A new method was developed for the direct synthesis of the second representative of the homologous series of diamond-like hydrocarbons, diamantane, in 65% yield by hydroisomerization of the norbornadiene dimer, endo-endo-heptacyclo[8.4.0.0₂₂.₆.₀₃₃.₀₇₇.₀₉₉.₀₁₁₁₃]tetradecane (binor-S) on treatment with concentrated sulfuric acid (98%). In the presence of H₂SO₄ of lower concentration (75–80%), the reaction stops after the hydrogenation step giving endo-endo-pentacyclo[7.3.1.1³⁵.₁⁸.₀³₇]tetradecane in 68% yield with excellent selectivity (100%).

**Abstract**

A new method was developed for the direct synthesis of the second representative of the homologous series of diamond-like hydrocarbons, diamantane, in 65% yield by hydroisomerization of the norbornadiene dimer, endo-endo-heptacyclo[8.4.0.0₂₂.₆.₀₃₃.₀₇₇.₀₉₉.₀₁₁₁₃]tetradecane (binor-S) on treatment with concentrated sulfuric acid (98%). In the presence of H₂SO₄ of lower concentration (75–80%), the reaction stops after the hydrogenation step giving endo-endo-pentacyclo[7.3.1.1³⁵.₁⁸.₀³₇]tetradecane in 68% yield with excellent selectivity (100%).

**Introduction**

Among the highly diverse polycyclic and cage compounds, an important place is occupied by diamond-like compounds called diamondoids, whose lower representatives belong to the homologous series C₄n+6H₄n+12. Owing to the rigid structure, diamondoids typically have high thermal stability and high reactivity compared with aliphatic and alicyclic saturated hydrocarbons and show peculiar chemical behavior.

Crude oil is known to be the main natural source of diamondoids. In the oil and gas field exploration, the presence of diamondoids is used to evaluate the field maturity. Whereas the synthesis and chemical reactivity of adamantane, the first member of the diamondoid homologous series, which is produced on an industrial scale (prepared by AlBr₃ or AlCl₃-induced skeletal isomerization of a petrochemical monomer, hydrogenated dicyclopentadiene) [1], have been studied rather extensively, the chemical behavior of diamantane, the second member of the diamondoid homologous series, has been poorly studied. The main cause of this situation is the lack of facile methods for its synthesis.

In the literature, diamantane (1) is prepared by skeletal isomerization of strained C₁₄H₂₀ polycyclic hydrocarbons [2-7]. In particular, the most suitable initial compounds for the preparation of diamantane are three isomeric polycyclic hydrocarbons C₁₄H₂₀ 3a–c, which are obtained
by hydrogenation of the norbornadiene dimer, heptacyclo[8.4.0.0\(^1\),2,7.0\(^{6,11}\),0\(^{11,13}\)]tetradecane (binor-S, 2). Binor-S is hydrogenated in the presence of a platinum catalyst (H\(_2\)PtCl\(_6\), PtO\(_2\)) in glacial acetic acid under high pressure conditions at 70 °C and 200 psi of H\(_2\) [8,9]. In the presence of superacid catalysts, such as B(OSO\(_2\)CF\(_3\))\(_3\), CF\(_3\)SO\(_2\)H/SbF\(_5\) 1:1, CF\(_3\)SO\(_2\)H/B(OSO\(_2\)CF\(_3\))\(_3\) 1:1 [10], NaBH\(_4\)/CF\(_3\)SO\(_2\)H [11], or zeolite Y in the NaH form (NaY) [12], hydrocarbons 3a–c isomerize to diamantane in up to 99% yield (Scheme 1).

As can be seen from Scheme 1, the synthesis of diamantane (1) from binor-S (2) is a two-step process, in which the hydrogenation performed in the first step is most complex and has always been an obstacle to the generation of large amounts of diamantane. In view of the foregoing, we set ourselves the task to develop a one-pot method for the synthesis of diamantane (1) from binor-S (2).

**Results and Discussion**

In this study, we developed a new method for the synthesis of pentacyclo[7.3.1.1\(^2\),5.1\(^8,10\),0\(^{11,13}\)]tetradecane (diamantane, 1) by skeletal hydroisomerization of endo-endo-heptacyclo[8.4.0.0\(^1\),2,7.0\(^{6,11}\),0\(^{11,13}\)]tetradecane (binor-S, 2) on treatment with sulfuric acid (Scheme 2).

The reaction selectivity and the yield of diamantane (1) considerably depend on the reaction conditions and the solvent nature. Indeed, at 20–40 °C, hydroisomerization of binor-S (2) in cyclohexane in the presence of 98% sulfuric acid ([2]/[H\(_2\)SO\(_4\)] = 1:10–50) during 7–15 h affords a mixture of endo-endo-pentacyclo[7.3.1.1\(^2,5\),1\(^8,10\)]tetradecane (tetrahydrobinor-S, 3c) and diamantane (1) (Table 1). An increase in the sulfuric acid ratio to binor-S (2) ([2]/[H\(_2\)SO\(_4\)] = 1:20–50) and rising the temperature to 40 °C lead to decreased product yield due to resinification. When the H\(_2\)SO\(_4\) ratio to binor-S (2) is 1:5, the conversion of compound 2 decreases to 10%. On the other hand, when the reactions are carried out in CS\(_2\) or without any solvent, the selectivity to diamantane (1) increases to 100%, with the maximum yield being 65% (Table 1, entry 12). A portion of binor-S (2) is converted to resinous products. When the reaction was ultrasonically assisted, the reaction time decreased to 2 h with the yield of diamantane (1) being retained (62%).

In order to answer the question of what is the hydrogen source in the hydroisomerization of binor-S (C\(_{14}\)H\(_{16}\), 2) containing 4 hydrogen atoms less than diamantane (C\(_{14}\)H\(_{20}\), 1), we carried out a series of control experiments using deuterated sulfuric acid (98%) in cyclohexane (C\(_6\)H\(_{12}\), experiment A), in deuterated cyclohexane (C\(_6\)D\(_{12}\)), or in carbon disulfide (CS\(_2\), experiment C).

In experiment A, the major isomer 1-D\(_2\), which is formed upon hydroisomerization of binor-S (2), contains two deuterium atoms. Two more hydrogen atoms are probably provided by cyclohexane. Unexpectedly, the reaction also gave undeuterated diamantane (1), which may be due to deuterium exchange with hydrogen of cyclohexane under the action of D\(_2\)SO\(_4\).
The major product 1-D₃, which is formed in experiment B with D₂SO₄ in C₈D₁₂ contains three deuterium atoms. The expected isomer with four deuterium atoms is formed in a minor amount. Evidently, binor-S (2) acts as the hydrogen source for the isomer C₁₄H₁₇D₃, 1-D₃. Our attempt to carry out the deuteration of diamantane (1) with D₂SO₄ in carbon disulfide for 7 h at 20 °C was unsuccessful. Evidently, the deuterium exchange, resulting in the formation of diamantanes 1-D₇ and 1-D₈ containing 7 and 8 deuterium atoms, occurs at the hydroisomerization step (experiment C).

As shown by further studies, when the sulfuric acid concentration decreases to 75–80%, the reaction stops at the intermediate step giving endo-endo-pentacyclo[7.3.1.1³,5,1⁸,1⁰,0⁴,7]tetradecane (tetrahydrobinor-S, 3c; Scheme 3). It should be emphasized that the reaction selectively gives only one of the possible isomers, hydrocarbon 3c, which is confirmed by ¹H and ¹³C NMR spectral data. The ¹³C NMR spectrum of compound 3c shows five characteristic carbon signals at 33.44, 35.64, 37.84, 38.30, and 40.49 ppm, coinciding with the reported values [13]. Since 75–80% H₂SO₄ contains 20–25% water, the participation of water as a hydrogen source in the reaction cannot be ruled out either.

Attempts to perform hydroisomerization of binor-S (2) to diamantane (1) on treatment with nitric or orthophosphoric acid were unsuccessful, with the starting binor-S (2) being recovered unchanged. The reaction of hydrocarbon 2 with hydrochloric acid proceeds with the addition of HCl to the cyclopropane ring and results in the formation of a mixture of mono- and dichloro derivatives, the synthesis of which has been reported [13,14]. When sulfuric acid is replaced by an ionic liquid prepared from triethylamine and sulfuric acid [15], the reaction follows a different route: Starting binor-S (2) is converted to two isomeric hexacyclic hydrocarbons, hexacyclo[8.4.0.0²,7.0³,1⁴,0⁴,8,0⁹,1³]tetradec-5-ene (4a) and hexacyclo[6.6.0.0²,6.0⁵,1⁴,0⁷,1²,0⁹,1³]tetradec-3-ene (4b), which are important precursors for the synthesis of triamantane [10,11,16-24] (Scheme 4).

**Conclusion**

Thus, we developed a new one-pot method for the synthesis of diamantane (1) by hydroisomerization of binor-S (2) on treatment with concentrated sulfuric acid (98%) in carbon disulfide.
or cyclohexane. It was found that both, sulfuric acid and cyclohexane can serve as the main hydrogen sources. In the presence of H$_2$SO$_4$ with a lower concentration (75–80%), the reaction stops at the step of formation of endo-endo-penta-cyclo[7.3.1.1$^2$.5,1$^8$.10,6$^3$.7]tetradecane (3c) in 68% yield.

**Experimental**

**General procedures and materials:** $^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance-III 400 Ascend instrument (400 MHz for $^1$H and 100 MHz for $^{13}$C in CDCl$_3$). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m × 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 (100 × 35 mm 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, evaporation temperature of 280 °C, and ionization energy of 70 eV). The characteristic data and graphical spectra of diamantane are almost identical with the literature data [25].

**Preparation of diamantane:** Heptacyclo[8.4.0.0$^2$.12,0$^3$.8,0$^4$.6,0$^5$.9,0$^{11}$.13]tetradecane (2, 0.368 g, 2 mmol) was charged into a glass reactor (V = 100 mL). Then, concentrated (98%) sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. When the whole amount of H$_2$SO$_4$ has been added, the reaction mixture was stirred at 20 °C for 15 h. After completion of the reaction, 10% NaOH was added to the reaction mixture, the organic phase was separated, and filtered through a silica gel layer (with petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 ethyl acetate/cyclohexane mixture. The characteristic data and graphical spectra of diamantane are almost identical with the literature data [25].

**Preparation of endo-endo-penta-cyclo[7.3.1.1$^2$.5,1$^8$.10,6$^3$.7]tetradecane (tetrahydrobinor-S, 3e):** Heptacyclo[8.4.0.0$^2$.12,0$^3$.8,0$^4$.6,0$^5$.9,0$^{11}$.13]tetradecane (2, 0.368 g, 2 mmol) was charged into a glass reactor (V = 100 mL) and dissolved in cyclohexane (10 mL). Then, 75–80% sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. When the whole amount of H$_2$SO$_4$ has been added, the reaction mixture was stirred at 20 °C for 7 h. After completion of the reaction, 10% NaOH was added to the reaction mixture, the organic part was separated, and filtered through a silica gel layer (with petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 ethyl acetate/cyclohexane mixture. Colorless crystals; 68% yield; mp 104–106 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.95–0.98 (m, 4H), 1.38 (s, 8H), 1.66–1.71 (m, 4H), 1.99–2.01 (m, 2H), 2.12–2.16 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 33.42 (C$^6$, C$^9$, C$^{13}$, C$^{14}$), 35.63 (C$^1$, C$^2$, C$^7$, C$^8$), 37.82 (C$^5$, C$^{10}$), 38.27(C$^3$, C$^{12}$), 40.47 (C$^4$, C$^{11}$); EIMS (70 eV, m/z): 188 [M]$^+$ (100), 187 (35), 159 (24), 145 (23), 131 (38), 117 (25), 105 (39), 91(82), 79 (57), 67 (29), 41 (47) %; Anal. calcd for C$_{14}$H$_{20}$: C, 89.29; H, 10.71; found: C, 89.14; H, 10.86.

**Preparation of hexacyclo[8.4.0.0$^2$.12,0$^3$.8,0$^4$.6,0$^5$.9,0$^{11}$.13]tetradec-5-ene (4a) and hexacyclo[6.6.0.0$^2$.26,0$^3$.8,0$^4$.14,0$^5$.9,0$^{10}$.13]tetradec-3-ene (4b):** Heptacyclo[8.4.0.0$^2$.12,0$^3$.8,0$^4$.6,0$^5$.9,0$^{11}$.13]tetradecane (2, 0.368 g, 2 mmol) was charged into a glass reactor (V = 100 mL) and dissolved in cyclohexane. Then, [Et$_3$NH]$^+$[H$_2$SO$_4$]$^-$ (1.99 g, 10 mmol) was added and the reaction mixture was stirred at 40 °C for 8 h. Then the reaction was cooled to room temperature, the reaction mixture extracted with petroleum ether, and filtered through a silica gel layer (with petroleum ether as the eluent). The characteristic data and graphical spectra of diamantane are almost identical with the literature data [25].

[Scheme 4: Isomerization of binor-S (2) to hydrocarbons 4a and b.]
Supporting Information

Supporting Information File 1
Experimental procedures, NMR, and mass spectral data.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-16-205-S1.pdf]

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