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Preprint Title Synthesis of polycyclic hydrocarbons C₁₄H₂₀ 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 H₂SO₄ and isomerization of the products to diamantane induced by ionic liquids

Authors Rishat Aminov and Ravil Khusnutdinov

Publication Date 18 März 2021

Article Type Full Research Paper

Supporting Information File 1 Scheme 1.cdx; 21.9 KB

Supporting Information File 2 Scheme 2.cdx; 20.1 KB

Supporting Information File 3 Scheme 3.cdx; 6.3 KB

Supporting Information File 4 Scheme 4.cdx; 4.7 KB

Supporting Information File 5 Supplementary material.doc; 1.1 MB

ORCID® IDs Rishat Aminov - <https://orcid.org/0000-0001-5427-6350>

Synthesis of polycyclic hydrocarbons C₁₄H₂₀ 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 H₂SO₄ and isomerization of the products to diamantane induced by ionic liquids

Rishat I. Aminov* and Ravil I. Khusnutdinov

Address:

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, pr. Oktyabrya 141, Ufa, 450075, Russian Federation

E-mail:

Rishat Aminov* - rishaminov@gmail.com

* Corresponding author

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, C₁₄H₂₀ **1**) 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 C₁₄H₂₀ 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 AlCl₃-containing melts, which makes them attractive for the use in catalysis [24-26]. According to published data [27,28], the ionic liquid [Et₃NH]⁺[Al₂Cl₇]⁻ exhibits high catalytic activity in the skeletal isomerizations of cyclohexane to methylcyclopentane and of polycyclic hydrocarbons C₁₂₋₁₅H₁₈₋₂₂ 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.

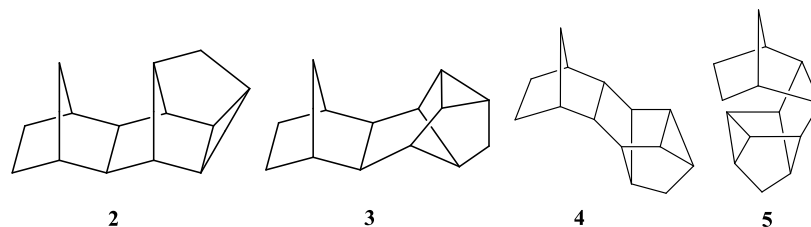


Figure 1: Hydrogenated hexacyclic norbornadiene dimers 2-5.

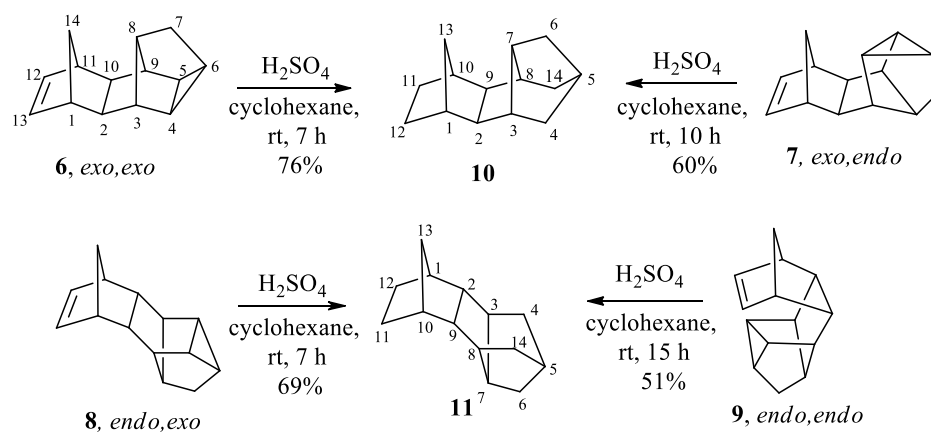
Hydrocarbons 2-5 were synthesized by hydrogenation of hexacyclic norbornadiene dimers 6-9 with hydrogen under mild conditions (20°C, 8 h, H₂ pressure of 1 atm) in the presence of Pd/C. Whereas the double bond of compounds 6-9 was readily hydrogenated, hydrogenolysis of the three-carbon ring with hydrogen in the presence of Pd/C could not be induced even under drastic conditions: 150°C, 50 atm of H₂.

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 (C₁₄H₂₀), 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[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradec-12-enes — with concentrated sulfuric acid (98%) to give pentacyclo[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]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**.

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[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]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 H₂SO₄ 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 C₁₄H₁₈D₂. According to ¹³C NMR data, compound (**10a**) contains two D atoms, one in the C¹² position, while the other one most likely in the C⁴ position. The location of deuterium at C¹² is indicated by a triplet with δC₁₂=29.03 ppm with a spin-spin coupling constant ²J_{13C-D}= 19.8 Hz. The α-isotope effect is ΔδC₁₂= - 0.26 ppm, whereas the β-isotope effect does not exceed - 0.1 ppm (δC₁=41.90 ppm, δC₁₁=29.29 ppm) [30].

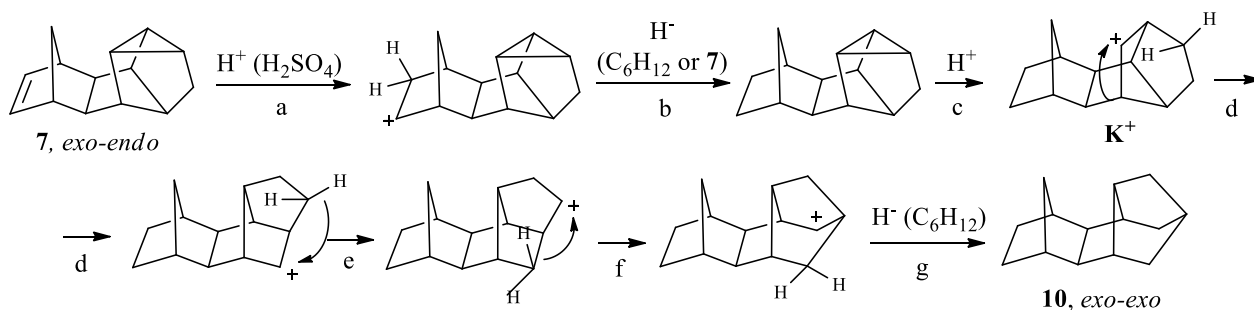
The characteristic upfield shifts of the signals with δC₃=45.03 ppm and δC₅=34.65 ppm by 0.1 ppm to 0.2 ppm attest to the presence of deuterium atom at δC₄=41.90 ppm. Unfortunately, the C–D coupling constant could not be determined due to signal overlap and to low intensity of the expected triplet.

On the other hand, if D₂-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 H₂SO₄ in dodecadeuterocyclohexane. The reaction gave compound (**10b**) containing one deuterium atom, with the molecular weight (m/z) of 189 Da and the formula C₁₄H₁₉D, which is indicative of partial involvement of cyclohexane in the hydrogenation reaction. When compound (**6**) was hydrogenated with H₂SO₄ 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 involved in NBD (**6-9**) hydrogenation are H₂SO₄, 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 H₂SO₄ 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^+).



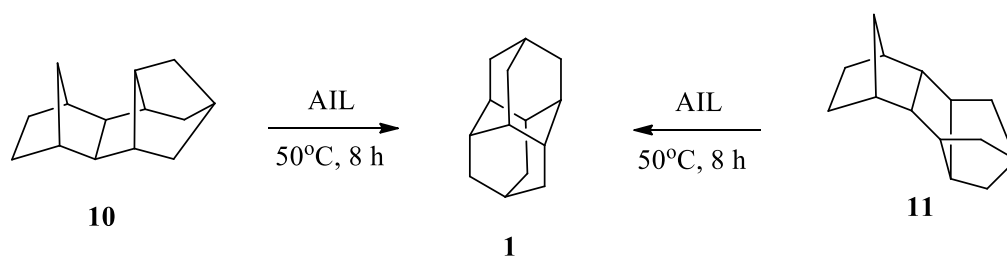
Scheme 2: Probable mechanism of formation of *exo-exo*-pentacyclo[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]tetradecane (**10**) from hydrocarbon (**7**).

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 H_2SO_4 (98%) from the heptacyclic norbornadiene dimer, binor-S, which has four H atoms less in the molecule than diamantane. This fact indicates that H_2SO_4 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 isocompositional *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%.



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

The skeletal rearrangement of *exo-exo*- (**10**) and *endo-exo*-pentacyclo[8.2.1.1^{5,8}.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.

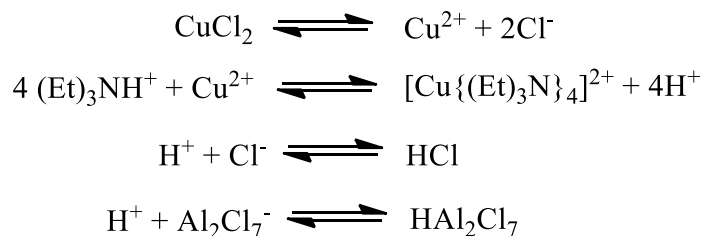
Table 1: Isomerization of *exo-exo*- (**10**) and *endo-exo*-pentacyclo[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]tetradecanes (**11**) to diamantane (**1**) induced by aluminate ionic liquids^a.

| 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] ⁻ | 10 | 49 | 47 |
| 4 | [Me ₃ NH] ⁺ [Al ₂ Cl ₇] ⁻ | 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] ⁻ -CuCl ₂ | 10 | - | 80 |
| 8 | [Et ₃ NH] ⁺ [Al ₂ Cl ₇] ⁻ -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] ⁺ [Al ₃ Cl ₁₀] ⁻ | 10 | - | 78 |
| 16 | [Et ₃ NH] ⁺ [Al ₃ Cl ₁₀] ⁻ | 11 | - | 81 |

^aReaction conditions: 50°C, 8 h, molar ratio hydrocarbon : AIL = 1:3. ^bDetermined by GC using C₁₂H₂₆ as the internal standard.

The highest yield of diamantane **1** was obtained when the ionic liquid prepared from Et₃N•HCl and 2-3 moles of AlCl₃ was used. The addition of copper(II) chloride to [Et₃NH]⁺[Al₂Cl₇]⁻ 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 CuCl₂ is due to complex formation with amines and the ability of CuCl₂ to catalyze some ionic

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_2Cl_7 are possible by the following mechanism:



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

It is clear that the formed HCl and HAl_2Cl_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 $[\text{Al}_3\text{Cl}_{12}\text{Cu}]^-$, 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^{5,8}.0^{2,9}.0^{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_2Cl_2 .

Conclusion

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

Experimental

General procedures and materials: ^1H and ^{13}C NMR spectra were measured on a Bruker Avance-II 400 Ascend instrument (400 MHz for ^1H and 100 MHz for ^{13}C in CDCl_3) and Bruker Avance-III HD 500 Ascend instrument (500 MHz for ^1H and 125 MHz for ^{13}C in CDCl_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 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 dimers, *exo-exo-* (**6**) [33], *exo-endo-* (**7**) [34], *endo-exo-* (**8**) [35], and *endo-endo-hexacyclo*[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradec-12-enes (**9**) [36], were prepared by reported procedures.

Synthesis of *exo-exo-pentacyclo*[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]tetradecane (10**):** The *exo-exo-* (**6**) or *exo-endo-hexacyclo*[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]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 (C^{11, 12}), 34.84 (C⁵), 34.88 (C⁶), 40.39 (C¹³), 41.99 (C^{1, 10}), 42.03 (C^{4, 14}), 45.13 (C^{3, 8}), 48.40 (C⁷), 57.86 (C^{2, 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*[8.2.1.1^{5,8}.0^{2,9}.0^{3,7}]tetradecane (10a**):** The *exo-exo-hexacyclo*[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]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; ^1H NMR (500 MHz, CDCl_3) δ 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) δ 29.03 (C^{12}), 29.29 (C^{11}), 34.65 (C^5), 34.87 (C^6), 40.29 (C^{13}), 41.90 ($\text{C}^{1, 4}$), 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[9.2.1.0 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_2SO_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; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 24.55 ($\text{C}^{11, 12}$), 36.71 (C^5), 34.90 (C^6), 41.02 ($\text{C}^{1, 10}$), 41.49 ($\text{C}^{3, 8}$), 43.80 ($\text{C}^{4, 14}$), 47.43 (C^{13}), 47.94 (C^7), 54.76 ($\text{C}^{2, 9}$); 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 $\text{C}_{14}\text{H}_{20}$: 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 $\text{Me}_3\text{N}\cdot\text{HCl}$, $\text{Et}_3\text{N}\cdot\text{HCl}$, EMIM-Cl, or BMIM-Cl.

$\text{Me}_3\text{N}\cdot\text{HCl}$, $\text{Et}_3\text{N}\cdot\text{HCl}$, 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.

ORCID® iDs

Rishat I. Aminov - <https://orcid.org/0000-0001-5427-6350>

Ravil I. Khusnutdinov - <https://orcid.org/0000-0003-1151-5248>

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