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Synthesis of diamantane by skeletal isomerization of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane induced by ionic liquids

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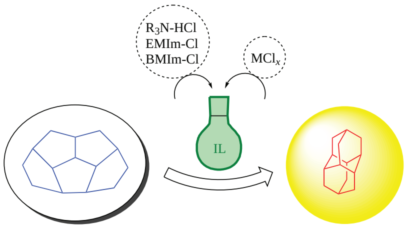
Diamantane was synthesized by skeletal isomerization of a new precursor pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane being the hydrogenated norbornadiene dimer of an unusual structure wholly composed of five-membered rings. The isomerization was induced by ionic liquids based on aluminum, iron, nickel, manganese, zinc, tin, and copper salts, among which aluminate ionic liquids were the most efficient ensuring diamantane yields of up to 85%.



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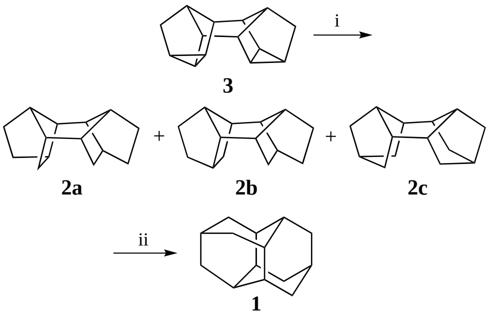
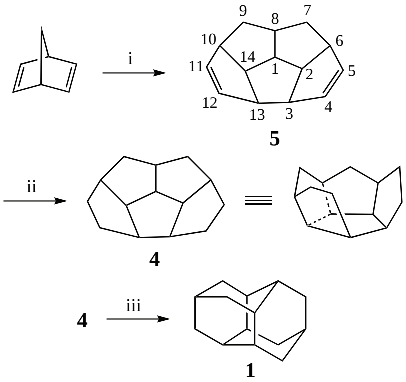
Among the huge variety of hydrocarbons, a special place is occupied by diamond-like hydrocarbons (diamondoids) which have been used in recent decades in organic and inorganic chemistry, materials science, bioengineering, and medicine.[1–8] Adamantane (tricyclo[3.3.1.1^{3,7}]decane), the first member of this family, is formed upon fusion of three cyclohexane rings in the chair conformation. The second representative of this series is diamantane, pentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane **1**. Whereas the synthesis and chemical transformations of adamantane have been studied rather extensively, the diamantane chemistry has been less investigated, which is caused by the absence of efficient methods for its synthesis. Several documented[9–15] preparative methods for the synthesis of diamantane **1** comprise the acid-catalyzed skeletal isomerization of polycyclic $C_{14}H_{18-20}$ hydrocarbons. In particular, the best precursors for the synthesis of diamantane **1** are three isomeric polycyclic hydrocarbons **2a–c**, obtained by hydrogenation of norbornadiene [4+4]-dimer, binor-S **3**. Hydrocarbons **2a–c** containing three cyclohexane rings each are readily isomerized to diamantane **1** on treatment with $AlBr_3$ (Scheme 1).

In this study, we intended to explore the possibility of synthesizing diamantane **1** from a new precursor, hydrogenated dimer of norbornadiene of an unusual structure composed exclusively of five-membered rings, namely, pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane **4**. We heterin obtained hydrocarbon **4** by hydrogenation of its unsaturated analogue **5**. Compound **5** being a norbornadiene dimer, *viz*. pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene, was previously described by Japanese chemists.[16] We carried out the hydrogenation of **5** with hydrogen gas under mild conditions: 20 °C, 8 h, H_2 pressure of 1 atm, in the presence of 10% Pd/C (Scheme 2).

Here we studied the catalytic activity of ionic liquids containing Al^{III}, Fe^{III}, Ni^{II}, Zn^{II}, Mn^{II}, Sn^{II} and Cu^{II} chlorides towards isomerization of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]-tetradecane **4** to diamantane **1** (see Scheme 2). In our previous study of the isomerization of hydrogenated hexacyclic norbornadiene dimers to diamantane **1** induced by aluminate ionic liquids (ILs), the highest yield was attained when the IL was used in a threefold molar excess relative to the substrate (reaction conditions: 50 °C, 6–8 h).[13] In a series of control experiments, we found that these conditions were also optimal for isomerization **4** → **1**. Raising the temperature to 70–80 °C led to a decrease in the yield of compound **1** due to resinification, while at lower temperatures (20–40 °C) the conversion of compound **4** was also lower. The ILs served simultaneously as catalysts and as solvents;



Scheme 1 *Reagents and conditions*: i, H_2/Pt, 200 °C, 305 atm; ii, $AlBr_3$, cyclohexane.



Scheme 2 *Reagents and conditions*: i, Ru(cod)(cot) (0.02 equiv.), dimethyl fumarate (0.2 equiv.), THF, 40 °C, 1 h; ii, H_2 (1 atm), 10% Pd/C (0.1 equiv.), hexane, room temperature, 8 h; iii, ionic liquid (3 equiv.), 50 °C, 6 h.

Table 1 Isomerization of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane **4** to diamantane **1** induced by ionic liquids.[a]

Entry	IL	Yield of **1** (%)	Entry	IL	Yield of **1** (%)
1	$[Et_3NH]^+[AlCl_4]^-$	33	10	$[BMIM]^+[Fe_2Cl_7]^-$	13
2	$[EMIM]^+[AlCl_4]^-$	23	11	$[Et_3NH]^+[Fe_2Cl_7]^-$	16
3	$[BMIM]^+[AlCl_4]^-$	29	12	$[BMIM]^+[NiCl_3]^-$	7
4	$[EMIM]^+[Al_2Cl_7]^-$	51	13	$[BMIM]_2{}^+[NiCl_4]^-$	6
5	$[BMIM]^+[Al_2Cl_7]^-$	56	14	$[Et_3NH]^+[Zn_2Cl_5]^-$	5
6	$[Me_3NH]^+[Al_2Cl_7]^-$	64	15	$[BMIM]^+[Mn_2Cl_5]^-$	10
7	$[Et_3NH]^+[Al_2Cl_7]^-$	76	16	$[Et_3NH]^+[Mn_2Cl_5]^-$	13
8	$[Et_3NH]^+[Al_2Cl_7]^-$–$CuCl_2$	85	17	$[Et_3NH]^+[Sn_2Cl_5]^-$	<1
9	$[BMIM]^+[FeCl_4]^-$	8	18	$[Et_3NH]^+[Cu_2Cl_5]^-$	<1

[a] Reaction conditions: 50 °C, 6 h, ratio **4**/IL = 1 : 3.

therefore, all experiments were carried out with a threefold excess of IL relative to hydrocarbon **4** at 50 °C for 6 h (see Scheme 2).

In the presence of ILs based on $ZnCl_2$, $CuCl_2$, and $SnCl_2$, the yields of diamantane **1** did not exceed 5%, while in the presence of ILs based on $FeCl_3$, $MnCl_2$, and $NiCl_2$, the yields were not higher than 16% (Table 1, entries 9–18). This is apparently related to the strength of Lewis acids, which decreases in the sequence $AlCl_3 > FeCl_3 > MnCl_2 > NiCl_2 > ZnCl_2 > CuCl_2 > SnCl_2$. Indeed, ionic liquids based on $AlCl_3$ proved to be most efficient. Moderate and good yields of diamantane **1** were observed in the presence of $[EMIM]^+[Al_2Cl_7]^-$, $[BMIM]^+[Al_2Cl_7]^-$, $[Me_3NH]^+[Al_2Cl_7]^-$, and $[Et_3NH]^+[Al_2Cl_7]^-$ (entries 1–7). As noted in our previous work,[15] the addition of $CuCl_2$ to ILs increased the yield of diamantane **1** due to the formation of a more efficient catalytic system. As shown by experiments, the highest (85%) yield of diamantane **1** was achieved using $[Et_3NH]^+[Al_2Cl_7]^-$ with $CuCl_2$ additive (entry 8).

In summary, the hydrogenated norbornadiene dimer of an unusual structure composed exclusively of five-membered rings, pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane **4**, was obtained for the first time and converted to diamantane **1** under the action of ionic liquids. Ionic liquid $[Et_3NH]^+[Al_2Cl_7]^-$ with the $CuCl_2$ additive was the most efficient catalyst for skeletal rearrangement of hydrocarbon **4** to diamantane **1,** providing 85% yield.

The results were obtained 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, registry no. FMRS-2022-0076.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.016.

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