# Selective Hydroxylation of Adamantane and Its Derivatives

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**Abstract**—A general method was developed for hydroxylation into the nodal position of adamantane and its 1- and 2-substituted derivatives employing systems $H_2O$–$CBr_4$ ($BrCCl_3$, $CCl_4$) in the presence of complexes of Pd, Ni, Ru, Co, Mo, W, and Fe. The oxidants in the systems are hypochlorous (HOCl) or hypobromous (HOBr) acids generated from water and halomethanes under the reaction conditions.

The adamantale series hydrocarbons are more prone to oxidation than alkanes and ordinary cycloalkanes [1, 2]. Versatile oxidants were applied to the catalytic oxidation of adamantane and its derivatives: oxygen, hydrogen peroxide, hydroperoxides, iodosobenzene, 2,6-dichloropyridine N-oxide [1–4]. The oxidation can be catalyzed by enzymes (cytochromes, cytochrome P-450), and by organometallic compounds of Co, Mn, Fe, Ru, Pt [1–4]. Due to the important involvement of radical processes these methods of adamantane oxidation are characterized by low selectivity and lead to the formation of mixtures of 1- and 2-hydroxyadamantanes and 2-adamantanone.

In the previous report [5] we demonstrated that applying the system $CBr_4$–$H_2O$–$Mo(CO)_6$ it was possible to carry out a selective oxidation of adamantane (**I**) to
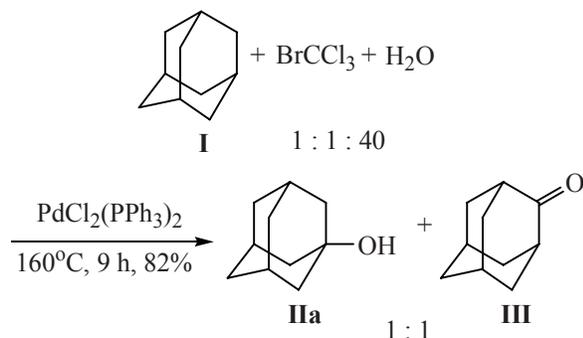


R = OH (**a**), Cl (**b**), Br (**c**), COCH₃ (**d**), NH₂ (**e**), CH(NH₂)CH₃ (**f**), COOH (**g**), COCl (**h**). **III**, R = O; **X**, R = Br (**a**), NH₂ (**b**); **XI**, R = O (**a**), Br (**b**), NH₂ (**c**).

1-adamantanol (**IIa**) which was obtained in 85% yield. In this system the oxidation was performed by hypobromous acid generated from $H_2O$ and $CBr_4$ under the action of $Mo(CO)_6$.

In this study we carried on the search for efficient catalysts for oxidation of adamantane (**I**) and its derivatives using halomethanes ($CBr_4$, $CBrCl_3$, $CCl_4$) and water.

The adamantane hydroxylation can be performed not only using the system $CBr_4$–$H_2O$–$Mo(CO)_6$, but also applying as catalyst complexes of Ru, W, Fe, Ni, Co, and Pd. In the reaction of adamantane (**I**) with a mixture $CBr_4$–$H_2O$, 1 : 80, in the presence of a ruthenium complex $Ru(OH)Cl_3$ ([AdH] : [Ru] = 100:1) at 140°C within 10 h 1-adamantanol (**IIa**) selectively formed in 33% yield. On raising the catalyst concentration to 3 mol% the yield of alcohol **IIa** increased to 55%. The adamantane (**I**) conversion and the yield of compound **IIa** depend decisively on water concentration, with a maximum efficiency at 40-fold water excess with respect to adamantane and $CBr_4$. The 8-fold decrease in water amount ($CBr_4$–$H_2O$, 1 : 10) resulted in diminishing of adamantane (**I**) conversion to 32% in spite of raising the reaction temperature (160°C, 9 h), and 1-bromoadamantane became the main reaction product.

At replacement of $CBr_4$ by $BrCCl_3$ in the composition of the oxidating system the adamantane (**I**) conversion grew to 89% (see the table, run no. 7). Whereas at the use of catalyst $NiCl_2(PPh_3)_2$, $NiCl_2[P(C_4H_9)_3]_2$, $CoCl_2[(Ph_2PCH_2)_2]_2$ the main reaction product is

Effect of the catalyst nature and reaction conditions on adamantane oxidation with a system $CHlg_4$–$H_2O$ under the action of transition metal complexes

| Run no. | Catalyst | $CHlg_4$ | Molar ratio [cat]:[AdH]:[$CHlg_4$]:[$H_2O$] | Temperature, °C | Time, h | Yield, % | |
|---|---|---|---|---|---|---|---|
| | | | | | | IIa | III |
| 1 | Without catalyst | $CBr_4$ | 0 : 1 : 1 : 1 | 140 | 10 | 3 | |
| 2 | $Ru(OH)Cl_3$ | " | 1 : 100 : 100 : 8000 | " | " | 33 | – |
| 3 | " | " | 3 : 100 : 100 : 8000 | " | " | 55 | – |
| 4 | " | " | 3 : 100 : 100 : 4000 | 160 | 9 | 62 | – |
| 5[a] | " | " | 3 : 100 : 100 : 2000 | " | " | 30 | – |
| 6[b] | " | " | 3 : 100 : 100 : 1000 | " | " | 28 | – |
| 7 | " | $CBrCl_3$ | " | " | " | 89 | – |
| 8 | $NiCl_2(PPh_3)_2$ | " | " | " | " | 55 | – |
| 9 | $NiCl_2[P(C_4H_9)_3]_2$ | " | " | " | " | 59 | – |
| 10 | $CoCl_2[(Ph_2PCH_2)_2]_2$ | " | " | " | " | 66 | – |
| 11 | $PdCl_2(PPh_3)_2$ | " | " | " | " | 41 | 41 |
| 12 | $Mo(CO)_6$ | " | " | " | " | 83 | – |
| 13 | $W(CO)_6$ | " | " | " | " | 78 | – |
| 14 | $Cr(CO)_6$ | " | " | " | " | 89 | – |
| 15 | $Fe_3(CO)_{12}$ | " | " | " | " | 64 | – |
| 16 | $Mo(CO)_6$ | $CCl_4$ | " | 140 | 13 | 70 | 10 |
| 17 | $Mo(CO)_6$–TBAB, 1:1 | " | " | " | " | 34 | 66 |

[a] Formed also 30% of 1-bromoadamantane (IIc). [b] Formed also 28% of 1-bromoadamantane (IIc).

1-adamantanol (IIa), in the presence of $PdCl_2(PPh_3)_2$ alongside compound IIa forms an equimolar quantity of 2-adamantanone (III).

Metal carbonyls $Mo(CO)_6$, $W(CO)_6$, $Cr(CO)_6$, and $Fe_3(CO)_{12}$ turned out to be sufficiently active catalysts of adamantane (I) hydroxylation in the oxidative system $BrCCl_3$–$H_2O$, 1:40. The reaction in their presence within 9 h at 160°C afforded 1-adamantanol (IIa) in 83, 78, 89, and 64% yield respectively.

Introducing $CCl_4$ into the composition of the oxidative system made it possible to reduce the temperature to



I

1 : 1 : 40

$Mo(CO)_6$–TBAB, 1 : 1
———————————→
140°C, 13 h, ~100%

IIa    1 : 2    III
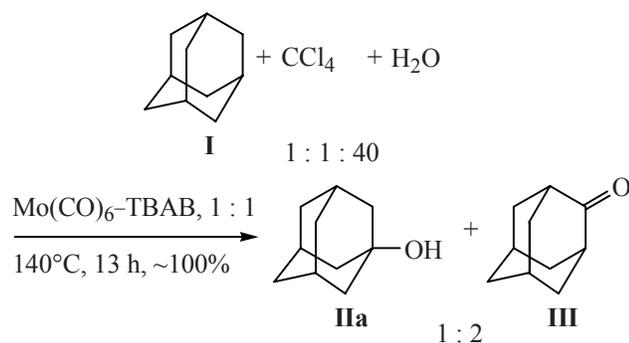
140°C, but the complete conversion of adamantane (I) required longer heating (13 h). The reaction involving $CCl_4$ occurred with a low selectivity: In the reaction mixture alongside alcohol IIa were found adamantanone III, 1,3-adamantanediol (IVa), and 3-chloroadamantan-1-ol (IVb) in a ratio 4:1:2:1. When the reaction was carried out in the presence of $Mo(CO)_6$ with the addition of phase-transfer catalyst tetrabutylammonium bromide (TBAB), 1:1, then the main product was adamantanone III.

The progress of adamantane (I) hydroxylation was monitored by GLC. We determined the optimum concentrations of the catalyst and reagents components, the reaction conditions suitable for preparation of 1-adamantanol (IIa) and adamantanone III (see the table).
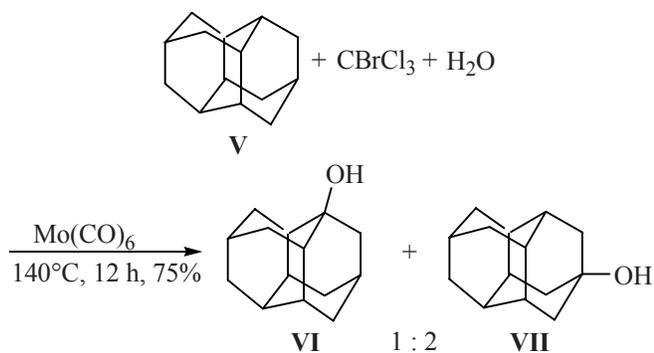
In the reaction mixture alongside compounds IIa and III GLC and GC-MS methods revealed the presence of bromoform and chloroform showing the involvement of $CBr_4$, $BrCCl_3$, and $CCl_4$ in the process of adamantane oxidation. The reaction does not proceed in the absence of halomethanes. The iodometric titration of the quickly cooled reaction mixture showed the presence of active bromine ($c$ 8.48 mg ml$^{-1}$) and active chlorine ($c$ 3.2 mg ml$^{-1}$)

demonstrating the formation of hypobromous (HOBr) and hypochlorous (HOCl) acids respectively. The formation of HOCl was confirmed by the appearance in the UV spectrum of a characteristic maximum in the region 229–236 nm. The data obtained suggest that the oxidation of adamantane and its derivatives is effected by HOBr and HOCl [5].

We succeeded in bringing into the hydroxylation reaction a homolog of adamantane (**I**), diamantane **V** whose oxidation with a system $CBrCl_3$–$H_2O$ in the presence of $Mo(CO)_6$ also occurred at the nodal carbon atoms giving a mixture of 1- and 4-diadamantanols (**VI, VII**) in a ratio 2:1 and an overall yield 75% (Scheme 1).

As showed the study of a series of substituted adamantanes, the oxidation system $H_2O$–$BrCCl_3$–$Mo(CO)_6$ ([cat] : [AdH] : [$BrCCl_3$] : [$H_2O$] = 1 : 100 : 100 : 4000) provided the hydroxylation of the following substrates: adamantanol (**IIa**), 1-chloro- (**IIb**), 1-bromo- (**IIc**), 1-acetyl- (**IId**), 1-amino- (**IIe**), 1-(1-aminoethyl)- (**IIf**)–adamantanes, 1-adamantanecarboxylic acid (**IIg**), and 1-adamantanecarbonyl chloride (**IIh**) (Scheme 2).
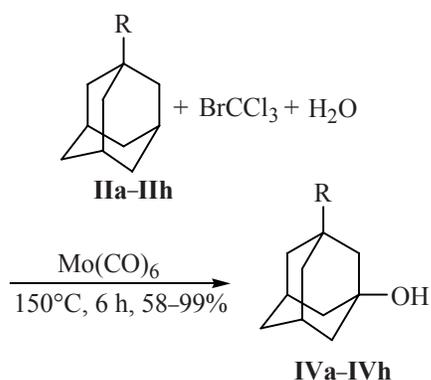
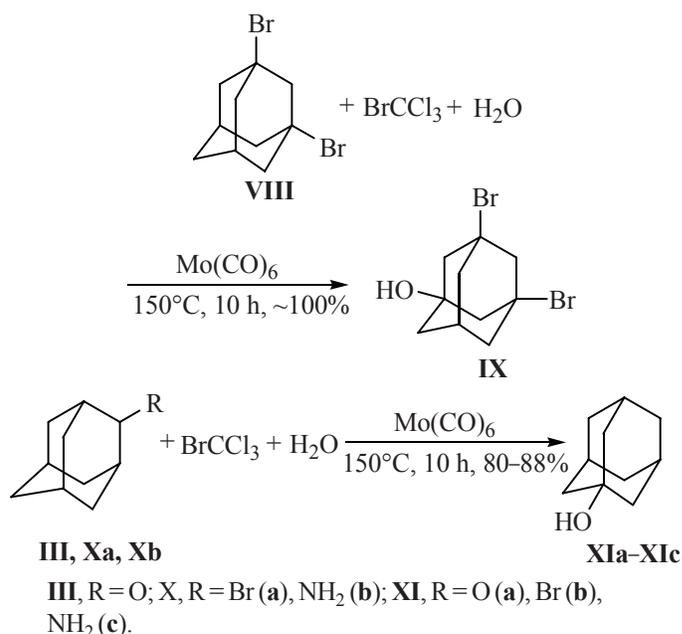The hydroxylation of compounds **IIa–IIh** in all cases proceeded chemoselectively at the free nodal carbon atom. For instance, the oxidation of 1,3-dibromo-adamantane (**VIII**) in the system $BrCCl_3$–$H_2O$–$Mo(CO)_6$ gave rise to 1,3-dibromo-5-adamantanol (**IX**).
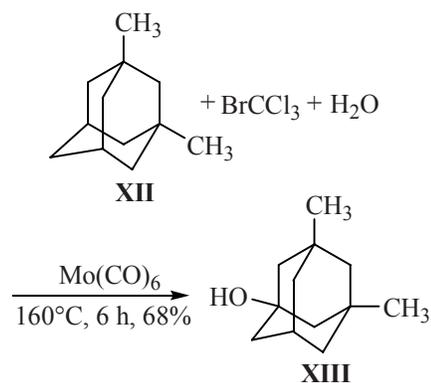
The hydroxylation direction to the nodal position is conserved also in the series of 2-substituted adamantanes: 2-adamantanone (**III**), 2-bromo- (**Xa**), and 2-adamantanamine (**Xb**).

4-Aminoadamantan-1-ol (**XIc**) formed as a mixture of two stereoisomers (*syn*/*anti* 1.6:1), distinguished by the relative positions of amino and hydroxy groups. The fact of the formation of mixture of *syn*- and *anti*-isomers **XIc** and their ratio were established by ^{13}C NMR spectroscopy

**Scheme 1.**



**Scheme 2.**



R = OH (**a**), Cl (**b**), Br (**c**), COCH₃ (**d**), NH₂ (**e**), CH(NH₂)CH₃ (**f**), COOH (**g**), COCl (**h**).

**Scheme 3.**



**III**, R = O; **X**, R = Br (**a**), NH₂ (**b**); **XI**, R = O (**a**), Br (**b**), NH₂ (**c**).

**Scheme 4.**

In the hydroxylation of adamantanes containing polar substituents a high activity was provided both by the carbonyl complexes of Mo, W, Fe and by phosphine complexes of Ni, Co, Pd, and Rh. The oxidation time essentially depended on the reaction temperature. Raising the temperature from 140 to 180°C accelerated the reaction more than 4-fold (3 h at 180°C, 5 h at 170°C, 10 h at 150°C, 13 h at 140°C). Prolonged reaction at high temperature (170–180°C) is unwanted for it results in the formation of chlorinated (brominated) products.

The hydroxylation of 1,3-dimethyladamantane (**XII**) occurred at the free nodal carbon atom; no oxidation products of the methyl group were detected (Scheme 4).

As follows from the data obtained, the best catalysts for hydroxylation of adamantane and its derivatives by the reagent $CBr_4$ ($BrCCl_3$, or $CCl_4$)–$H_2O$ besides $Mo(CO)_6$ are ruthenium and chromium complexes. At employing as catalyst $PdCl_2(PPh_3)_2$ a deeper oxidation of adamantine occurred giving 2-adamantanone in 41% yield.

## EXPERIMENTAL

The purity of compounds obtained was checked and the composition of reaction products was determined by GLC on a chromatograph Chrom-5, column 1.2 m × 3 mm, stationary phase 5% SE-30 on Chromaton N-AW-HMDS, ramp from 50 to 280°C at a rate 8 deg/min, carrier gas helium.

IR spectra were recorded on a spectrophotometer Specord 75IR (from films or mulls in mineral oil) in the range 550–3600 cm$^{-1}$. $^{13}C$ NMR spectra were registered on a spectrometer JEOL FX 90Q with operating frequency 90 MHz in $CDCl_3$, chemical shifts were measured with respect to TMS. Mass spectra were measured on a GC-MS instrument Finnigan MAT-112S in the electron impact mode at ionizing energy 70 eV and the temperature of ion source 22°C. Elemental composition of compounds was determined on an analyzer Karlo Erba, model 1106.

**Hydroxylation of adamantane and its derivatives.** Into a pressure microreactor of stainless steel (*V* 17 ml) or in a glass ampoule (*V* 20 ml) (the results of parallel runs were practically identical) was charged under argon 0.1–0.3 mmol of catalyst, 10 mmol of adamantane (or its derivative), 10 mmol of $CBr_4$ ($BrCCl_3$ or $CCl_4$), and 400–800 mmol of water. The reactor was hermetically closed (the ampoule was sealed), and the reaction mixture was

stirred at 140–180°C for 3–12 h. On completion of the reaction the reactor or ampoule was cooled to room temperature, opened, the product was extracted into dichloromethane (3×5 ml), the solvent was distilled off, and the residue was either distilled in a vacuum or crystallized from hexane or ethanol. The yields are given calculated on the consumed adamantane (GLC analysis, internal reference). The structure of compounds was confirmed by comparison with authentic samples and handbook references.

**1-Adamantanol (IIa)**. Yield 89%, mp 282–283°C (subl.) {283–284°C (subl.) [6]}. $^{13}C$ NMR spectrum, δ, ppm: 30.85 (C$^{3,5,7}$), 36.15 (C$^{4,6,10}$), 45.32 (C$^{2,8,9}$), 67.90 (C$^{1}$). Mass spectrum, *m/z* ($I_{rel}$, %): 152 [*M*]$^+$ (24), 109 (5), 96 (7), 95 (100), 94 (14), 79 (5), 77 (7), 67 (5), 55 (5), 43 (15), 41 (12), 39 (10), 29 (7). Found, %: C 78.87; H 10.57. $C_{10}H_{16}O$. Calculated, %: C 78.89; H 10.59.

**2-Adamantanone (III)**. Yield 66%, mp 256–257°C (subl.) {256–258°C [7]}. $^{13}C$ NMR spectrum, δ, ppm: 27.64 (C$^{5,7}$), 36.31 (C$^{6}$), 39.20 (C$^{4,8,9,10}$), 46.92 (C$^{1,3}$), 216.59 (C$^{2}$). Found, %: C 79.78; H 9.12. $C_{10}H_{14}O$. Calculated, %: C 79.95; H 9.39.

**1,3-Adamantanediol (IVa)**. Yield 86%, mp 308–309°C (subl.) {310°C [8]}. $^{13}C$ NMR spectrum, δ, ppm: 31.17 (C$^{5,7}$), 43.45 (C$^{4,8,9,10}$), 51.94 (C$^{2}$), 69.52 (C$^{1,3}$). Found, %: C 71.08; H 9.42. $C_{10}H_{16}O_2$. Calculated, %: C 71.39; H 9.58.

**3-Chloroadamantan-1-ol (IVb)**. Yield 80%, mp 205°C (subl.) {205.5°C [9]}. $^{13}C$ NMR spectrum, δ, ppm: 26.95 (C$^{5,7}$), 36.94 (C$^{6}$), 44.77 (C$^{8,9}$), 47.90 (C$^{4,10}$), 54.05 (C$^{2}$), 69.24 (C$^{3}$), 72.94 (C$^{1}$). Found, %: C 64.21; H 7.89; Cl 18.82. $C_{10}H_{15}ClO$. Calculated, %: C 64.33; H 8.39; Cl 18.99.

**3-Bromoadamantan-1-ol (IVc)**. Yield 92%, mp 158–159°C (hexane) {159–160°C (petroleum ether) [10]}. $^{13}C$ NMR spectrum, δ, ppm: 73.54 (C$^{1}$), 54.48 (C$^{2}$), 68.59 (C$^{3}$), 48.37 (C$^{4,10}$), 26.19 (C$^{5,7}$), 37.26 (C$^{6}$), 44.13 (C$^{8,9}$). Mass spectrum, *m/z* ($I_{rel}$, %): 166 [*M*]$^+$ (lacking), 230 (5), 152 (31), 151 (94), 133 (7), 109 (7), 107 (10), 96 (26), 95 (100), 94 (14), 93 (17), 92 (7), 91 (17), 81 (8), 79 (7), 77 (16), 67 (16), 67 (13), 65 (7), 55 (14), 42 (12), 41 (19), 39 (20), 29 (48). Found, %: C 51.77; H 6.48; Br 34.52. $C_{10}H_{15}BrO$. Calculated, %: C 51.96; H 6.54; Br 34.57.

**1-(3-Hydroxy-1-adamantyl)ethanone (IVd)**. Yield 98%, mp 86–87°C (hexane) {89–91°C (ethyl acetate–hexane) [11]}. IR spectrum, ν, cm$^{-1}$: 3395 (OH), 1680 (C=O). $^{13}C$ NMR spectrum, δ, ppm: 67.92 (C$^{1}$), 45.64

($C^2$), 49.70 ($C^3$), 37.02 ($C^{4,10}$), 30.13 ($C^{5,7}$), 35.21 ($C^6$), 44.19 ($C^{8,9}$), 212.58 (C=O), 24.39 ($CH_3$). Mass spectrum, $m/z$ ($I_{rel}$, %): 194 [$M$]$^+$ (7), 152 (9), 151 (100), 133 (7), 109 (7), 107 (19), 95 (36), 93 (48), 91 (7), 81 (11), 79 (8), 77 (9), 67 (11), 65 (7), 59 (9), 55 (9), 43 (38), 41 (12), 39 (9), 29 (7). Found, %: C 74.05; H 9.29. $C_{12}H_{18}O_2$. Calculated, %: C 74.19; H 9.34.

**3-Aminoadamantan-1-ol (IVe)**. Yield 80%, mp 264–265°C (267°C [9]). $^{13}$C NMR spectrum, δ, ppm: 68.25 ($C^1$), 45.71 ($C^2$), 47.18 ($C^3$), 46.10 ($C^{4,10}$), 30.38 ($C^{5,7}$), 36.81 ($C^6$), 45.39 ($C^{8,9}$). Found, %: C 71.43; H 10.07; N 8.42. $C_{10}H_{17}NO$. Calculated, %: C 71.81; H 10.25; N 8.37.

**3-(1-Aminoethyl)adamantan-1-ol (IVf)**. Yield 99%, mp 111–112°C (ethanol). $^{13}$C NMR spectrum, δ, ppm: 16.56 ($CH_3$), 28.32 ($C^{5,7}$), 35.61 ($C^{4,10}$), 36.69 ($C^6$), 36.88 ($C^2$), 44.80 ($C^{8,9}$), 45.74 ($C^1$), 55.54 ($CHNH_2$), 66.42 ($C^3$). Found, %: C 73.79; H 10.84; N 7.17. $C_{12}H_{21}NO$. Calculated, %: C 73.48; H 10.71; N 6.95.

**3-Hydroxy-1-adamantanecarboxylic acid (IVg)**. Yield 58%, t.subl. 120°C (2 mm Hg). $^{13}$C NMR spectrum, δ, ppm: 28.53 ($C^{5,7}$), 36.03 ($C^6$), 38.29 ($C^{4,10}$), 42.91 ($C^3$), 44.51 ($C^{8,9}$), 48.23 ($C^2$), 68.74 ($C^1$), 183.13 (COOH). Found, %: C 67.19; H 8.15. $C_{11}H_{16}NO_3$. Calculated, %: C 67.32; H 8.21.

**3-Hydroxy-1-adamantanecarbonyl chloride (IVh)**. Yield 91%, t.subl. 111–112°C (1 mm Hg). $^{13}$C NMR spectrum, δ, ppm: 27.37 ($C^{5,7}$), 37.26 ($C^6$), 41.18 ($C^{4,10}$), 45.76 ($C^{8,9}$), 48.53 ($C^2$), 53.55 ($C^3$), 67.76 ($C^1$), 178.32 (COCl). Found, %: C 61.32; H 6.89; Cl 16.48. $C_{11}H_{15}ClO_2$. Calculated, %: C 51.53; H 7.04; Cl 16.51.

**Diamantan-1-ol (VI)** [12]. Yield 50%. $^{13}$C NMR spectrum, δ, ppm: 25.33 ($C^4$), 30.56 ($C^9$), 32.60 ($C^{3,14}$), 36.81 ($C^6$), 37.68 ($C^{8,10}$), 38.05 ($C^5$), 40.02 ($C^{7,11}$), 43.44 ($C^{2,12}$), 46.40 ($C^{13}$), 70.82 ($C^1$). Mass spectrum, $m/z$ ($I_{rel}$, %): 204 [$M$]$^+$ (51), 186 (100), 130 (36), 129 (26), 95 (85), 94 (87), 92 (22), 91 (24), 79 (20). Found, %: C 82.21; H 9.83. $C_{14}H_{20}O$. Calculated, %: C 82.30; H 9.86.

**Diamantan-4-ol (VII)** [12]. Yield 25%. $^{13}$C NMR spectrum, δ, ppm: 25.36 ($C^9$), 35.92 ($C^{1,7,11}$), 36.81, 37.15 ($C^{8,10,13}$), 41.90 ($C^{2,6,12}$), 45.83 ($C^{3,5,14}$), 67.87 ($C^4$). Mass spectrum, $m/z$ ($I_{rel}$, %): 204 [$M$]$^+$ (100), 183 (3), 109 (20), 108 (14), 107 (18), 96 (15). Found, %: C 82.15; H 9.78. $C_{14}H_{20}O$. Calculated, %: C 82.30; H 9.86.

**3,5-Dibromoadamantan-1-ol (IX)**. Yield ~100%, t.subl. 98°C (1 mm Hg). $^{13}$C NMR spectrum, δ, ppm: 29.98 ($C^7$), 45.25 ($C^6$), 49.20 ($C^{8,10}$), 53.70 ($C^{4,9}$), 55.90 ($C^2$), 65.08 ($C^{1,3}$), 72.97 ($C^5$). Found, %: C 38.63; H 4.41;

Br 49.98. $C_{10}H_{14}Br_2O$. Calculated, %: C 38.74; H 4.55; Br 51.55.

**1-Hydroxyadamantan-4-one (XIa)**. Yield 85%, mp 320–321°C (subl.) {319–322°C (CCl$_4$) [13]}. $^{13}$C NMR spectrum, δ, ppm: 29.95 ($C^7$), 38.95 ($C^{8,10}$), 45.18 ($C^{2,6,9}$), 46.85 ($C^{3,5}$), 67.78 ($C^1$), 216.21 ($C^4$). Mass spectrum, $m/z$ ($I_{rel}$, %): 166 [$M$]$^+$ (25), 148 (6), 109 (6), 108 (10), 107 (5), 97 (10), 96 (20), 95 (100), 94 (10), 80 (7), 79 (8), 77 (6), 67 (5), 55 (10), 53 (11), 43 (12), 41 (24), 39 (23). Found, %: C 77.48; H 8.46. $C_{10}H_{16}O_2$. Calculated, %: C 72.25; H 8.49.

**4-Bromoadamantan-1-ol (XIb)**. Yield 80%, t.subl. 89°C (2 mm Hg). $^{13}$C NMR spectrum, δ, ppm: 32.58 ($C^{1,3}$), 33.49 ($C^7$), 36.51 ($C^{8,10}$), 41.87 ($C^{4,9}$), 44.50 ($C^6$), 62.25 ($C^2$), 72.09 ($C^5$). Found, %: C 51.82; H 6.45; Br 34.49. $C_{10}H_{15}BrO$. Calculated, %: C 51.96; H 6.96; Br 34.57.

**4-Aminoadamantan-1-ol (XIc)**. Yield 88%, mp 256–260°C (ethanol) {258–260°C (toluene) [14]}. $^{13}$C NMR spectrum, δ, ppm, *syn*-isomer: 29.73 ($C^7$), 36.29 ($C^{6,10}$), 37.68 ($C^{3,5}$), 38.80 ($C^{2,9}$), 45.64 ($C^8$), 54.07 ($C^4$), 67.52 ($C^1$); *anti*-isomer: 67.45 ($C^1$), 44.88 ($C^{2,9}$), 36.92 ($C^{3,5}$), 54.55 ($C^4$), 29.50 ($C^{6,10}$), 30.07 ($C^7$), 45.83 ($C^8$). Found, %: C 71.48; H 19.97; N 8.48. $C_{10}H_{17}NO$. Calculated, %: C 71.81; H 10.25; N 8.37.

**3,5-Dimethyladamantan-1-ol (XIII)**. Yield 68%, mp 95–96°C (ethanol) {95.2–96.2°C [15]}. $^{13}$C NMR spectrum, δ, ppm: 23.58 ($C^7$), 30.37 ($CH_3$), 33.49 ($C^{3,5}$), 43.23 ($C^{6,10}$), 45.72 ($C^8$), 50.59 ($C^4$), 54.47 ($C^{2,9}$), 72.96 ($C^1$). Found, %: C 79.85; H 11.05. $C_{12}H_{20}O$. Calculated, %: C 79.94; H 11.18.

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