Synthesis of polycyclic hydrocarbons C_{14}H_{20} by hydrogenation of exo-exo-, exo-endo-, endo-exo-, and endo-endo-hexacyclo[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradec-12-enes with H_{2}SO_{4} and isomerization of the products to diamantane induced by ionic liquids

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18 März 2021

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Synthesis of polycyclic hydrocarbons \( \text{C}_{14}\text{H}_{20} \) by hydrogenation of exo-exo-, exo-endo-, endo-exo-, and endo-endo-hexacyclo[9.2.1.0\(^{2,10}\).0\(^{3,8}\).0\(^{4,6}\).0\(^{5,9}\)]tetradec-12-enes with \( \text{H}_2\text{SO}_4 \) and isomerization of the products to diamantane induced by ionic liquids

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Keywords:
diamantane; hexacyclic norbornadiene dimers, isomerization, ionic liquids, sulfuric acid

Abstract
A new method was developed for hydrogenation of unsaturated hexacyclic norbornadiene dimers, exo-exo-, exo-endo-, endo-exo-, and endo-endo-hexacyclo[9.2.1.0\(^{2,10}\).0\(^{3,8}\).0\(^{4,6}\).0\(^{5,9}\)]tetradec-12-enes, using sulfuric acid (98%), giving pentacyclo[8.2.1.1\(^{5,8}\).0\(^{2,9}\).0\(^{3,7}\)]tetradecanes, which were subjected to skeletal rearrangement under the action of ionic liquids to form diamantane in up to 84% yield.

Introduction
Diamantane (pentacyclo[7.3.1.1\(^{4,12}\).0\(^{2,7}\).0\(^{6,11}\)]tetradecane, \( \text{C}_{14}\text{H}_{20} \)) is the second representative of the homologous series of diamondoids. It is promising for the preparation of medicinal agents, polymer materials, and solvent-resistant rubbers and can serve as the raw material for the synthesis of thermally stable synthetic lubricating oils and transmission fluids [1-3].

The known methods for diamantane synthesis (1) are based on the skeletal isomerization of strained, thermodynamically less stable \( \text{C}_{14}\text{H}_{20} \) polycyclic hydrocarbons [4-8].
Inorganic ionic liquids (ILs) have been widely used in the last two decades. In particular, ILs are employed as immersion media [9,10] in electrochemical methods of analysis, for the design of sensing devices and biosensors [11-13]. Also, ILs are used in the synthesis of polymers [14,15] and as electrolyte components of lithium batteries and capacitors [16-19].

The most promising field of application of ILs is homogeneous and heterogeneous catalysis, as noted in a number of recent reviews and monographs [20-23]. Inorganic ionic liquids may have Brønsted or Lewis acidity or behave as superacids. In particular, superacid properties are inherent in AlCl$_3$-containing melts, which makes them attractive for the use in catalysis [24-26]. According to published data [27,28], the ionic liquid [Et$_3$NH][Al$_2$Cl$_7$] exhibits high catalytic activity in the skeletal isomerizations of cyclohexane to methylcyclopentane and of polycyclic hydrocarbons C$_{12-15}$H$_{18-22}$ to adamantane and diamantane derivatives.

In a previous study [29], we performed the first synthesis of diamantane by hydroisomerization of hydrogenated norbornadiene [4π+2π]-dimers (NBDs), that is, endo-endo- (2), exo-exo- (3), exo-endo- (4), and endo-exo-hexacyclo[9.2.1.0$^{2,10}$.0$^{3,8}$.0$^{4,6}$.0$^{5,9}$]tetradecanes (5) (with two carbon atoms less in the molecules than in the diamantane molecule) induced by ionic liquids.

![Figure 1: Hydrogenated hexacyclic norbornadiene dimers 2-5.](image)

Hydrocarbons 2-5 were synthesized by hydrogenation of hexacyclic norbornadiene dimers 6–9 with hydrogen under mild conditions (20°C, 8 h, H$_2$ pressure of 1 atm) in the presence of Pd/C. Whereas the double bond of compounds 6-9 was readily hydrogenated, hydrogenolysis of the three-carbon ring with hydrogen in the presence of Pd/C could not be induced even under drastic conditions: 150°C, 50 atm of H$_2$.

Therefore, the goal of the present study was to develop a method for hydrogenation of both the double bond and the three-carbon ring of hydrocarbons 6-9 to obtain hydrocarbons (C$_{14}$H$_{20}$), iso-compositional with diamantane, and to perform
subsequently a skeletal rearrangement of these products to diamantane (1) under the action of ionic liquids.

Result and Discussion
In this study, we developed for the first time a method for complete hydrogenation of cyclopropane-containing hexacyclic norbornadiene dimers (NBDs) — exo-exo- (6), exo-endo- (7), endo-exo- (8), and endo-endo- (9) hexacyclo[9.2.1.0².10.0³.8.0⁴.6.0⁵.9]tetradec-12-enes — with concentrated sulfuric acid (98%) to give pentacyclo[8.2.1.1⁵.8.0₂.⁹.0³.⁷]tetradecanes (10) and (11), identical to diamantane in the composition. The reactions proceed via C₁₂–C₁₃ double bond hydrogenation and C₄–C₅ cyclopropane ring hydrogenolysis.

![Scheme 1: Hydrogenation of hexacyclic norbornadiene dimers 6-9.](image)

The optimal reaction conditions and the preferable ratios of NBDs 6-9 and sulfuric acid were determined in a series of experiments. The reaction of hydrocarbons 6-9 with H₂SO₄ proceeds most smoothly at room temperature and at the [6-9]:[H₂SO₄] molar ratio of 1:10 in cyclohexane, which is taken in excess. An increase in the amount of sulfuric acid with respect to hydrocarbons 6-9 and temperature rise to 40°C result in decreasing yields of products due to resinification. When the H₂SO₄ excess over 6-9 is decreased (1 : 5), the conversion of hydrocarbons decreases to 10%. Conducting the reaction without a solvent induces pronounced resinification, and the yields of hydrocarbons (10) and (11) do not exceed 8%.

It is noteworthy that complete conversion of the starting hydrocarbons 6-9 depends on the duration of the reaction. The required reaction time is 7 h in the case of exo-exo- (6) and endo-exo- (7) hexacyclo[9.2.1.0².10.0³.8.0⁴.6.0⁵.9]tetradec-12-enes, 10 h for the exo-endo isomer (8), and 15 h for the endo-endo-isomer (9).
In order to confirm the involvement of H$_2$SO$_4$ into hydrogenation of dimers 6-9, we carried out a control experiment on hydrogenation of NBD 6 with deuterated sulfuric acid (96-98%; 99% atomic fraction of D) in cyclohexane. According to gas chromatography/mass spectrometry analysis data, the molecular weight (m/z) of the obtained product (10a) was 190 Da, which corresponds to the molecular formula C$_{14}$H$_{18}$D$_2$. According to $^{13}$C NMR data, compound (10a) contains two D atoms, one in the C$^{12}$ position, while the other one most likely in the C$^{4}$ position. The location of deuterium at C$^{12}$ is indicated by a triplet with δC$_{12}$=29.03 ppm with a spin-spin coupling constant $^2$J$_{13C}$-D= 19.8 Hz. The α-isotope effect is ΔδC$_{12}$= -0.26 ppm, whereas the β-isotope effect does not exceed -0.1 ppm (δC$_1$=41.90 ppm, δC$_{11}$=29.29 ppm) [30].

The characteristic upfield shifts of the signals with δC$_3$=45.03 ppm and δC$_5$=34.65 ppm by 0.1 ppm to 0.2 ppm attest to the presence of deuterium atom at δC$_4$=41.90 ppm. Unfortunately, the C–D coupling constant could not be determined due to signal overlap and low intensity of the expected triplet.

On the other hand, if D$_2$-sulfuric acid alone was the hydrogen donor in the hydrogenation of dimers (6-9), the molecular weight (m/z) of hydrogenation products would be 192 Da. Presumably, cyclohexane also acts as a hydrogen donor. In order to clarify this issue, we carried out hydrogenation of hydrocarbon (6) with H$_2$SO$_4$ in dodecadeuterocyclohexane. The reaction gave compound (10b) containing one deuterium atom, with the molecular weight (m/z) of 189 Da and the formula C$_{14}$H$_{19}$D, which is indicative of partial involvement of cyclohexane in the hydrogenation reaction. When compound (6) was hydrogenated with H$_2$SO$_4$ in carbon disulfide, the hydrocarbon conversion decreased to 38%, which means that not only cyclohexane, but also the proper hydrocarbon (6) participates in hydrogenation.

Thus, presumably, the hydrogen donors involed in NBD (6-9) hydrogenation are H$_2$SO$_4$, cyclohexane, and the hydrocarbons (6-9) themselves.

As can be seen from the structure of products (10) and (11), the reactions of hydrocarbons (6) and (8) with H$_2$SO$_4$ were not accompanied by skeletal rearrangements and gave products of the expected structure. As regards hydrocarbons (7) and (9), which contain the most shielded three-carbon ring, they reacted with sulfuric acids to give products structurally identical to adducts (10) and (11), obtained from hydrocarbons (6) and (8), respectively. Evidently, hydrogenation of compounds (7) and (9) proceeds...
by a more complex pathway. The first step is protonation of the double bond, which is followed by the hydride ion transfer from cyclohexane (or from hydrocarbon 7), thus completing hydrogenation. Then the carbocation skeletal rearrangement takes place, which starts with the protonation of compound (3) at the cyclopropane ring to give the carbocation (K⁺).

Scheme 2: Probable mechanism of formation of exo-exo-pentacyclo[8.2.1.1^5,8.0^2,9.0^3,7]tetradecane (10) from hydrocarbon (7).

Compound (11) is formed from hydrocarbon (9) by a similar pathway.
Attempts to perform hydrogenation of hydrocarbons 6-9 using hydrochloric, nitric, or orthophosphoric acid were unsuccessful: after the reaction, the starting NBDs 6-9 were recovered unchanged.

In a previous study [31], we accomplished direct synthesis of diamantane (1) using H₂SO₄ (98%) from the heptacyclic norbornadiene dimer, binor-S, which has four H atoms less in the molecule than diamantane. This fact indicates that H₂SO₄ promotes hydrogenation and isomerization of binor-S. In the case of reaction of hexacyclic dimers 6-9 with sulfuric acid, the reaction stops after hydrogenolysis of the three-carbon ring to give pentacyclotetradecanes 10 and 11.

In the next stage of investigation, we carried out skeletal isomerization of iso-compositional exo-exo- (10) and endo-exo-pentacyclo[8.2.1.1^5,8.0^2,9.0^3,7]tetradecanes (11) to diamantane (1). The inorganic ionic liquids containing Al (III), Fe (III), Zn (II), Mn (II), Sn (II), and Cu (II) chlorides were tested as catalysts (Scheme 3). As shown by experiments, high activities in the skeletal isomerization of hydrocarbons 10 and 11 to diamantane (1) were shown by aluminate ionic liquids (AIL), which provided up to 84% yields of diamantane (1). In the presence of other ILs, the yields of diamantane did not exceed 10-12%.
The skeletal rearrangement of exo-exo- (10) and endo-exo-pentacyclo[8.2.1.1\(^5\).0\(^2\).9\(^0\).3\(^7\)]tetradecanes (11) to diamantane (1) gives the product in a high yield when the [10; 11] : [AIL] molar ratio is 1:3. The examples of using AIL are summarized in Table 1.

**Scheme 3:** Isomerization of hydrocarbons (6) and (7) to diamantane (1).

![Scheme 3](image)

The highest yield of diamantane 1 was obtained when the ionic liquid prepared from Et\(_3\)N-HCl and 2-3 moles of AlCl\(_3\) was used. The addition of copper(II) chloride to [Et\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)]\(^-\) in the isomerization of hydrocarbons (10) and (11) increased the yield of diamantane (1) to 80 and 84\%, respectively. Most likely, the activating effect of CuCl\(_2\) is due to complex formation with amines and the ability of CuCl\(_2\) to catalyze some ionic reactions.

### Table 1: Isomerization of exo-exo- (10) and endo-exo-pentacyclo[8.2.1.1\(^5\).0\(^2\).9\(^0\).3\(^7\)]tetradecanes (11) to diamantane (1) induced by aluminate ionic liquids\(^a\).

| entry | AILs | hydrocarbon 10 or 11 | Yield [%]\(^b\) 10 or 11 | 1 |
|-------|------|----------------------|-----------------|---|
| 1     | [Et\(_3\)NH]\(^+\)[AlCl\(_4\)]\(^-\) | 10     | 88   | -  |
| 2     | [Et\(_3\)NH]\(^+\)[AlCl\(_4\)]\(^-\) | 11     | 91   | -  |
| 3     | [Me\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)] \(\cdot\)CuCl\(_2\) | 10     | 49   | 47 |
| 4     | [Me\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)] \(\cdot\)CuCl\(_2\) | 11     | 38   | 59 |
| 5     | [Et\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)] | 10     | -    | 69 |
| 6     | [Et\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)] | 11     | -    | 74 |
| 7     | [Et\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)] \(\cdot\)CuCl\(_2\) | 10     | -    | 80 |
| 8     | [Et\(_3\)NH]\(^+\)[Al\(_2\)Cl\(_7\)] \(\cdot\)CuCl\(_2\) | 11     | -    | 84 |
| 9     | [EMIM]\(^+\)[AlCl\(_4\)]\(^-\) | 10     | 88   | 12 |
| 10    | [EMIM]\(^+\)[AlCl\(_4\)]\(^-\) | 11     | 85   | 15 |
| 11    | [EMIM]\(^+\)[Al\(_2\)Cl\(_7\)] | 10     | 29   | 60 |
| 12    | [EMIM]\(^+\)[Al\(_2\)Cl\(_7\)] | 11     | 25   | 66 |
| 13    | [BMIM]\(^+\)[Al\(_2\)Cl\(_7\)] | 10     | 24   | 62 |
| 14    | [BMIM]\(^+\)[Al\(_2\)Cl\(_7\)] | 11     | 22   | 68 |
| 15    | [Et\(_3\)NH]\(^+\)[AlCl\(_3\)] \(\cdot\)CuCl\(_2\) | 10     | -    | 78 |
| 16    | [Et\(_3\)NH]\(^+\)[AlCl\(_3\)] \(\cdot\)CuCl\(_2\) | 11     | -    | 81 |

\(^a\)Reaction conditions: 50\(^\circ\)C, 8 h, molar ratio hydrocarbon : AIL = 1:3. \(^b\)Determined by GC using C\(_{12}\)H\(_{26}\) as the internal standard.
processes. In view of the fact that ionic liquids are polar media in which solid salts can readily dissociate into the corresponding cations and anions, the complex formation between triethylamine and copper ions and also the formation of HCl and HAl\textsubscript{2}Cl\textsubscript{7} are possible by the following mechanism:

\[
\text{CuCl}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{Cl}^-
\]

\[
4 \text{(Et)}_3\text{NH}^+ + \text{Cu}^{2+} \rightleftharpoons [\text{Cu(\text{(Et)}_3\text{N})}_4]^{2+} + 4\text{H}^+
\]

\[
\text{H}^+ + \text{Cl}^- \rightleftharpoons \text{HCl}
\]

\[
\text{H}^+ + \text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{HAl}_2\text{Cl}_7
\]

**Scheme 4:** Putative mechanism of complex formation of triethylamine with copper ions.

It is clear that the formed HCl and HAl\textsubscript{2}Cl\textsubscript{7} increase the acidity of the medium, thus promoting an increase in the rate of formation of carbocations involved in the reaction. On the other hand, according to published data [32], the increase in the diamantane (1) yield upon the addition of copper(II) chloride to the ionic liquid may be attributed to the formation of the anionic complex species [Al\textsubscript{3}Cl\textsubscript{12}Cu], which are catalytically active. It is noteworthy that the aluminate ionic liquids perform two functions in the isomerization of exo-exo- (10) and endo-exo-pentacyclo[8.2.1.1\textsuperscript{5,8}.0\textsuperscript{2,9}.0\textsuperscript{3,7}]tetradecanes (11) to diamantane (1): they serve as both catalysts and the reaction medium. The use of solvents is undesirable, as the yield of diamantane (1) decreases to 5% upon the addition of hexane or CH\textsubscript{2}Cl\textsubscript{2}.

**Conclusion**

Thus, we developed a new method for the synthesis of polycyclic hydrocarbons, pentacyclo[8.2.1.1\textsuperscript{5,8}.0\textsuperscript{2,9}.0\textsuperscript{3,7}]tetradecanes 10, 11, by hydrogenation of unsaturated hexacyclic norbornadiene dimers (exo-exo-, exo-end-endo-, endo-exo-, and endo-endo-isomers) with concentrated sulfuric acid (98%). Under the action of aluminane ionic liquids, pentacyclo[8.2.1.1\textsuperscript{5,8}.0\textsuperscript{2,9}.0\textsuperscript{3,7}]tetradecanes 10, 11 are converted to diamantane (1) in 80 and 84% yields.

**Experimental**

**General procedures and materials:** $^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance-II 400 Ascend instrument (400 MHz for $^1$H and 100 MHz for $^{13}$C in CDCl\textsubscript{3}) and Bruker Avance-III HD 500 Ascend instrument (500 MHz for $^1$H and 125 MHz for $^{13}$C in CDCl\textsubscript{3}). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass
spectrometer (SPB-5 capillary column, 30m×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 [2m×3mm column, SE-30 silicone (5%) on Chromat 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 dimers, exo-exo- (6) [33], exo-endo- (7) [34], endo-exo- (8) [35], and endo-endo-hexacyclo-[9.2.1.02.10.03.8.04.6.05.9]tetradec-12-enes (9) [36], were prepared by reported procedures.

**Synthesis of exo-exo-pentacyclo[8.2.1.15.8.02.9.03.7]tetradecane (10):** The exo-exo- (6) or exo-endo-hexacyclo[9.2.1.02.10.03.8.04.6.05.9]tetradec-12-ene (7, 0.368 g, 2 mmol) was placed into a glass reactor (V=100 mL) and dissolved in cyclohexane (10 mL). Then 98% sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. After the whole amount of H₂SO₄ was added, the reaction mixture was stirred at 0–20°C for 7–10 h. After completion of the reaction, a 10% solution of NaOH was added to the reaction mixture, and the organic phase was separated and filtered through a silica gel layer (elution with petroleum ether). The solvent was distilled off. Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.87–0.91 (m, 2H), 1.07–1.09 (m, 2H), 1.37 (s, 3H), 1.46 (s, 1H), 1.59 (d, J = 10 Hz, 1H), 1.82–1.94 (m, 7H), 2.02 (s, 2H), 2.44 (s, 1H), 2.49 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 29.40 (C₁₁, 12), 32.23 (C₁), 34.84 (C⁵), 34.88 (C⁶), 40.39 (C¹₃), 41.99 (C¹, 10), 42.03 (C⁴, 14), 45.13 (C³, 8), 48.40 (C⁷), 57.86 (C², 9); EIMS (70 eV, m/z): 188 [M]+ (69), 159 (29), 147 (25), 121 (100), 105 (25), 91 (64), 79 (76), 66 (53), 41 (41); Anal. calcd for C₁₄H₂₀: C, 89.29; H, 10.71; found: C, 89.36; H, 10.64.

**Synthesis of exo-exo-dideuteriopentacyclo[8.2.1.15.8.02.9.03.7]tetradecane (10a):** The exo-exo-hexacyclo[9.2.1.02.10.03.8.04.6.05.9]tetradec-12-ene (6, 0.184 g, 1 mmol) was placed into a glass reactor (V=100 mL) and dissolved in cyclohexane (5 mL). Then deuterated sulfuric acid (96-98%; 99% atomic fraction of D) (1 g, 10 mmol) was added in portions with vigorous stirring. After the whole amount of D₂SO₄ was added, the reaction mixture was stirred at 20°C for 15 h. After completion of the reaction, a 10%
solution of NaOH was added to the reaction mixture, and the organic phase was separated and filtered through a silica gel layer (elution with petroleum ether). The solvent was distilled off. Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.87–0.91 (m, 2H), 1.06–1.07 (m, 2H), 1.37 (s, 3H), 1.48 (d, \(J = 11.5\) Hz, 1H), 1.59 (d, \(J = 10.5\) Hz, 1H), 1.82–1.87 (m, 5H), 1.92 (d, \(J = 13.5\) Hz, 2H), 2.02 (s, 2H), 2.44 (s, 1H), 2.49 (s, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 29.03 (C\(_{12}\)), 29.29 (C\(_{11}\)), 34.65 (C\(_5\)), 34.87 (C\(_6\)), 40.29 (C\(_{13}\)), 41.90 (C\(_{11}\)), 41.99 (C\(_{10}\)), 42.03 (C\(_{14}\)), 45.03 (C\(_3\)), 45.13 (C\(_8\)), 48.31 (C\(_7\)), 57.85 (C\(_2\)), 57.86 (C\(_9\)); EIMS (70 eV, \(m/z\)): 190 [M]+ (68).

**Synthesis of endo-exo-pentacyclo[8.2.1.1\(^5\).8.0\(^2\).9.0\(^3\).7\]tetradecane (11):** The endo-exo- (8) or endo-endo-hexacyclo[9.2.1.1\(^2\).10.0\(^3\).8.0\(^4\).6.0\(^5\).9\]tetradec-12-ene (9, 0.368 g, 2 mmol) was placed into a glass reactor (V=100 mL) and dissolved in cyclohexane (10 mL). Then 98% sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. After the whole amount of H\(_2\)SO\(_4\) was added, the reaction mixture was stirred at 0–20°C for 7–15 h. After completion of the reaction, a 10% solution of NaOH was added to the reaction mixture, and the organic phase was separated and filtered through a silica gel layer (elution with petroleum ether). The solvent was distilled off. Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.89–0.91 (m, 3H), 1.07–1.09 (m, 2H), 1.37 (s, 4H), 1.61 (d, \(J = 10\) Hz, 1H), 1.83–1.94 (m, 7H), 2.02 (s, 2H), 2.49 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 24.55 (C\(_{10}\)), 36.71 (C\(_5\)), 34.90 (C\(_6\)), 41.02 (C\(_{11}\)), 41.49 (C\(_3\)), 43.80 (C\(_4\)), 47.43 (C\(_{13}\)), 47.94 (C\(_7\)), 54.76 (C\(_2\)); EIMS (70 eV, \(m/z\)): 188 [M]+ (67), 159 (28), 147 (26), 121 (100), 93 (39), 91 (61), 79 (73), 66 (54), 41 (38); Anal. calcd for C\(_{14}\)H\(_{20}\): C, 89.29; H, 10.71; found: C, 89.44; H, 10.56.

**Preparation of ionic liquids:** The ionic liquids were prepared by the reaction of AlCl\(_3\), FeCl\(_3\), ZnCl\(_2\), or SnCl\(_2\) with Me\(_3\)N•HCl, Et\(_3\)N•HCl, EMIM-Cl, or BMIM-Cl. Mes\(_3\)N•HCl, Et\(_3\)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. In experiments with CuCl\(_2\), copper chloride (0.05 mmol) was added to the prepared ionic liquid, and the mixture was stirred for an additional 1 h at room temperature.

**Preparation of diamantane:** Hydrocarbon (10) or (11) (1 mmol) and pre-synthesized ionic liquid (3 mmol) were charged into a glass reactor (V=50 mL) under argon. The
reaction was conducted 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 characteristic data and graphical spectra of diamantane are almost identical with the literature data [29].

Supporting Information
Supporting Information File 1
Experimental procedures, NMR, and mass spectral data.

Funding
The results were obtained with the financial support of the Russian Ministry of Education and Science (project no. 2019-05-595-000-058) on unique equipment at the 'Agidel' Collective Usage Center (Ufa Federal Research Center, Russian Academy of Sciences) and carried out within the RF state assignment, reg. no. AAAA-A19-119022290009-3.

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