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A new method for the synthesis of diamantane by hydroisomerization of binor-S on treatment with sulfuric acid

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Keywords:

diamantane; binor-S; tetrahydrobinor-S; hydroisomerization; sulfuric acid

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 norbornadiene dimer, *endo*-*endo*-heptacyclo[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecane (binor-S) on treatment with concentrated sulfuric acid (98%). In the presence of H_2SO_4 of lower concentration (75-80%), the reaction stops after hydrogenation step giving *endo*-*endo*-pentacyclo[7.3.1.$1^{2,5}$.$1^{8,10}$]tetradecane in 68% yield.

Introduction

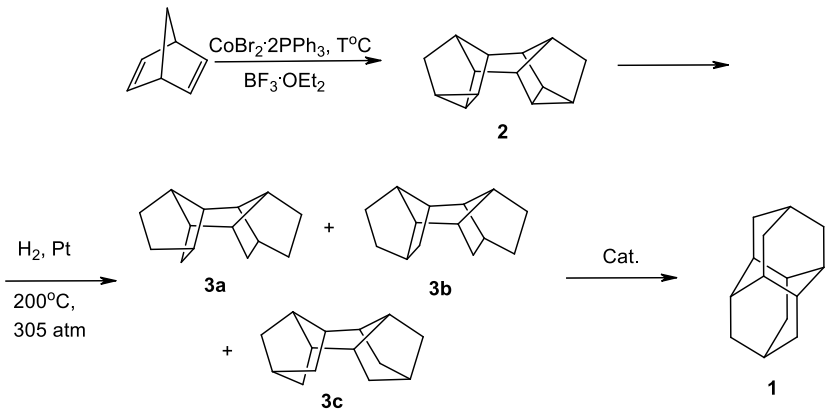
Among the highly diverse polycyclic and cage compounds, an important place is occupied by diamond-like compounds called diamondoids, whose lower representatives belong to homologous series $C_{4n+6}H_{4n+12}$. Owing to the rigid structure, diamondoids typically have high thermal stability and high reactivity 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 $AlBr_3$- or $AlCl_3$-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 diamandoid 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 $C_{14}H_{20}$ polycyclic hydrocarbons [2-7].

In particular, the most suitable initial compounds for the preparative synthesis of diamantane are three isomeric polycyclic hydrocarbons $C_{14}H_{20}$ **3a-c**, which are obtained by hydrogenation of norbornadiene dimer, heptacyclo[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecane (binor-S) **2**. Binor-S is hydrogenated in the presence of a platinum catalyst (H_2PtCl_6, PtO_2) in glacial acetic acid under drastic conditions: 200°C and 305 atm of H_2 [8,9]. In the presence of superacid catalysts: $B(OSO_2CF_3)_3$, CF_3SO_3H-SbF_5 (1:1), CF_3SO_3H-$B(OSO_2CF_3)_3$ (1:1) [10], $NaBH_4$/CF_3SO_3H [11], or zeolite Y in the NaH form [12], hydrocarbons **3a-c** isomerize to diamantane in up to 99% yield (Scheme 1).



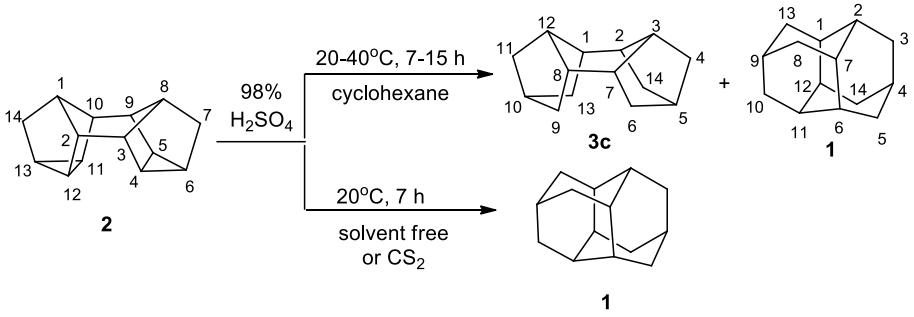
Scheme 1. Isomerization of **3a-c** to diamantane **1**.

As can be seen from Scheme 1, the synthesis of diamantane **1** from binor-S **2** is a two-step process, in which hydrogenation performed in the first step is most complex and has always been an obstacle to 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^{4,12}.0^{2,7}.0^{6,11}]tetradecane (diamantane) **1** by skeletal hydroisomerization of *endo*-*endo*-heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane (binor-S) **2** on treatment with sulfuric acid.



Scheme 2. Isomerization of binor-S **2** to diamantane **1**.

The reaction selectivity and the yield of diamantane **1** considerably depend on the reaction conditions and the solvent nature. Indeed, at 20-40°C, hydroizomerization of binor-S **2** in cyclohexane in the presence of 98% sulfuric acid ([**2**]:[H_2SO_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_2SO_4]=1:20–50) and temperature rise to 40°C lead to decreasing product yield due to resinification. When the H_2SO_4 ratio to binor-S **2** is 1 : 5, the conversion of binor-S decreases to 10%. When the reactions are carried out in CS_2 or without a 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.

Table 1. Hydroisomerization of binor-S **2** in the presence of sulfuric acid

Entry	Ratio **2**: H_2SO_4	Solvent	Temp. [°C]	Time [h]	Product Ratio [%][a]		
					2	**3c**	**1**
1	1:50	cyclohexane	40	7	2	10	23
2	1:50	cyclohexane	20	7	3	26	10
3	1:20	cyclohexane	40	7	3	52	28
4	1:20	cyclohexane	20	7	12	46	22
5	1:20	cyclohexane	20	15	-	55	31

6	1:10	cyclohexane	20	7	22	41	36
7	1:10	cyclohexane	20	15	16	47	34
8	1:5	cyclohexane	40	15	56	31	2
9	1:20	carbon disulfide	20	7	21	-	36
10	1:20	carbon disulfide	20	15	15	-	44
11	1:10	carbon disulfide	20	7	24	-	52
12	1:10	carbon disulfide	20	15	-	-	65
13	1:5	carbon disulfide	40	7	78	-	10
14	1:5	carbon disulfide	20	7	90	-	-
15	1:10	-	20	7	-	-	8
16[b]	1:10	cyclohexane	20	2	9	64	26
17[b]	1:10	carbon disulfide	20	2	-	18	62
18[b]	1:10	-	20	2	-	-	6

[a] Determined by GC using $C_{12}H_{26}$ as the internal standard. [b] The reaction was conducted under ultrasonic irradiation

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_6H_{12}) (experiment A), in deuterated cyclohexane (C_6D_{12}) (experiment B), or in carbon disulfide (CS_2) (experiment C).

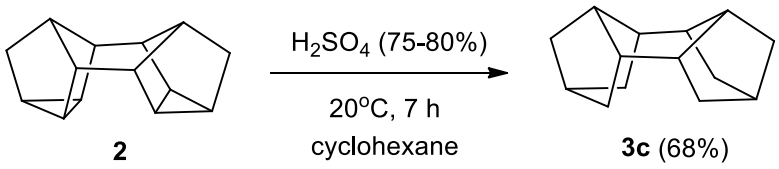
In experiment A, the major isomer **1-D_2**, which is formed upon hydroisomerization of binor-S **2**, contains two deuterium atoms. Two more hydrogen atoms are probably provided by cyclohexane. Unexpectedly, the reaction gave undeuterated diamantane **1**, which may be due to deuterium exchange with hydrogen of cyclohexane under the action of D_2SO_4.

The major product **1-D_3**, which is formed in experiment C with D_2SO_4 in C_6D_{12} 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 $C_{14}H_{17}D_3$ **1-D_3**.

Our attempt to carry out deuteration of diamantane **1** with D_2SO_4 in carbon disulfide for 7 h at 20°C was unsuccessful. Evidently, the deuterium exchange, resulting in the formation of diamantanes **1-D_7** and **1-D_8** containing 7 and 8 deuterium atoms, occurs at the hydroisomerization step.

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[7.3.1.1^{2,5}.1^{8,10}]tetradecane (tetrahydrobinor-S) **3c**. It should be emphasized that the reaction selectively gives only one of the possible isomers, hydrocarbon **3c**, which is confirmed by ^{1}H and ^{13}C NMR spectral data. The ^{13}C 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].

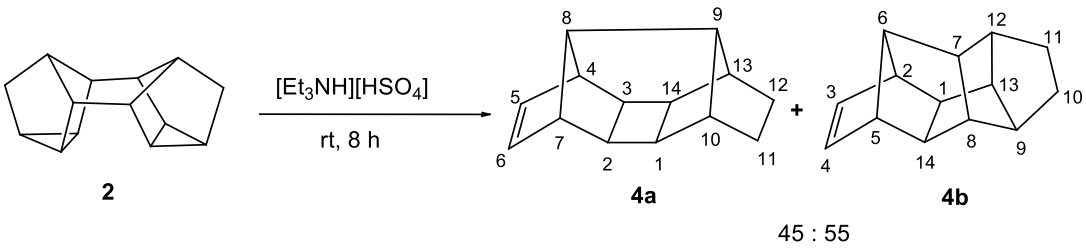
Since 75-80% H_2SO_4 contains 20-25% water, the participation of water as a hydrogen source in the reaction cannot be ruled out either.



Scheme 3. Selective synthesis of tetrahydrobinor-S **3c** from binor-S **2**.

Attempts to perform hydroisomerization of binor-S **2** to diamantane **1** on treatment with nitric or orthophosphoric acid were unsuccessful, the starting binor-S **2** being recovered unchanged. The reaction of hydrocarbon **2** with hydrochloric acid proceeds as 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 was reported in.[13,14]

When sulfuric acid is replaced by an ionic liquid prepared from triethylamine and sulfuric acid,[15] the reaction follows a different route: binor-S **2** is converted to two isomeric hexacyclic hydrocarbons, hexacyclo[8.4.0.0^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradec-5-ene **4a** and hexacyclo[6.6.0.0.^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-3-ene **4b**, which are important precursors for the synthesis of triamantane [10,11,16-24].



Scheme 4. Isomerization of binor-S **2** with hydrocarbons **4a, b**.

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_2SO_4 with a lower concentration (75-80%), the reaction stops at the step of formation of *endo-endo*-pentacyclo[7.3.1.1^{5,8}.0.0^{3,7}]tetradecane **3c** in 68% yield.

Experimental Section

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, 30m×0.25 mm, helium as the carrier gas, temperature programming from 40 to 300ºC at 8ºC/min, evaporation temperature of 280ºC, ion source temperature of 200ºC, 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 270ºC at 8ºC/min, helium as the carrier gas (47 mL/min)].

The sonication was carried out with an ultrasound generator IL10–0.63 (INLAB LTD) for 180 min at a frequency of 22 kHz with a submerged of 15 mm diameter titanium horn, with output power 150 W. The reactions were carried out in a 100 × 35 mm glass reactor equipped with a jacket to maintain the required temperature (20°C).

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) and the solvent were 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_2SO_4 was added, the reaction mixture was stirred at 20ºC 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.

Diamantane **1**. White crystals, yield 65%, mp 244–245°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.72–1.80 (m, 20H).^{13}C NMR (100 MHz, $CDCl_3$): δ=25.95 (C,^{4}C^{9}), 37.64 (C,^{3} C,^{5} C,^{8} C,^{10} C,^{13} C^{14}), 38.37 (C,^{1} C,^{2} C,^{6} C,^{7} C,^{11} C^{12}). MS(EI, 70 eV): m/z (%)=188 $[M]^+$ (100), 189 (15), 187 (18), 159 (10),145 (8), 131 (23), 130 (18), 117 (12), 105 (13), 93 (12), 92 (11), 91(28), 77 (15), 67 (8). Calcd for $C_{14}H_{20}$: C, 88.29; H, 11.71; found C, 88.75; H, 11.25.

Preparation of endo-endo-pentacyclo[7.3.1.1^{5,8}.0.0^{3,7}]tetradecane (tetrahydrobinor-S).
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_2SO_4 was 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.

Tetrahydrobinor-S **3c**. White crystals, 68% yield, mp 104-106°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=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, $CDCl_3$): δ=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}). MS(EI, 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). 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^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradec-5-ene and hexacyclo [6.6.0.0.^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-3-ene
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 $[Et_3NH]^+[HSO_4]^-$ (1.99 g, 10 mmol) was added, and the reaction mixture was stirred at 40°C for 8 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 (with petroleum ether as the eluent).

Hexacyclo[8.4.0.$0^{2,7}$.$0^{3,14}$.$0^{4,8}$.$0^{9,13}$]tetradecene-5 **4a** and hexacyclo[6.6.0.0.^{2,6}.$0^{5,14}$.$0^{7,12}$.$0^{9,13}$]tetradecene-3 **4b** (45:55)**.** Colorless oil, 78% yield; **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 7.2 Hz, 2H), 1.41 (d, *J* = 7.6 Hz, 2H), 1.95 (s, 2H), 2.09 (d, *J* = 7.2 Hz, 4H), 2.21 (d, *J* = 7.2 Hz, 2H) 2.56 (s, 2H), 5.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=26.27 (C,^{11} C^{12}), 34.62 (C,^{10} C^{13}), 36.34 (C,^{1} C^{14}), 37.27 (C,^{2} C^{3}), 40.68 (C,^{4} C^{7}), 44.68 (C^{8}), 52.88 (C^{9}), 134.82 (C,^{5} C^{6}). MS(EI, 70 eV): m/z (%)=184 $[M]^+$ (44), 169 (14), 155 (16), 142 (34), 117 (100), 115 (37), 105 (22), 91 (73), 80 (38), 65 (17), 41 (21). **4b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19–1.24 (m, 1H), 1.31–1.36 (m, 1H), 1.48 (s, 1H), 1.56–1.59 (m, 2H), 1.71 (t, *J* = 6 Hz, 1H) 2.03–2.06 (m, 3H), 2.15–2.17 (m, 2H), 2.22 (s, 1H), 2.52 (s, 2H), 2.59 (s, 1H), 5.96–5.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=24.08 (C^{10}), 27.16 (C^{11}), 40.52 (C^{1}), 40.93 (C^{12}), 42.30 (C^{14}), 45.66 (C^{9}), 47.38 (C^{2}), 47.94 (C^{13}), 48.61 (C^{7}), 50.20 (C^{8}), 54.09 (C^{5}), 60.05 (C^{6}), 133.69 (C^{4}), 133.75 (C^{3}). MS (EI, 70 eV): m/z (%)=184 $[M]^+$ (40), 169 (21), 155 (45), 141 (45), 129 (51), 117 (100), 115 (53), 91 (88), 78 (43), 65 (21), 41 (20).

Supporting Information

Supporting information includes experimental procedures, NMR and mass spectra data.

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