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SHORT COMMUNICATIONS

Synthesis of Diamantane via Skeletal Isomerization of Hydrogenated Cyclohepta-1,3,5-triene Dimers in Ionic Liquid $[Et_3NH]^+ [Al_2Cl_7]^-$

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Abstract—Diamantane was synthesized in 91–97% yield by skeletal isomerization of a mixture of hydrogenated cyclohepta-1,3,5-triene dimers, pentacyclo[$8.4.0.0^{3,7}.0^{4,14}.0^{6,11}$]tetradecane and pentacyclo[$7.5.0.0^{2,8}.0^{5,14}.0^{7,11}$]tetradecane, at a ratio of 3 : 2 in the presence of ionic liquid $[Et_3NH]^+ [Al_2Cl_7]^-$.

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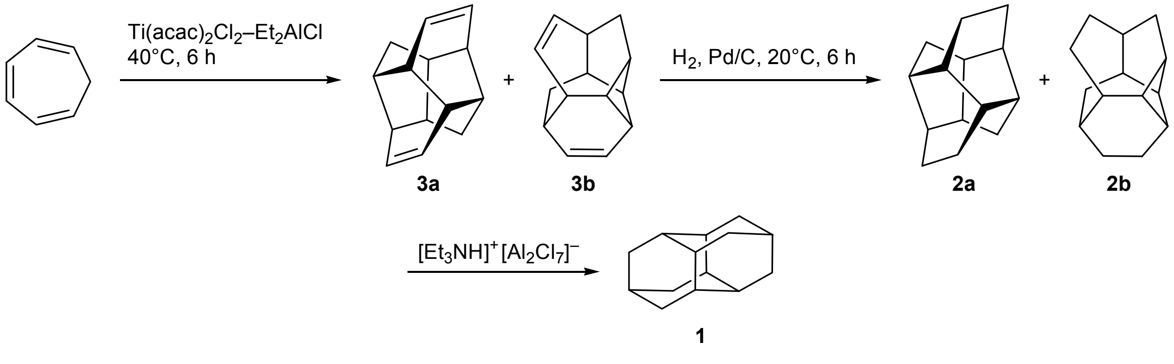
Diamantane (**1**) is the second member of the homologous series of diamond-like hydrocarbons (adamantanoids). It is used in the synthesis of heat-resistant synthetic lubricating oils (e.g., cable oil) or their components, solvent-resistant polymeric materials and rubbers, and medicinal agents [1–4].

The most widely known method of synthesis of diamantane (**1**) is based on skeletal isomerization of $C_{14}H_{20}$ hydrocarbons resulting from hydrogenation of heptacyclic norbornadiene dimer Binor-S. The yield of diamantane (**1**) in the isomerization of tetrahydro-Binor-S in the presence of CS_2–$AlBr_3$ [5], superacid catalysts $B(OSO_2CF_3)_3$, CF_3SO_3H–SbF_5, and CF_3SO_3H–$B(OSO_2CF_3)_3$ [6], and Na-Y zeolite [7] was 60–98%. Diamantane was also obtained in 89% yield by skeletal isomerization of individual hydrogenated cyclohepta-1,3,5-triene dimers, pentacyclo[$8.4.0.0^{3,7}.0^{4,14}.0^{6,11}$]tetradecane (**2a**) and pentacyclo[$7.5.0.0^{2,8}.0^{5,14}.0^{7,11}$]tetradecane (**2b**) [8]. The isomerization of **2a** and **2b** to diamantane (**1**) was accomplished in the presence of $AlCl_3$ at a ratio of 4.8 : 1 on heating in boiling methylene chloride for 12 h.

Inorganic ionic liquids are unique subjects of chemical studies; since the end of the XX century, they have been widely used in catalysis and organic synthesis. Inorganic ionic liquids exhibit properties of Brønsted or Lewis acids, as well as superacidic properties. In particular, superacidic properties are intrinsic to melts containing aluminum chloride, which makes them attractive for use as catalysts [9]. For example, the ionic liquid $[Et_3NH]^+ [Al_2Cl_7]^-$ showed a high catalytic activity in the isomerization of cyclohexane to methylcyclopentane [10].

We have found that $[Et_3NH]^+ [Al_2Cl_7]^-$ efficiently catalyzes the isomerization of a 3 : 2 mixture of pentacyclo[$8.4.0.0^{3,7}.0^{4,14}.0^{6,11}$]tetradecane (**2a**) and penta-



Synthesis of diamantane (**1**) by skeletal isomerization of a 3 : 2 mixture of pentacyclo[8.4.0.$0^{3,7}$.$0^{4,14}$.$0^{6,11}$]tetradecane (**2a**) and pentacyclo[7.5.0.$0^{2,8}$.$0^{5,14}$.$0^{7,11}$]tetradecane (**2b**)

Molar ratio (**2a**+**2b**)/ ionic liquid	Temperature, °C	Time, h	Conversion, %	Yield of **1**, %
3 : 1[a]	50	8	12	12
2 : 1[a]	50	8	53	53
1 : 1[a]	50	8	91	91
1 : 1[a]	80	8	79	79
1 : 2	50	8	100	93
1 : 2	50	4	94	94
1 : 2	50	5	100	97
1 : 2	80	2	100	97
1 : 2	20	40	100	95

[a] In cyclohexane.

cyclo[7.5.0.$0^{2,8}$.$0^{5,14}$.$0^{7,11}$]tetradecane (**2b**) to diamantane (**1**) in up to 97% yield. Hydrocarbon mixture **2a**/**2b** was obtained by cyclodimerization of cyclohepta-1,3,5-triene (6 h) [11], followed by hydrogenation of dimer mixture **3a**/**3b** (3 : 2) over Pd/C at room temperature. The best yield of **1** was achieved at a molar ratio of mixture **2a**/**2b** and the ionic liquid of 1 : 2. Depending on the reaction time (2–40 h) and temperature (20–80°C), the yield of **1** varied from 93 to 97%. When the ratio of **2a**/**2b** to $[Et_3NH]^+$ $[Al_2Cl_7]^-$ ranged from 1 : 1 to 3 : 1, the conversion decreased to 12% (see table); these ratios required the use of cyclohexane as solvent.

Thus, the ionic liquid $[Et_3NH]^+$ $[Al_2Cl_7]^-$ is an efficient catalyst for the isomerization of a 3 : 2 mixture of pentacyclo[8.4.0.$0^{3,7}$.$0^{4,14}$.$0^{6,11}$]tetradecane (**2a**) and pentacyclo[7.5.0.$0^{2,8}$.$0^{5,14}$.$0^{7,11}$]tetradecane (**2b**) to diamantane (**1**).

Isomer mixture 2a/2b. A glass reactor was charged with 0.5 g of Pd/C, 5 g of a 3 : 2 mixture of pentacyclo[8.4.0.$0^{3,7}$.$0^{4,14}$.$0^{6,11}$]tetradeca-8,12-diene (**3a**) and pentacyclo[7.5.0.$0^{2,8}$.$0^{5,14}$.$0^{7,11}$]tetradeca-3,12-diene (**3b**), and 15 mL of hexane, and hydrogen was supplied at a pressure of 1 atm at room temperature. When the reaction was complete, the mixture was filtered through a layer of silica gel, the sorbent was washed with hexane, and the solvent was distilled off. Yield 4.9 g (98%), isomer ratio **2a**/**2b** 3 : 2.

Pentacyclo[8.4.0.$0^{3,7}$.$0^{4,14}$.$0^{6,11}$]tetradecane (2a). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 46.88 (C^1, C^6), 41.85 (C^7, C^{14}), 41.52 (C^3, C^4), 34.42 (C^{10}, C^{11}), 32.52 (C^2, C^5), 26.04 (C^9, C^{12}), 22.03 (C^8, C^{13}). Mass spectrum, *m*/*z* (I_{rel}, %): 188 (30) $[M]^+$, 145 (28), 131 (35), 117 (26), 105 (32), 95 (38), 91 (89), 79 (100), 67 (46), 41 (43).

Pentacyclo[7.5.0.$0^{2,8}$.$0^{5,14}$.$0^{7,11}$]tetradecane (2b). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 51.34 (C^1), 50.96 (C^8), 43.12 (C^7), 43.01 (C^9), 41.38 (C^{14}), 41.02 (C^2), 35.86 (C^{11}), 35.78 (C^5), 31.33 (C^{10}), 31.30 (C^6), 25.43 (C^{12}), 25.12 (C^{13}), 24.17 (C^4), 23.91 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 188 (100) $[M]^+$, 173 (16), 117 (24), 92 (30), 91 (47), 79 (40), 67 (17), 41 (20).

Diamantane (1). A 50-mL glass reactor was charged under argon with 0.3 g (1 mmol) of isomer mixture **2a**/**2b** and 1.29 g (2 mmol) of preliminarily prepared $[Et_3NH]^+$ $[Al_2Cl_7]^-$ [12]. The mixture was stirred for 5 h at 50°C, cooled to room temperature, and extracted with petroleum ether. The extract was filtered through a layer of silica gel, the sorbent was washed with petroleum ether, the solvent was distilled off, and the residue was recrystallized from ethyl acetate–cyclohexane (1 : 1). Yield 0.291 g (97%), white crystals, mp 244–245°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 37.76 (C^1, C^2, C^6, C^7, C^{11}, C^{12}), 38.51 (C^3, C^5, C^8, C^{10}, C^{13}, C^{14}), 26.18 (C^4, C^9). Mass spectrum, *m*/*z* (I_{rel}, %): 188 (100) $[M]^+$, 160 (5), 159 (10), 145 (8), 131 (13), 130 (18), 120 (7), 105 (15), 91 (28), 79 (25), 67 (15). Found, %: C 88.75; H 11.25. $C_{14}H_{20}$. Calculated, %: C 88.29; H 10.71.

The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance III-500 spectrometer at 500 and 125 MHz, respectively, using $CDCl_3$ as solvent; the chemical shifts are given relative to tetramethylsilane. The mass spectra were obtained on a Shimadzu GCMS-QP2010 Plus instrument (SPB-5 capillary column, 30 m×0.25 mm; carrier gas helium, oven temperature programming from 40 to 300°C at a rate of 8 deg/min; injector temperature 280°C, ion source temperature 200°C; electron impact, 70 eV). Chromatographic analysis was performed on Shimadzu GC-9A and GC-2014 instruments (2 m × 3-mm column packed with 5% SE-30 on Chromaton N-AW-HMDS, oven temperature programming from 50 to 270°C at a rate of 8 deg/min; carried gas helium, flow rate 47 mL/min).

Cyclohepta-1,3,5-triene, triethylamine hydrochloride, cyclohexane, $AlCl_3$, and 10% Pd/C were commercial products.

The structural studies were performed using unique equipment of the Agidel Joint Regional Center.

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