represent media in which salts easily dissociate into cations and anions, and, therefore, a complex is formed between the components directly during the synthesis of the

catalytic system. The better promoting effect of $CuSO_4$ can be attributed to higher polarity.

The most efficient catalysts, ionic liquids based on aluminum(III) and iron(III) chlorides, were used subsequently to carry out isomerization of other hydrogenated hexacyclic norbornadiene dimers **5-7**.

Diamantane **1** was obtained in the highest yield (96%) by isomerization of *endo-exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **5**. The reaction was performed under the action of $[Et_3NH]^+[Al_2Cl_7]^-$–$CuSO_4$ system under the chosen conditions: 50°C, 6 h, and **5** to IL molar ratio of 1 : 3 (Table 2).

Table 2 Hydroisomerization of *endo-exo*-hexacyclo-[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **5** in the presence of ionic liquids.[a]



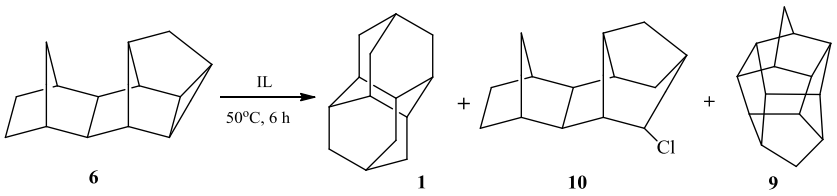
Entry	ILs	Ratio **5**:IL	Yield (%)[b]		
			1	**8**	**9**
1	$[BMIM]^+[Fe_2Cl_7]^-$	1:3	81	19	-
2	$[BMIM]^+[Fe_2Cl_7]^-$	1:1	28	54	18
3	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:3	96	4	-
4	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:1	83	17	-
5	$[Et_3NH]^+[Al_2Cl_7]^-$	1:3	54	43	3
6	$[Et_3NH]^+[Al_2Cl_7]^-$	1:1	41	52	-

[a]Reaction conditions: 50°C, 6 h.

[b]Determined by GC using $C_{12}H_{26}$ as the internal standard.

It was found that another isomer, *exo-exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **6**, is converted in the presence of $[Et_3NH]^+[Al_2Cl_7]^-$–$CuSO_4$ to give diamantane **1** in 85% yield (Table 3). The highest yields of diamantane **1** (85-87%) are observed at the [**6**] : [IL] molar ratio of 1 : 3 and in the presence of the $[Et_3NH]^+[Al_2Cl_7]^-$ ionic liquid, either with or without copper sulfate. It is noteworthy that a lower ratio of IL to hydrocarbon **6** leads to the predominant formation of chloropentacyclo[8.2.1.$1^{5,8}$.$0^{2,9}$.$0^{3,7}$]tetradecane **10**, resulting from the addition of HCl to hydrocarbon **6** (Table 3).

Table 3 Hydroisomerization of *exo-exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **6** in the presence of ionic liquids.[a]



6 1 10 9

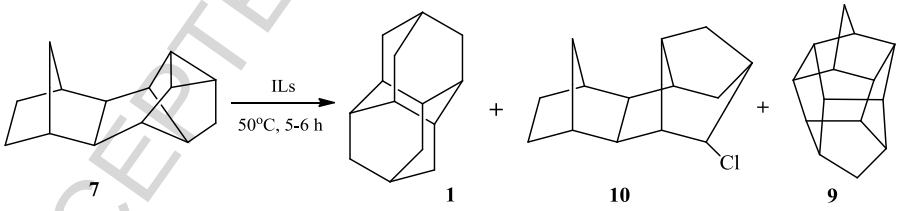
Entry	ILs	Ratio **6**:IL	Yield (%)[b]		
			1	**10**	**9**
1	$[BMIM]^+[Fe_2Cl_7]^-$	1:3	64	26	-
2	$[BMIM]^+[Fe_2Cl_7]^-$	1:1	10	76	14
3	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:3	87	10	-
4	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:1	71	29	-
5	$[Et_3NH]^+[Al_2Cl_7]^-$	1:3	85	13	-
6	$[Et_3NH]^+[Al_2Cl_7]^-$	1:1	69	31	-

[a]Reaction conditions: 50°C, 6 h.

[b]Determined by GC using $C_{12}H_{26}$ as the internal standard.

exo-endo-Hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **7** undergoes an equally efficient isomerization to diamantane **1** in the presence of $CuSO_4$-pomoted aluminate ionic liquids (Table 4).

Table 4 Hydroisomerization of *exo-endo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecane **7** in the presence of ionic liquids.[a]



7 1 10 9

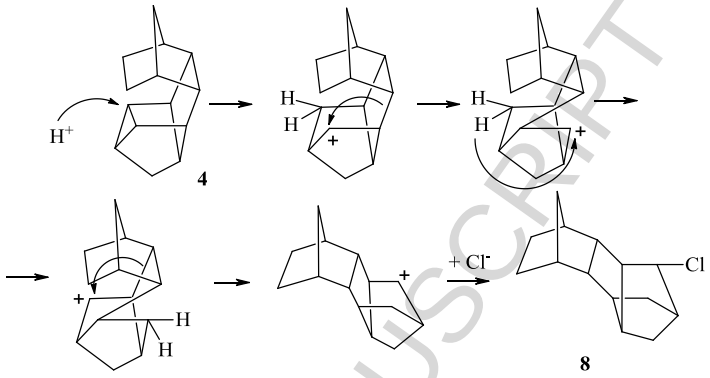
Entry	ILs	Ratio **7**:IL	Yield (%)[b]		
			1	**10**	**9**
1	$[BMIM]^+[Fe_2Cl_7]^-$	1:3	58	40	2
2	$[BMIM]^+[Fe_2Cl_7]^-$	1:1	19	67	14
3	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:3	83	15	2
4	$[Et_3NH]^+[Al_2Cl_7]^-$-$CuSO_4$	1:1	40	55	5
5	$[Et_3NH]^+[Al_2Cl_7]^-$	1:3	72	13	6
6	$[Et_3NH]^+[Al_2Cl_7]^-$	1:1	43	45	12

[a]Reaction conditions: 50°C, 6 h.

[b]Determined by GC using $C_{12}H_{26}$ as the internal standard.

A high yield of diamantane **1** (83%) is observed upon isomerization of the *exo-endo*-dimer **7** in the $[Et_3NH]^+[Al_2Cl_7]^- – CuSO_4$ system (1:3) .

Attention is attracted by the structure of chlorinated derivatives **8** and **10**, which are formed from hydrocarbons **4** and **7**, respectively, containing the most shielded three-carbon rings. Obviously, this occurs *via* a skeletal rearrangement the starting step of which is protonation of the cyclopropane ring with hydrogen chloride. In particular, the formation of compound **8** from hydrocarbon **4** can be depicted by the following scheme:



Scheme 2. Probable mechanism of formation of compound **8** from hydrocarbon **4**.

Compound **10** is formed from hydrocarbon **7** by a similar pathway.

Upon interaction between HCl and hydrocarbons **4** and **7**, the formation of chlorine derivatives **8** and **10** accompanied by the skeletal rearrangement was not unexpected. We observed the same transformation in the alkylation of benzene with hydrocarbons **4** or **6** in the presence of the $[Et_3NH]^+[Al_2Cl_7]^-$ ionic liquid [35].

These results concerning isomerization of hexacyclic dimers to diamantane are unexpected, as the molecules of hydrocarbons **4-7** ($C_{14}H_{18}$) contain less hydrogen atoms than diamantane. Most likely, components of the ionic liquid serve as the main hydrogen donors. Meanwhile, it cannot be ruled out that the proper hydrocarbons **4-7** can serve as additional sources of hydrogen, since they are partly converted to hydrocarbon **9**, which has the composition $C_{14}H_{16}$. It is unlikely that HCl would serve as a hydrogen donor. Indeed, experiments on isomerization of hydrocarbons **4-7** in the presence of the $[Et_3ND]^+[Al_2Cl_7]^-$ ionic liquid did not meet with success: no dideuterodiamantane was detected. This implies that the major hydrogen donors are the ethyl and butyl groups of triethylamine and 1-ethyl- and 1-butyl-3-methylimidazolium cations incorporated in the ionic liquid.

4. Conclusions

Thus, new methods were developed for the preparation of diamantane in high yield by hydroisomerization of partially hydrogenated hexacyclic norbornadiene dimers: *endo-endo-*, *exo-exo-*, *exo-endo-*, and *endo-exo-*hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecanes **4-7** induced by inorganic ionic liquids, $[Et_3NH]^+[Al_2Cl_7]^-$ or $[BMIM]^+[Fe_2Cl_7]^-$, under the following conditions: 50^{o}C, 5-6 h, [**4-7**]:[IL] = 1:3.

It was found that the isomerizations of *endo-endo-*, *exo-exo-*, *exo-endo-*, and *endo-exo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradecanes **4-7** to diamantane were promoted by ionic liquids.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:/

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Highlights

- Ionic liquids catalyze diamantane synthesis
- A new route to diamantane is based on skeletal rearrangement of $C_{14}H_{18}$ hydrocarbon
- The highest yields of diamantane are 80-96%
- $[Et_3NH]^+[Al_2Cl_7]^-$ and $[BMIM]^+[Fe_2Cl_7]^-$ are the most efficient catalysts

Graphical abstract