

# Synthesis of 1,3-Dimethyladamantane by Skeletal Rearrangement of C<sub>12</sub>H<sub>18</sub> and C<sub>12</sub>H<sub>20</sub> Hydrocarbons over Na/H-Y-Zeolite

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**Abstract**—Granular binder-free Y-zeolite with a degree of Na<sup>+</sup>/H<sup>+</sup> ion exchange of 0.97 efficiently catalyzed isomerization of tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane and (2aR,5aα,8aR,8bα)-dodecahydroacenaphthene (perhydroacenaphthene) to 1,3-dimethyladamantane.

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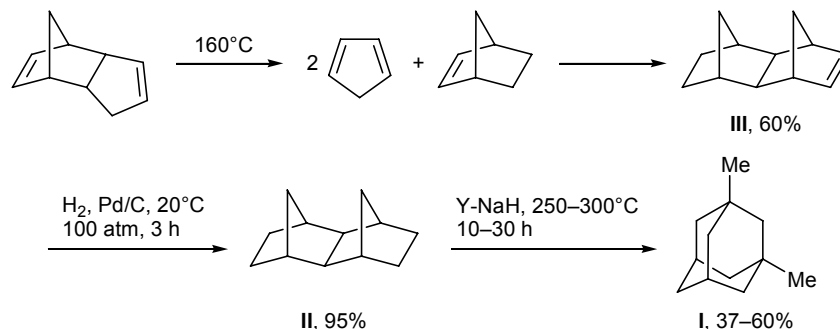
Adamantane and its derivatives are widely used in the synthesis of valuable chemical compounds for various branches of industry. Due to high thermal stability, adamantane derivatives have found application for the preparation of heat-resistant polymeric materials. They are also starting materials for the preparation of oils, hydraulic liquids, and antimicrobial lubricant additives. Another field of application of adamantane is the synthesis of antiviral and neurotropic drugs. 1,3-Dimethyladamantane (**I**) is one of the most important adamantane derivatives; it is used as starting compound for the synthesis of 3,5-dimethyladamantan-1-amine which is the active component of Memantine, an efficient drug for the treatment of Alzheimer's disease and other disorders of the central nervous system at early stages [1–4].

Several known methods of synthesis of 1,3-dimethyladamantane (**I**) are based on the isomerization of

C<sub>12</sub>H<sub>20</sub> cyclic hydrocarbons in the presence of acid catalysts. Most of these methods are not free from essential disadvantages, such as drastic conditions, the use of anhydrous aluminum halides or inorganic acids as catalysts, formation of a lot of wastes, and poor yields of the target product.

The present study was aimed at searching for inorganic acid catalysts ensuring isomerization of C<sub>12</sub>H<sub>18</sub> and C<sub>12</sub>H<sub>20</sub> hydrocarbons into 1,3-dimethyladamantane (**I**). As starting compound we initially selected hydrogenated adduct of norbornene and cyclopentadiene, tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (**II**). The reaction of norbornene with dicyclopentadiene (the latter undergoes retro-Diels–Alder reaction to give two cyclopentadiene molecules) in the presence of NiCl<sub>2</sub>·Ph<sub>3</sub>P as catalyst at 160°C (reaction time 12 h) gave tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodec-4-ene (**III**) in 60% yield. Hydrogenation of **III** in hexane over Pd/C at a hydro-

Scheme 1.



**Table 1.** Isomerization of tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (**II**) over Na/H-Y-zeolite (hexane, 300°C)

Catalyst		Reaction time, h	Conversion of <b>II</b> , %	Yield, %			
degree of Na <sup>+</sup> /H <sup>+</sup> exchange, %	amount, wt %			<b>I</b>	<b>IV</b>	<b>V</b>	<b>VIa</b>
40	70	30	85	37	25	10	15
40	70	20	90	49	24	9	11
40	90	30	70	24	15	7	9
40	90	10	60	17	15	4	4
40	120	10	70	18	21	8	10
97	100	10	30	6	9	3	5
97	100	30	50	10	8	3	5
97	120	10	90	67	22	2	6

gen pressure of 100 atm (20°C, 3 h) afforded 95% of compound **II** (Scheme 1).

Skeletal isomerization of tetracyclododecane **II** was performed at 250–300°C (reaction time 10–30 h) in the presence of granular binder-free Y-zeolite (H,Na). Samples of Y-zeolite with a degree of Na<sup>+</sup>/H<sup>+</sup> exchange of 0.40 to 0.97 were tested in an amount of 50–120 wt % with respect to tetracyclododecane **II**. The most efficient catalyst for the rearrangement of **II** into 1,3-dimethyladamantane (**I**) was Y-zeolite with a degree of Na<sup>+</sup>/H<sup>+</sup> exchange of 0.97; it ensured the maximum conversion of tetracyclododecane **II** and the highest yield of 1,3-dimethyladamantane (**I**). Obviously, this catalyst is characterized by the maximum concentration of acid centers [5].

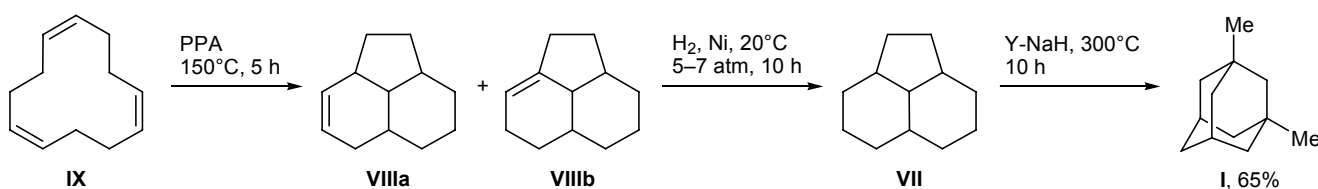
Insofar as tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (**II**) molecule contains less hydrogen than does 1,3-dimethyladamantane (**I**), we presumed that the source of hydrogen is a hydrocarbon solvent, hexane or cyclohexane. It is known that zeolites catalyze hydride transfer reactions [6–10]. Under solvent-free conditions, the conversion of **II** did not exceed 20%, and the yield of 1,3-dimethyladamantane (**I**) was less than 5%. Presumably, this is the result of fast deactivation of active centers of the catalyst via carburization at high reactant concentration. Preliminary results showed that hexane is a better solvent; cyclohexane underwent complex transformations to produce unsaturated com-

pounds which also favored carburization of the catalyst [11].

The results of the isomerization of compound **II** are given in Table 1. The best yield of **I** was 67%, the conversion of **II** being 90% (300°C, 10 h). Apart from 1,3-dimethyladamantane (**I**), the reaction mixture contained isomeric 1,4- and 1,2-dimethyladamantanes **IV** and **V** and 1-ethyladamantane (**VIa**).

Perhydroacenaphthene (**VII**) contains two cyclohexane rings, and its hydrocarbon composition coincides with that of 1,3-dimethyladamantane (**I**). Therefore, it may be possible to synthesize compound **I** via skeletal rearrangement of hydrocarbon **VII**. Perhydroacenaphthene (**VII**) was prepared in two steps. Initially, the isomerization of 1,3,5-cyclododecatriene (**IX**) in the presence of polyphosphoric acid (PPA) according to [12] gave a mixture of isomeric octahydroacenaphthenes **VIIIa** and **VIIIb**. The reaction was carried out at a **IX**-to-PPA ratio of 5:1; after 5 h at 150°C, the yield of **VIIIa/VIIIb** was 80%. Isomer mixture **VIIIa/VIIIb** was subjected to hydrogenation over nickel catalyst (nickel supported on GM-3 kieselguhr) at a hydrogen pressure of 5–7 atm at 20°C; the yield of **VII** was 95% (Scheme 2).

The isomerization of perhydroacenaphthene (**VII**) into 1,3-dimethyladamantane (**I**) was catalyzed by Y-zeolite with a degree of Na<sup>+</sup>/H<sup>+</sup> exchange of 0.97. The reaction was carried out in hexane at 300–320°C

**Scheme 2.**

**Table 2.** Synthesis of 1,3-dimethyladamantane (**I**) by skeletal isomerization of perhydroacenaphthene (**VII**) over Na/H-Y-zeolite

Weight ratio <b>VII</b> –catalyst–hexane	Temperature, °C	Reaction time, h	Yield, %
100:50:50	300	10	34
100:50:50	320	7	30
100:50:100	300	5	38
100:50:100	320	4	32
100:100:50	320	4	55
100:100:50	300	15	63
100:100:50	300	10	65
100:100:50	320	7	61
100:100:0	300	7	53
100:100:100	300	7	56
100:100:100	300	5	55
100:100:100	300	3	58

(reaction time 3–15 h; catalyst concentration 50–100 wt % with respect to **VII**). The results are collected in Table 2. After 10 h at 300°C, the major product was 1,3-dimethyladamantane (**I**), the conversion of perhydroacenaphthene (**VII**) was complete, and the maximum yield of **I** was 65%. As follows from the data in Table 2, the yield of 1,3-dimethyladamantane (**I**) is strongly determined by the amount of the catalyst. The best yield of **I** was obtained at a substrate-to-catalyst weight ratio of 1:1. Reduction of the amount of the catalyst from 100 to 50 wt % (relative to **VII**) led to almost twofold reduction of the yield of **I**. As in the isomerization of tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (**II**), the reaction mixture also contained isomeric alkyl-substituted adamantanes **IV–VI** in an overall yield of 10–15%.

Like the catalysis by aluminum halides, the isomerization in the presence of Y-zeolite follows a carbenium ionic mechanism and involves intramolecular rearrangements with rupture of C–C bonds. The rate-determining step in the isomerization of alkyladamantanes is the formation of *tert*-adamantyl cation [13]. The rearrangements are accompanied by reduction of the internal molecular strain and increase of the degree of branching.

The isomerization of tricyclic non-adamantane hydrocarbons into hydrocarbons of the adamantane series usually leads to thermodynamically less stable structures, such as ethyl- and methyl-substituted adamantanes in which one of the substituents does not occupy bridgehead position (1,2-dimethyl-, 1,3,4-trimethyladamantanes, etc.) [14]. These compounds are kineti-

cally preferred, and they accumulate among the products due to low rate of isomerization

Under the examined conditions, 1,3-dimethyladamantane (**I**) and isomeric alkyladamantanes were the main products of the transformation of perhydroacenaphthene (**VII**). In addition, small amounts of other compounds were also formed, in particular paraffin, mono- and bicyclic naphthene, and aromatic hydrocarbons. Their concentration in the reaction mixture appreciably increased with rise in the reaction temperature. The main reasons for the reduction of the overall yield of 1,3-dimethyladamantane (**I**) upon extension of the reaction time (24 h) are cracking and isomerization of targeted 1,3-dimethyladamantane (**I**) via methyl group transfer to positions 2 and 4. This conclusion is confirmed by the results of isomerization of 1,3-dimethyladamantane (**I**) in the presence of Y-zeolite (Table 3).

In fact, compound **I** in the temperature range from 200 to 320°C in the presence of Y-zeolite (Na<sup>+</sup>/H<sup>+</sup> 0.97) underwent isomerization via methyl group shift. The rate of the isomerization was appreciable even at 200°C. The conversion of **I** increased with rise in temperature and increase of the reaction time. Among the isomerization products, the major one was 1,4-dimethyladamantane (**IV**), while the amount of 1,2-dimethyladamantane (**V**) was smaller by a factor of 3–4. In addition, 1- and 2-ethyladamantanes **VIa** and **VIb** were detected. Thus the most probable reason for the reduced yield of **I** when the reaction time is longer than 7 h is isomerization of **I** into 1,2- and 1,4-dimethyladamantanes and 1- and 2-ethyladamantanes.

**Table 3.** Isomerization of 1,3-dimethyladamantane (**I**) over Na/H-Y-zeolite

Temperature, °C	Reaction time, h	Yield, %					decomposition products
		<b>I</b>	<b>IV</b>	<b>V</b>	<b>VIa</b>	<b>VIb</b>	
200	1	80	12	3	<1	–	4
200 <sup>a</sup>	1	89	1	–	<1	–	10
200	3	88	7	2	–	–	4
200 <sup>a</sup>	3	82	12	3	2	<1	1
300	2	79	14	4	–	–	–
300	5	81	6	2	2	2	7
320	3	48	20	6	6	–	21
320 <sup>a</sup>	3	54	19	6	4	3	15

<sup>a</sup> Hexane was used as solvent; in the other cases, no solvent was added.

The concentration of these compounds in the reaction mixture is not high since the equilibrium is strongly displaced toward 1,3-dimethyladamantane (**I**) due to considerable difference in the thermodynamic stabilities of 1,2- and 1,3-dimethyladamantanes.

Mutual transformations of 1,2-, 1,3-, and 1,4-dimethyladamantanes may be described with the aid of both 1,2-hydride and methyl shifts and structural isomerization of the adamantane skeleton whose mechanism is similar to the mechanism of the isomerization of 2-methyladamantane into 1-methyladamantane in the presence of AlBr<sub>3</sub> [15].

To conclude, we have found that Y-zeolite with a degree of Na<sup>+</sup>/H<sup>+</sup> exchange of 0.97 effectively catalyzes isomerization of tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (**II**) and (2a*R*,5a*α*,8a*R*,8b*α*)-dodecahydroacenaphthene (**VII**, perhydroacenaphthene) to 1,3-dimethyladamantane (**I**). The zeolite catalyst used in this work is advantageous due to its accessibility, facile isolation of the target product, the lack of corrosion, and simple equipment.

## EXPERIMENTAL

The IR spectra were recorded in KBr or mineral oil on a Bruker-Vertex 79V spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance-400 spectrometer at 400.13 and 100.62 MHz, respectively, using CDCl<sub>3</sub> as solvent and tetramethylsilane as reference. The mass spectra were obtained on a Shimadzu GCMS-QP2010Ultra instrument (Supelco PTE-5 capillary column, 60 m×0.25 mm; carrier gas helium; oven temperature programming from 40 to 280°C at a rate of 8 deg/min; injector temperature 260°C; electron impact, 70 eV; ion source temperature 200°C).

Chromatographic analyses were carried out on a Carlo Erba GC 6000 Vega Series 2 chromatograph equipped with a 3-m column packed with 15% of PEG-6000 on Chromaton N-AW-HMDS; oven temperature programming from 50 to 180°C at a rate of 8 deg/min; carrier gas helium, 47 ml/min. The elemental compositions were determined on a Carlo Erba 1108 analyzer.

Commercial GM-3-supported nickel was used (TU 38.101396-89E). The catalyst was reduced for 2 h at 400°C in a stream of pure hydrogen. Initial Y-zeolite (Na form) was synthesized according to the procedure described in [16]. Samples of granular Y-zeolite with different degrees of Na<sup>+</sup>/H<sup>+</sup> exchange were prepared following standard procedure [6]. The catalyst was activated by thermal treatment of decationized samples at 450°C over a period of 3–5 h on exposure to air. The reactions were carried out in a stainless-steel high-pressure microreactor or in a glass ampule placed in a high-pressure microreactor under controlled heating and stirring. Octahydroacenaphthenes were synthesized as described in [12]. Polyphosphoric acid was commercial product (from Acros Organics; 84% of phosphorus as P<sub>2</sub>O<sub>5</sub>).

1,2-Dimethyl-, 1,4-dimethyl-, and 1-ethyladamantanes were identified by comparing their retention times and stabilities [14]. Naphthene hydrocarbons were identified in reaction mixtures by mass spectrometry (by comparing *m/z* values of the molecular and fragment ions with reference data).

**Tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodec-4-ene (**III**).** A 20-ml glass ampule was charged with a mixture of 10 g (0.07 mol) of dicyclopentadiene and 11 g (0.11 mol) of norbornene and catalytic amounts of NiCl<sub>2</sub>·2Ph<sub>3</sub>P and bisphenol. The ampule was sealed and placed into

a high-pressure microreactor, the reactor was tightly closed and heated for 12 h at 160°C. When the reaction was complete, the ampule was cooled to 20°C and opened, and the mixture was extracted with methylene chloride (3×5 ml). The solvent was distilled off from the extract, and the residue was distilled under reduced pressure. Yield 7.2 g (60%), colorless oily substance, bp 55–60°C (0.2 mm). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1583 (C=C), 890 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.906–0.983 m (2H, 11-H), 1.13–1.17 m (4H, 9-H, 10-H), 1.28–1.47 m (4H, 2-H, 7-H), 1.57–1.69 m (2H, 12-H), 2.17–2.39 m (2H, 1-H, 8-H), 2.79–2.85 m (2H, 3-H, 6-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 31.86 (C<sup>9</sup>, C<sup>10</sup>), 33.74 (C<sup>1</sup>, C<sup>8</sup>), 37.83 (C<sup>11</sup>), 46.63 (C<sup>12</sup>), 48.61 (C<sup>3</sup>, C<sup>6</sup>), 53.74 (C<sup>2</sup>, C<sup>7</sup>), 135.21 (C<sup>4</sup>, C<sup>5</sup>). Found, %: C 89.83; H 10.17. C<sub>12</sub>H<sub>16</sub>. Calculated, %: C 89.94; H 10.06.

**Tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (II).** A high-pressure hydrogenation reactor was charged with 5 g of GM-3-supported nickel catalyst, 7.2 g of tetracyclopent-4-ene (III), and 45 ml of hexane. The reactor was tightly closed and hydrogen was supplied at a pressure of 100 atm for 3 h at 20°C. When the reaction was complete, the reactor was opened, the mixture was filtered, and the solvent was distilled off from the filtrate. Yield 95%.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.94–1.00 m (4H, 11-H, 12-H), 1.41–1.53 m (8H, 4-H, 5-H, 9-H, 10-H), 1.67–2.1 m (4H, 1-H, 3-H, 6-H, 8-H), 2.23–2.30 m (2H, 2-H, 7-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 24.38 (C<sup>4</sup>, C<sup>5</sup>, C<sup>9</sup>, C<sup>10</sup>), 31.24 (C<sup>1</sup>, C<sup>3</sup>, C<sup>6</sup>, C<sup>8</sup>), 41.24 (C<sup>11</sup>, C<sup>12</sup>), 50.07 (C<sup>2</sup>, C<sup>7</sup>). Found, %: C 88.73; H 11.27. C<sub>12</sub>H<sub>18</sub>. Calculated, %: C 88.82; H 11.18.

**(2aR,5aα,8aR,8bα)-Dodecahydroacenaphthene (VII, perhydroacenaphthene).** GM-3-supported nickel catalyst, 5 g, was added in a stream of helium to a solution of 10 g (0.061 mol) of isomeric octahydroacenaphthenes VIIIa and VIIIb in 40 ml of hexane, the mixture was transferred to a high-pressure hydrogenation reactor, the reactor was tightly closed, and the mixture was stirred for 10 h at 20°C under a hydrogen pressure of 5–7 atm. When the reaction was complete, the reactor was opened, the mixture was filtered, and the solvent was distilled off from the filtrate. Yield 9.5 g (95%), colorless oily substance.  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 19.62 (C<sup>3</sup>, C<sup>6</sup>), 27.20 (C<sup>4</sup>, C<sup>5</sup>), 28.24 (C<sup>2</sup>, C<sup>7</sup>), 29.57 (C<sup>12</sup>), 32.63 (C<sup>9</sup>, C<sup>10</sup>), 38.84 (C<sup>1</sup>, C<sup>8</sup>), 40.82 (C<sup>11</sup>). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 164 (24) [ $M$ ]<sup>+</sup>, 136 (26) [ $M - 28$ ]<sup>+</sup>, 121 (100) [ $M - 43$ ]<sup>+</sup>. Found, %: C 87.68; H 12.24. C<sub>12</sub>H<sub>20</sub>. Calculated, %: C 87.73; H 12.27.  $M$  164.1565.

**1,3-Dimethyladamantane (I).** *a.* A 20-ml glass ampule was charged with 0.8 g (5 mmol) of tetracyclo-

[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecane (II), 0.96 g of Y-zeolite (Na/H 0.97), and 1 ml of hexane. The ampule was sealed and placed into a high-pressure microreactor, and the reactor was tightly closed and heated for 10 h at 300°C. When the reaction was complete, the ampule was cooled to room temperature and opened, the mixture was filtered, and the solvent was distilled off from the filtrate. The residue was distilled under reduced pressure. Yield 60%.

*b.* A 20-ml glass ampule was charged with 3 g of (2aR,5aα,8aR,8bα)-decahydroacenaphthene (VII), 3 g of Y-zeolite (Na/H 97%), and 1.5 ml of hexane. The ampule was sealed and placed into a high-pressure microreactor, and the reactor was tightly closed and heated for 10 h at 300°C. The mixture was then treated as described in *a*. Yield 65%. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2890 (CH<sub>3</sub>), 1449 (CH<sub>2</sub>).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.79–0.81 m (6H, CH<sub>3</sub>), 1.90–1.92 m (2H, CH<sub>2</sub>), 1.39–1.58 m (10H, CH<sub>2</sub>), 2.26–2.32 m (2H, CH<sub>2</sub>).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 29.50 (C<sup>5</sup>, C<sup>8</sup>), 30.70 (C<sup>1</sup>, C<sup>3</sup>), 31.15 (CH<sub>3</sub>), 36.30 (C<sup>7</sup>), 44.00 (C<sup>2</sup>, C<sup>4</sup>, C<sup>8</sup>, C<sup>10</sup>), 51.95 (C<sup>2</sup>). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 164 (16) [ $M$ ]<sup>+</sup>, 149 (100) [ $M - 15$ ]<sup>+</sup>. Found, %: C 87.73; H 12.27. C<sub>12</sub>H<sub>20</sub>. Calculated, %: C 87.79; H 12.33.  $M$  164.1565.

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