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Synthesis of diamantane from new polycyclic hydrocarbons C_{14} under the action of ionic liquids

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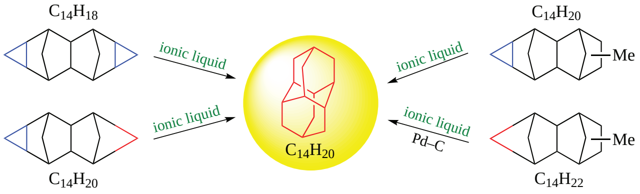
Diamantane was obtained by skeletal rearrangement of three new polycyclic hydrocarbons $C_{14}H_{18}$, $C_{14}H_{20}$ and $C_{14}H_{22}$ under the action of aluminate ionic liquids. For the successful isomerization of hydrocarbon $C_{14}H_{22}$ containing two hydrogen atoms more, the addition of Pd/C to the reaction medium is necessary.



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Diamondoids represent a group of three-dimensional cyclohexane ring alkanes comprising symmetrical and deformation-free diamond-like structures with fused rings in a chair conformation.[1–3] The simplest diamondoid is adamantane, which is followed by homologous diamantane **1**, triamantane, tetramantane, pentamantane, and hexamantane.[4] Diamondoids are characterized by unique physicochemical properties, including chemical and physical stability, high melting point and specific heat.[5–11] The adamantane chemistry has been extensively studied, and its derivatives are applied, most often, as antiviral agents and for treatment of diseases of the central nervous system.[12–17] The chemical transformations of diamantane **1** have been investigated much less, which is mainly due to the absence of efficient methods for its synthesis.

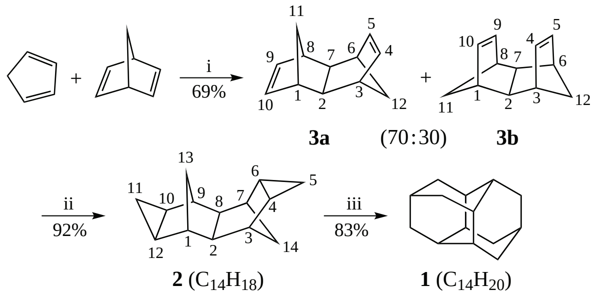
According to published data, diamantane **1** can be isolated from crude oil, however, its content is low.[18,19] Preparative methods for the synthesis of diamantane **1** from norbornadiene dimers (NBD),[20–26] cycloheptatriene,[27,28] and spiro[2.4]hepta-4,6-diene[29] include the use of acid catalysts. Diamantane **1** is of considerable interest as a precursor for the synthesis of pharmaceutical agents, polymer materials, solvent-resistant rubbers, and thermally stable synthetic lubricating oils or their components, in particular, cable oil.[1,30] Therefore, the search for new promising methods for the synthesis of diamantane **1** is relevant. It is noteworthy that adamantane and diamantane derivatives and some other highly strained polycyclic compounds, including cyclopropane-containing hydrocarbons, have been actively studied in the last decade owing to their thermal stability, high density, high calorific value, and good low-temperature characteristics. The unique properties make these compounds promising energy intensive fuels for aircraft and rocket engines.[31–37]

In this study, new methods for the synthesis of diamantane $C_{14}H_{20}$ **1** from three new cyclopropane-containing hydrocarbons avalilable from norbornadiene, 5-methylnorbornene, and cyclopentadiene are reported. These precursors have different compositions, $C_{14}H_{18}$, $C_{14}H_{20}$ and even $C_{14}H_{22}$ with two extra hydrogen atoms.

Hydrocarbon $C_{14}H_{18}$, namely, *exo*,*endo*-hexacyclo[7.3.1.1^{3,7}.0^{2,8}.0^{10,12}]tetradecane **2**, was obtained for the first time from a mixture of *exo*,*endo*- and *endo*,*endo*-tetracyclo[6.2.1.0^{2,7}.0^{3,6}]dodeca-4,9-dienes **3a** and **3b**, respectively, by cyclopropanation of their double bonds with diiodomethane–triethylaluminum system.[38] According to NMR spectroscopy data, cyclopropanation of isomers **3a** and **3b** gave only one, the most stable *exo*,*endo*-isomer **2** in 92% yield (Scheme 1). As regards hydrocarbons **3a**,**b** prepared by cycloaddition of cyclopentadiene with norbornadiene at 190 °C for 18 h,[39] their ^{1}H NMR spectra exhibited signals at 6.23, 6.06, and 0.97 ppm, characteristic of olefinic protons and bridging group protons for the *exo*-substituted norbornane moiety of **3a**. Also, the ^{1}H NMR spectrum of compound **3b** showed a signal at 5.33 ppm; according to published data,[40,41] this signal was assigned to the olefinic protons of the *endo*-disubstituted norbornene moiety of hydrocarbon **3b**.

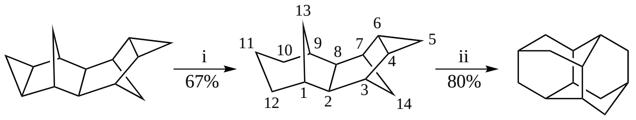
Previously,[23] we ascertained that the conversion of norbornadiene dimers $C_{14}H_{18}$ to diamantane ($C_{14}H_{20}$) was catalyzed by ionic liquids (ILs), with the $[Et_3NH]^+[Al_2Cl_7]^-$ being the most efficient and selective. In view of the fact that molecule **2** contains two hydrogen atoms less than the diamantane molecule, one may assume that the IL would induce conversion of hydrocarbon **2** to diamantane **1**. In fact, the action of $[Et_3NH]^+[Al_2Cl_7]^-$ on hydrocarbon **2** did really cause its selective conversion into diamantane in 83% yield. The reaction proceeded at 50 °C for 6 h (see Scheme 1).

Relying on previous study[24] in which diamantane **1** was prepared from binor-S (heptacyclic NBD dimer containing two



Scheme 1 *Reagents and conditions*: i, 190 °C, 18 h; ii, CH_2I_2, $AlEt_3$, CH_2Cl_2, room temperature, 10 h; iii, $[Et_3NH]^+[Al_2Cl_7]^-$, 50 °C, 6 h.

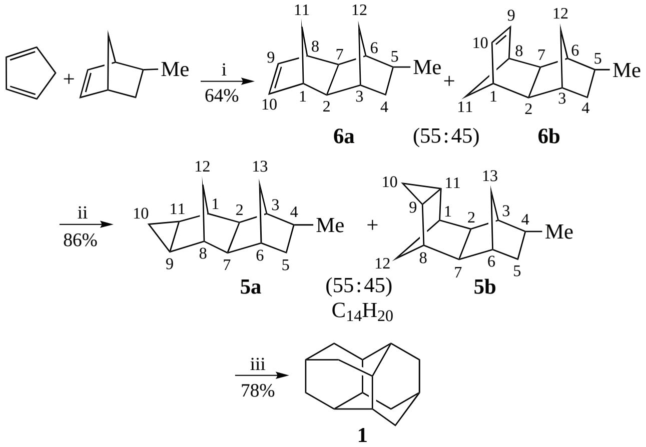
cyclopropane rings) on treatment with concentrated sulfuric acid, one may assume that hydrocarbon **2** would behave similarly. However, the reaction of hexacyclic hydrocarbon **2** with H_2SO_4 in cyclohexane followed a different pathway, namely, hydrogenolysis of one, less shielded three-carbon ring took place, resulting in pentacyclo[7.3.1.1^{3,7}.0^{2,8}.0^{4,6}]-tetradecane **4** in 67% yield. The structure of compound **4** was confirmed by gas chromatography/mass spectrometry and by NMR spectroscopy. Hydrocarbon **4** has the same composition $C_{14}H_{20}$ as diamantane **1**. Its further treatment with IL $[Et_3NH]^+[Al_2Cl_7]^-$ selectively afforded diamantane **1** in up to 80% yield (Scheme 2).



2 ($C_{14}H_{18}$) **4** ($C_{14}H_{20}$) **1**

Scheme 2 *Reagents and conditions*: i, H_2SO_4, cyclohexane, room temperature, 7 h; ii, $[Et_3NH]^+[Al_2Cl_7]^-$, 50 °C, 6 h.

4-Methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecanes **5a**,**b** $C_{14}H_{20}$ contain methyl group and cyclopropane ring (Scheme 3). Their mixture was prepared by cyclopropanation of *exo,exo*/*endo,exo*-5-methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-enes **6a**,**b** with diiodomethane–Et_3Al system. In turn, hydrocarbons **6a,b** were accessed by the Diels–Alder reaction of cyclopentadiene with 5-methylbicyclo[2.2.1]hept-2-enes at 190 °C for 20 h.[39] Under the action of IL $[Et_3NH]^+[Al_2Cl_7]^-$, methyl-containing hydrocarbons **5a**,**b** readily isomerized to diamantane **1** under typical conditions (see Scheme 3).



6a (55 : 45) **6b**

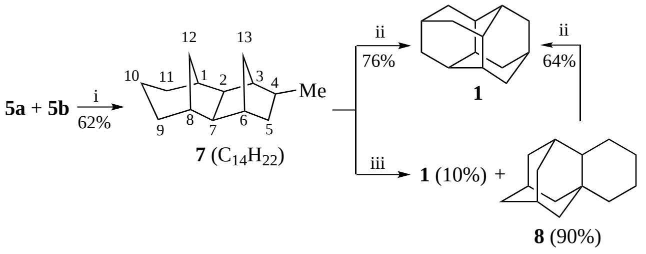
5a (55 : 45) **5b**

$C_{14}H_{20}$

1

Scheme 3 *Reagents and conditions*: i, 190 °C, 20 h; ii, CH_2I_2, $AlEt_3$, CH_2Cl_2, room temperature, 6 h; iii, $[Et_3NH]^+[Al_2Cl_7]^-$, 50 °C, 6 h.

Treatment of *exo*,*exo*/*endo*,*exo*-isomer mixture **5a**,**b** with H_2SO_4 in cyclohexane led to hydrogenolysis of the cyclopropane ring to give a $C_{14}H_{22}$ hydrocarbon **7** with two hydrogen atoms more than diamantane **1**. According to the data of NMR spectroscopy, compound **7** was formed as individual *exo,exo*-isomer (Scheme 4). It was found that for smooth and selective conversion of compound **7** to diamantane **1** the addition of Pd/C to the ionic liquid was required. Evidently, the addition of Pd/C promoted the elimination of a hydrogen molecule in the course of the transformation. When the process was carried out in the absence of Pd/C, the reaction was non-selective, and the reaction mixture was dominated by 1,2-butanoadamantane **8** ($C_{14}H_{22}$). An additional experiment showed that the processing of hydrocarbon **8** in IL in the presence of Pd/C under similar conditions (50 °C for 6 h) afforded diamantane **1** in a yield of 64% (see Scheme 4).



7 ($C_{14}H_{22}$) **1** **1** (10%) + **8** (90%)

Scheme 4 *Reagents and conditions*: i, H_2SO_4, cyclohexane, room temperature, 7 h; ii, $[Et_3NH]^+[Al_2Cl_7]^-$ + Pd/C, 50 °C, 6 h; iii, $[Et_3NH]^+[Al_2Cl_7]^-$, 50 °C, 6 h.

To conclude, the synthesis of diamantane by skeletal isomerization of new hydrocarbons $C_{14}H_{18}$, $C_{14}H_{20}$, and $C_{14}H_{22}$ under the action of the $[Et_3NH]^+[Al_2Cl_7]^-$ ionic liquid was accomplished. The precursor hydrocarbons were obtained by [4 + 2]-cycloaddition of cyclopentadiene to norbornadiene or 5-methylnorbornene followed by cyclopropanation of the olefinic bond and hydrogenolysis of the cyclopropane ring.

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The results were obtained on unique equipment at the ‘Agidel’ Collective Usage Center (Ufa Federal Research Center, Russian Academy of Sciences).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.022.

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