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Functionalization of Homodiamantane: Oxygen Insertion Reactions without Rearrangement with Dimethyldioxirane

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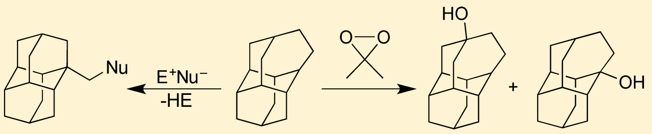
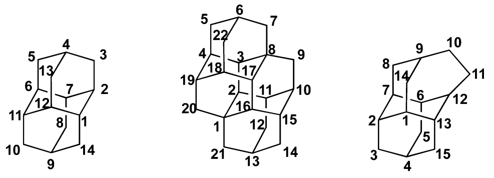
Supporting Information



ABSTRACT: Homodiamantane bromination and nitroxylation are accompanied by contraction of the seven-membered ring to give the corresponding substituted 1-diamantylmethyl derivatives. In contrast, CH-bond hydroxylations with dimethyldioxirane retain the cage and give both apically and medially substituted homodiamantanes. The product ratios are in accord with the barriers for the oxygen insertion computed with density functional theory methods only if solvation is included through a polarizable continuum model. B3LYP-D3 and M06-2X computations with a 6-31G(d,p) basis set on the oligomeric van der Waals complexes predict the potential of homodiamantane derivatives for surface modifications with conformationally slightly flexible diamondoid homologues.

Diamondoids[1] are defined as a group of nanometer-size saturated hydrocarbons, whose structures resemble part of the diamond lattice; i.e., these are hydrogen-terminated nanodiamonds. Among many others, diamantane (**1**) and [121]tetramantane (**2**) (Figure 1) are accessible in sizable quantities from crude oil.[2] The theoretically predicted[3] ability of diamondoid-based materials to resemble the properties of diamond, in particular, its negative electron affinity (NEA), was proven experimentally for self-assembled monolayers (SAMs) of diamondoid thiols on Au and Ag surfaces.[4] These new photocathode devices display monochromatic emission with up to 70% electron yield,[5] which is far beyond the efficiency of bulk hydrogen-capped diamond.[4,6,7] Conformational flexibility is one of the key factors that determine SAM properties. Very recently it was shown that conformational disorder enhances electron transfer through alkyl monolayers.[8] Near-edge X-ray absorption fine structure spectroscopic[9] and other measurements[10] demonstrated that the self-assembly of thiols on gold surfaces occurs in two steps whereby closer packing follows preliminary aggregation, a process that may involve conformational changes that affect the density and the electronic properties of SAMs.



1 **2** **3**

Figure 1. Structures of diamantane (**1**), [121]tetramantane (**2**), and homodiamantane (**3**) with numbering of carbon atoms.

Homodiamantane (**3**, Figure 1)[11] is the simplest nonspherical diamondoid homologue that displays modest conformational flexibility due to the presence of a seven-membered ring similar to that of homoadamantane.[12] The interconversion of two degenerate C_1-minima (bridge flip) occurs through the C_s-symmetric structure and is barrierless at various DFT (B3LYP, B3LYP-D3, M06-2X, B3PW91) and *ab initio* (MP2) levels of theory. This makes **3** the first relevant candidate for testing the self-assembly of moderately flexible homologated diamondoids on surfaces.

Diamondoid self-assembly is effective due to intermolecular dispersion interactions between the neighboring CH-terminated diamond–like surfaces.[13] Recently, we have experimentally confirmed that such type of bonding is responsible for strengthening the central CC bonds in diamondoid dimers[14] that are structurally related to graphane dimers.[15,16] To predict the differences in the self-association of **3** vs conformationally rigid parent **1** we optimized the structures of their van der Waals tetramers, in an attempt to model the clustering of these hydrocarbons on surfaces. In order to account for the noncovalent interactions we utilized the M06-2X functional[17] that is parametrized to include medium range electron correlation. For clean-cut comparisons of the dispersion contributions we also employed the *a posteriori* D3 dispersion corrections (B3LYP-D3).[18] The B3LYP-D3/6-31G(d,p) computed association energies of **1** and **3** to the respective tetramers (Figure 2A and B) are 26.9 and 28.4 kcal mol^{-1},

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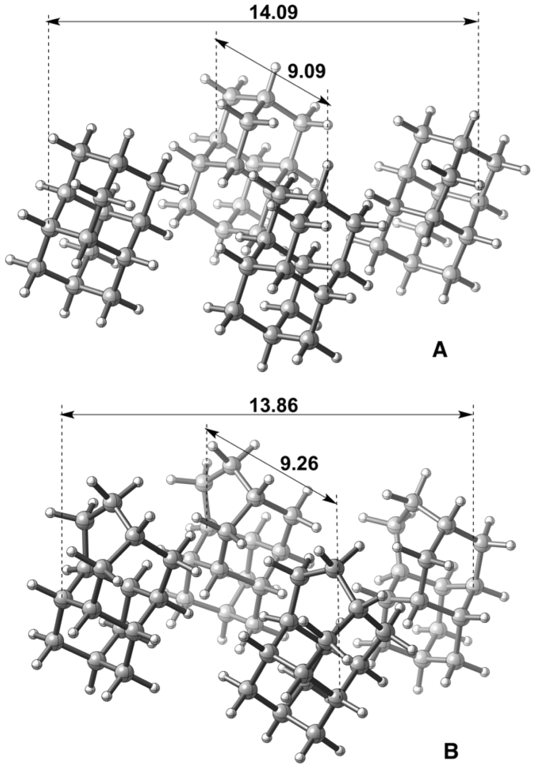


Figure 2. The B3LYP-D3/6-31G(d,p) optimized van der Waals tetramers of diamantane (A) and homodiamantane (B) (selected interatomic distances in Å).

respectively. Even though the dimensions of these complexes are almost identical (Figure 2), the higher association energy for the tetramer of homodiamantane (Figure 2B) is due to a larger number of intermolecular HH contacts. Similar trends were observed at M06-2X/6-31G(d,p) where, although the absolute complexation energies are ca. 10 kcal mol^{-1} lower than those at B3LYP-D3/6-31G(d,p), the tetramerization of **3** still is 2.1 kcal mol^{-1} more favorable than that of **1**. We envisage that the SAM morphologies are expected to be similar for **1** and **3**, but the latter hydrocarbon may form more densely packed and therefore likely also more stable monolayers.

For the preparation of **3** we took the route through the homologation of diamantanone (**4**)[19] with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. Further Wolff−Kishner reduction of thus obtained mixture of homodiamantanones gave **3** in 87% overall preparative yield (Scheme 1).

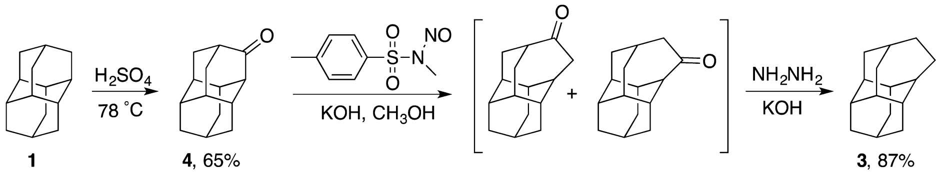
In order to study the self-assembly properties of **3**, surface attachment points must be introduced into its structure; these are typically −OH, −SH, −COOH as well as other nucleophilic functional groups. The presence of the six different types of tertiary C−H bonds makes the selective functionalization of **3** rather challenging. As the functionalizations of diamondoids usually are most selective with electrophiles,[20] we first tested the reactivity of **3** toward bromine[21] and 100% nitric acid,[22] where the positively polarized bromine ($\mathrm{Br}_n^{+}\mathrm{Br}_m^{-}$)[23] and nitronium nitrate ($\mathrm{NO_2^{+}NO_3^{-}}$)[24] constituents achieve oxidative CH activations. Previously we successfully utilized these reagents for the functionalizations of diamantane,[20] triamantane,[25] [121],[25] [123],[26] [1(2)3][27] tetramantanes, T_d-pentamantane,[28] and cyclohexamantane.[27] As the selectivities of the functionalizations of diamondoids with electrophiles correlate well with the stabilities of carbocations in the chosen positions of the cage,[27,29−31] we first estimated the relative ΔH_{298} of the tertiary carbocations derived from **3**. Again, we employed B3LYP-D3 and M06-2X, as the latter was particularly useful to describe the highly delocalized charge in diamondoid cations.[32] We found that the relative stabilities of the tertiary carbocations derived from **3** vary substantially, whereby **3a** with the charge in the medial C^{12}-position is the most favorable at both B3LYP-D3 and M06-2X with a 6-31G(d,p) basis set (Figure 3). This is due to the combination of two factors, namely (*i*) location of the carbocationic center in the seven-membered ring that reduces the strain and (*ii*) more effective delocalization of the charge within the cage as seen from the electrostatic potential distributions (Figure 3).

The 4 kcal mol^{-1} energy gap between cations **3a** and **3b** (ca.) implies that the reaction of **3** with electrophiles will be directed predominantly into the medial C^{12}-position. We found, however, that although bromination of **3** does occur at the computationally predicted position, it is accompanied by ring contraction to furnish 1-bromomethyldiamantane (**5**) as the main product (Scheme 2). The analogous rearrangement of parent homoadamantane in the presence of bromine was documented earlier where it was suggested that contraction occurs upon ionization of the halogenated product.[33−36] As C−H brominations with neat bromine occur through H-coupled electron transfer involving highly polarized transitions structures[23] leading to complexes of the respective carbocation with protonated bromine (HBr_{2n}^{+}), the rearrangement of the homodiamantane cage may occur already at the CH-functionalization step. As it was shown that the transition structures for the reaction of cage hydrocarbons with $\mathrm{HNO_3}$ (modeled with an $\mathrm{NO_2^{+}\cdots HNO_3}$ complex)[20] are early along the reaction coordinate, i.e., less carbocation-like than those for the reaction with polarized halogens,[23] we hoped that the nitroxylation of **3** may retain the homoadamantane cage upon CH-substitution.

However, the reaction of **3** with 100% nitric acid, under conditions previously used for the oxidations of a variety of cage hydrocarbons,[27] followed by hydrolysis of the reaction mixture, solely gave the rearranged product (1-hydroxymethyldiamantane, **7**).

To prevent the potential rearrangement of the intermediate homodiamantane nitroxy derivatives (if formed) we attempted quenching the reaction mixture with $\mathrm{NaHCO_3}$ and reduction of the intermediate nitrate with $\mathrm{H_2/PtO_2}$, but we still obtained the rearranged products **7** and **8** (the X-ray crystal structure of **8** is

Scheme 1. Preparation of Homodiamantane (3)



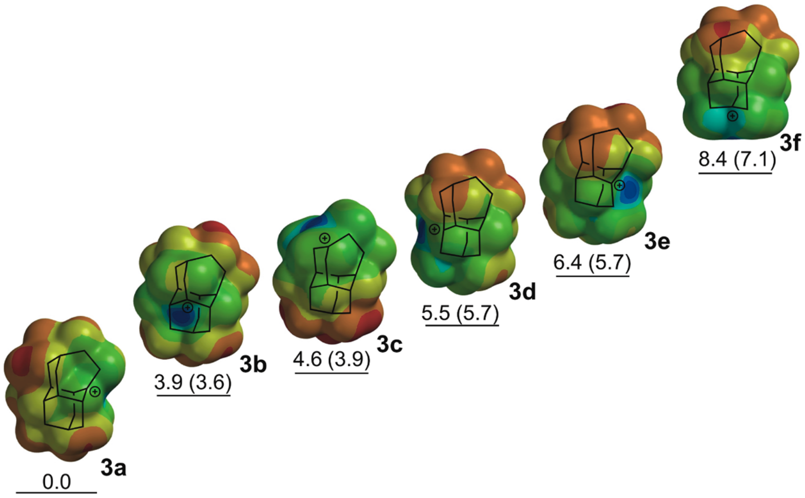
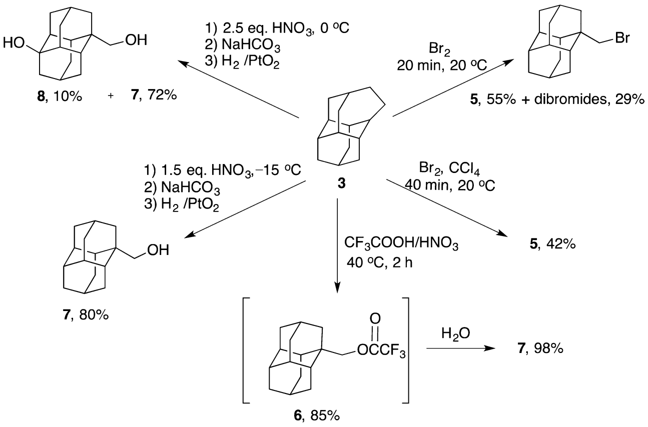


Figure 3. Electrostatic potential surfaces and relative stabilities of tertiary homodiamantyl cations **3a**−**f** (ΔH_{298}, kcal mol^{-1} at B3LYP-D3 (M06-2X)/6-31G(d,p)).

Scheme 2. Yields of Isolated Products for the Functionalizations of 3 with Electrophiles



shown in the SI). Decreasing the nitroxylation temperature to −15 °C as well as nitroxylation of **3** in CF_3COOH also resulted in rearrangement (Scheme 2). We conclude that the preparation of medial tertiary homodiamantane derivatives cannot be achieved with common electrophilic reagents. Even though the attack of electrophiles occurs at the C^{12}-position of **3**, the intermediate cationic intermediates contract and the homodiamantane cage cannot be retained.

We alternatively attempted the C(sp^3)−H functionalizations utilizing reagents that circumvent the formation of cationic intermediates. Dioxiranes[37,38] were particularly successful for the incorporation of hydroxyl functions into a number of cage compounds such as adamantane,[39] dehydroadamantanes,[40] and diamantane[20] with remarkable 3°/2° selectivities, even when the cage is deactivated with electron-withdrawing groups. We utilized dimethyldioxirane (DMD) that can readily be prepared from acetone and oxone $(KHSO_5)_2 \times KHSO_4 \times K_2SO_4$.[41] The CH-functionalizations with DMD mechanistically are very different from the reactions with other electrophiles and can be viewed as concerted insertion[40,42] or as radical abstraction followed by fast rebound.[43] In any case carbocationic transition structures or intermediates are not involved in such transformations. The computed transition structures (Figure 4) for the reaction of DMD with **3** at M06-2X/6-31G(d,p) and B3LYP-D3/6-31G(d,p) show that the attack of the reagent on the C^{12}−H position of **3** through **TS1** dominates and the functionalization is expected to proceed with the same positional selectivity as found above. As **TS3** is substantially

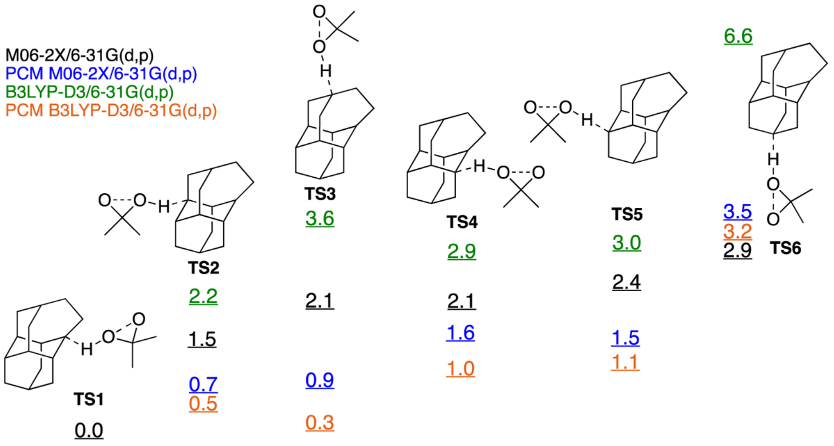


Figure 4. The M06-2X/6-31G(d,p) (black), PCM(CH_2Cl_2)-M06-2X/6-31G(d,p) (blue), B3LYP-D3/6-31G(d,p) (green), and PCM(CH_2Cl_2)-B3LYP-D3/6-31G(d,p) (light brown) relative barriers for the CH-insertions to **3** with dimethyldioxirane (ΔH_{298}, kcal mol^{-1}).

higher in energy than the medial transition structures **TS2** and **TS4**, the formation of apical derivatives is *not* expected based on the gas phase computations. The fact that the most sterically hindered position is attacked preferentially (**TS1**) demonstrates the dominance of electronic[43] over steric[44,45] factors in the reaction of **3** with DMD. The transition structures are highly polarized, and their relative energies nicely mirror the stabilities of the respective carbocations (Figure 3).

As we found that accounting for solvent effects in the CH-bond activations with uncharged electrophiles such as diacetyl changes the positional selectivities,[46] we utilized the polarizable continuum model (PCM) in our computations with DMD in dichloromethane (ε = 8.93) as a model solvent. While the differences in the barriers for the H-insertions into the C^{12}- and other positions of **3** are sizable (2.2 kcal mol^{-1} at B3LYP), accounting for the solvent effects changes this picture considerably (Figure 4): transition structures (**TS1**−**TS3**) become close in energy (within 1 kcal mol^{-1}) implying that the reaction of **3** with DMD will be directed not only to the medial C^1 and C^{12} but also to the apical C^9-position. This is due to generally higher polarizabilities of the apical transition structures[46] and in accord with previous solvent effect studies[47] that demonstrated extraordinary high polarization of the transition structures for reactions with dioxiranes. Although the barriers for the oxygen insertion vary only slightly, the formation of substantial amounts of apical product through **TS3** is expected based on the PCM−DFT computations.

The reaction of **3** with *in situ* generated DMD gave a mixture of alcohols from which the main products, homodiamantan-9-ol (**9**) and homodiamantan-12-ol (**10**), were isolated and characterized individually in good preparative yields (Figure 5); the product distribution is in accord with our computations.

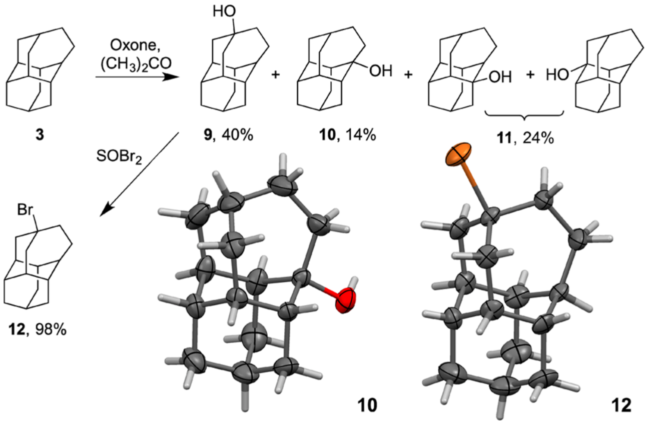


Figure 5. Preparative yields of the products for the reaction of homodiamantane (**3**) with dimethyldioxirane and the X-ray crystal structures of homodiamantan-12-ol (**10**) and 9-bromohomodiamantane (**12**).

The structure of **10** was confirmed by X-ray crystal structure analysis. We were able to perform functional group exchange without rearrangement of the cage; e.g., the reaction of **9** with $SOBr_2$ gave 9-bromohomodiamantane (**12**), whose structure was also confirmed by X-ray crystal structure data analysis (Figure 5). The structures of **9**, **10**, and **12** were fully characterized through the NMR data (see SI for details).

We conclude that the functionalizations of **3** with commonly employed electrophiles (Br_2 and HNO_3) inevitably are accompanied by ring contraction and formation of the corresponding medial 1-diamantylmethyl derivatives. The situation with DMD is clearly different, and **3** can be oxidized with DMD without cage rearrangement. The apical alcohol **9** and medial alcohol **10** that result from high-yielding oxygen insertion into the tertiary CH-bonds of the seven-membered ring are easily separable. Such product distributions are in accord with computed hydrogen abstraction barriers only if solvent effects are accounted in the computations. Hence, DMD, in contrast to the reaction with other electrophiles, allows the preparation of both apical and medial derivatives of homodiamantane. These are valuable building blocks for surface modifications with moderately conformationally flexible diamondoid analogs.

■ EXPERIMENTAL SECTION

General Information. NMR spectra were recorded at 400 and 600 MHz (^1H) spectrometers with TMS as the internal standard. High-resolution mass spectra (HRMS) were recorded using electron impact ionization on a focusing sector-type mass spectrometer. Products were purified by chromatography on 100−160 mesh silica gel. All melting points were determined without correction. Commercially available reagents and solvents were used without further purification.

Homodiamantane (3). A solution of KOH (5.4 g, 96 mmol) in a mixture of 10.2 mL of CH_3OH and 10.2 mL of water was added dropwise to a well-stirred solution of 3.1 g (15 mmol) of diamantanone (**4**)[19] and 16.4 g (76 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 64.2 mL of CH_3OH at 0−3 °C, and the reaction mixture was stirred for 10 h at rt. The reaction mixture was extracted with $CHCl_3$ (5 × 15 mL), the combined extracts were washed with water and brine and dried over Na_2SO_4, and solvent was evaporated. The residual mixture of the isomeric homodiamantanones (3.2 g) and 1.6 mL of hydrazine hydrate ($N_2H_4{\cdot}H_2O$) was heated in 30 mL of diethylene glycol for 2 h at 140 °C. The reaction mixture was cooled, and 3.58 g of KOH was added; water was evaporated, then the reaction mixture was heated for 3 h at 180 °C, cooled, and extracted with hexane (5 × 15 mL), and the combined extracts were washed with water, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (pentane) to give homodiamantane **3** (2.7 g, 13 mmol, 87%), which was identical to the material described previously.[11]

Bromination of Homodiamantane (3) with Neat Br_2. A mixture of 0.2 g of homodiamantane **3** and 1.4 mL of neat bromine (distilled) was stirred for 15 min at rt, quenched with $NaHSO_3$ solution, and extracted with $CHCl_3$ (4 × 10 mL). The combined extracts were washed with water and brine and were dried over Na_2SO_4. Evaporation gave 0.5 g of a mixture of monobromide **5** and dibromides. Purification by column chromatography (hexane/ether 95/5) gave 0.153 g (55%) of **5** as a colorless solid. Mp = 117−118 °C. ^1H NMR (400 MHz, $CDCl_3$): 3.53 (s, 2 H), 2.05−1.39 (m, 19 H). ^{13}C NMR: 45.9 (CH_2), 41.6 (CH_2), 38.7 (CH), 38.6 (CH_2), 38.3 (CH), 37.8 (CH_2), 37.5 (CH), 37.1 (C), 32.6 (CH_2), 27.4 (CH), 25.6 (CH). MS (*m*/*z*): 201 (100%), 145 (10%), 131 (12%), 117 (15%), 105 (19%), 91 (25%). Anal. Calcd for $C_{15}H_{21}Br$: C, 64.06; H, 7.53. Found: C, 64.18; H, 7.63.

Bromination of Homodiamantane (3) with Br_2 in CCl_4. A mixture of 0.2 g of **3** and 0.5 mL of neat bromine (distilled) was stirred in 4 mL of CCl_4 for 40 min at rt, quenched with $NaHSO_3$ solution, and extracted with $CHCl_3$ (4 × 15 mL). The combined extracts were washed with water and brine and were dried over Na_2SO_4. Purification by column chromatography (hexane/ether 95/5) gave 0.116 g (42%) of monobromide **5** as a colorless solid, whose spectral properties were identical to those described above.

Oxidation of Homodiamantane (3) with HNO_3 in CH_2Cl_2. 0.2 g of **3**, CH_2Cl_2 (5 mL), and 1 mL of HNO_3 (100%) was mixed and stirred for 20 min at 0 °C and then 40 min at rt, and then diluted with water (5 mL). CH_2Cl_2 was then evaporated, and the reaction mixture was refluxed for 1.5 h. Then the reaction mixture was extracted with $CHCl_3$ (5 × 10 mL), and the combined extracts were washed with

10% Na_2CO_3 and water and dried over Na_2SO_4. Column chromatography on silica gel (eluent of hexane/ethylacetate = 4/1) gave 0.172 g (80%) 1-hydroxymethyl diamantane (**7**) as a colorless solid with ^1H and ^{13}C NMR spectra identical to literature data.[48]

Oxidation of Homodiamantane (3) with HNO_3 in CF_3COOH. A mixture of 0.2 g of **3** and 3 mL of HNO_3 (65%) was stirred in 4.5 mL of CF_3COOH for 2 h at 40 °C. The reaction mixture was poured into 30 mL of water and extracted with $CHCl_3$ (5 × 10 mL), and the combined extracts were washed with 10% Na_2CO_3 and water and dried over Na_2SO_4. GC/MS analysis of the reaction mixture indicated the formation of diamantylmethyl trifluoroacetate **6** (85%), MS (*m*/*z*): 314 (3%), 201 (8%), 187 (100%), 131 (13%), 117, 115 (14%), 91 (43%), 69 (35%). The reaction mixture was diluted with 10% KOH ethanol solution and stirred at rt for 4 h. The reaction mixture was poured into 50 mL of water and was extracted with $CHCl_3$ (5 × 10 mL), and the combined extracts were washed with water and brine and dried over Na_2SO_4. Column chromatography on silica gel (eluent of hexane/ethylacetate = 4/1) gave 0.180 g (83%) of 1-hydroxymethyldiamantane (**7**) as a colorless solid with ^1H and ^{13}C NMR spectra identical to literature data.[48]

Oxidation of Homodiamantane (3) with HNO_3. A solution of 2 mL of HNO_3 (100%) in 5 mL of CH_2Cl_2 was added dropwise to a mixture of 0.2 g of **3** and 5 mL of CH_2Cl_2 at 0 °C, which was stirred for 10 min at 0 °C, and then 10 mL of CH_2Cl_2 were added to a reaction mixture; excess HNO_3 was neutralized by the addition of dry $NaHCO_3$ in small portions. When gas evolution stopped, the solution was decanted from the solid. Then the solid was washed twice with 5 mL portions of CH_2Cl_2, the extracts were combined, and the solvent was evaporated giving 0.255 g of the crude reaction mixture as a yellow oil. The reaction mixture was diluted with 20 mL of dry methanol, 20 mg of PtO_2 were added, and the reaction mixture was stirred under a H_2 atmosphere for 3 h. The reaction mixture was filtered under an argon atmosphere, and the filtrate was evaporated in vacuo. Column chromatography of the residue on silica gel gave 0.155 g (72%) of 1-hydroxymethyldiamantane (**7**) (eluent of hexane/ethylacetate = 4/1) as a colorless solid with ^1H and ^{13}C NMR spectra identical to literature data[48] and 0.045 g (10%) of 1-hydroxy-6-hydroxymethyldiamantane (**8**) (eluent hexane/ethylacetate = 1/1) as a colorless solid. Mp = 180−181 °C. ^1H NMR (400 MHz, $CDCl_3$): 3.51 (s, 2 H), 2.28 (d, 2 H), 2.01 (m, 3 H), 1.82 (t, 1 H), 1.78 (s, 2 H), 1.66 (s, 2 H), 1.61 (s, 2 H), 1.55 (s, 2 H), 1.38 (d, 4 H). ^{13}C NMR: 71.7 (C), 67.9 (C), 48.1 (CH_2), 44.9 (CH), 41.1 (CH), 40.8 (CH_2), 38.9 (CH), 33.2 (CH_2), 31.5 (CH), 30.7 (CH_2), 28.3 (CH_2). MS (*m*/*z*): 234 (11%), 216 (5%), 203 (100%), 185 (54%), 143 (9%), 129 (16%), 117 (7%), 105 (9%), 95 (10%), 91 (18%). EI-HRMS (*m*/*z*): found 234.1623, calcd for $C_{15}H_{22}O_2$ 234.1620.

Oxidation of Homodiamantane 3 with DMD. To a mixture of 0.75 g (3.7 mmol) of **3**, 10.2 g of Na_2CO_3, 7.3 mL of CH_2Cl_2, 10.2 mL of acetone, and 10.2 mL of distilled water, a solution of 10.3 g (33.5 mmol) of oxone in 15 mL of distilled water was added dropwise under intense stirring at 0 °C over 1 h. The reaction mixture was stirred at rt for 3 h and extracted with $CHCl_3$ (5 × 10 mL), and the combined extracts were washed with water and brine and dried over Na_2SO_4. Solvent evaporation gave 0.72 g of a mixture of monohydroxy derivatives of homodiamantane. Column chromatography on silica gel (eluent of pentane/diethyl ether = 1/1) gave 0.13 g (16%) of 12-homodiamantanol (**10**), 0.34 g (42%) of 9-homodiamantanol (**9**), and 0.21 g of the mixture of 6-homodiamantanol and 1-homodiamantanol (26%).

9-Homodiamantanol (**9**): Mp = 137−138 °C. ^1H NMR (400 MHz, $CDCl_3$): 1.92 (m, 1H), 1.90−1.84 (m, 8 H), 1.81 (m, 1 H), 1.80−1.76 (m, 6 H), 1.76−1.70 (m, 3 H), 1.68 (s, 2 H), 1.62 (s, 1 H). ^{13}C NMR: 71.8 (C), 47.8 (CH), 44.5 (CH_2), 42.8 (CH), 40.7 (CH), 40.0 (CH_2), 38.6 (CH), 37.6 (CH_2), 36.6 (CH_2), 28.3 (CH), 27.0 (CH_2). MS (*m*/*z*): 218 (80%), 200 (100%), 143 (10%), 109 (21%), 91 (47%). EI-HRMS (*m*/*z*): found 218.1668, calcd for $C_{15}H_{22}O$ 218.1671.

12-Homodiamantanol (**10**): Mp = 154−155 °C. ^1H NMR (400 MHz, $CDCl_3$): 2.42 (d, 2 H), 2.0−1.85 (m, 7 H), 1.75−1.6 (m, 7 H), 1.55−1.55 (m, 5 H), 1.3 (s, 1 H). ^{13}C NMR: 76.1 (C), 45.3 (CH), 41.7 (CH_2), 39.7 (CH_2), 39.2 (CH), 38.7 (CH_2), 36.8 (CH), 34.5 (CH_2), 31.3 (CH_2), 28.5 (CH), 25.5 (CH). MS (*m*/*z*): 218 (10%), 200 (100%), 143 (10%), 129 (17%), 109 (45%), 91 (23%). EI-HRMS (*m*/*z*): found 218.1669, calcd for $C_{15}H_{22}O$ 218.1671.

Reaction of Homodiamantan-9-ol (10) with $SOBr_2$. A mixture of 50 mg (0.18 mmol) of 9-hydroxyhomodiamantane (**9**), 16 mg (0.2 mmol) of pyridine, 41 mg (0.2 mmol) of $SOBr_2$, and 2 mL of CH_2Cl_2 was stirred at 0 °C for 15 min. Then the temperature was increased to rt, the reaction mixture was poured into a solution of 10 mL of CH_2Cl_2 and 10 mL of water, which was extracted with CH_2Cl_2 (4 × 10 mL). The combined extracts were washed with water and brine and were dried over Na_2SO_4. Evaporation gave 63 mg (98%) of 9-bromohomodiamantane (**12**) as a white solid. Mp = 123−124 °C (hexane). ^1H NMR (400 MHz, $CDCl_3$): 2.75 (dd, 2 H), 2.57 (dd, 2 H), 2.35 (m, 2 H), 1.92 (m, 1 H), 1.91−1.75 (m, 3 H), 1.75−1.60 (m, 9 H), 1.67−1.57 (m 2 H). ^{13}C NMR: 72.9 (C), 51.4 (CH_2), 47.4 (CH_2), 44.5 (CH), 40.1 (CH_2), 39.9 (CH), 39.8 (CH), 38.4 (CH_2), 36.2 (CH), 31.2 (CH_2), 26.8 (CH). Anal. Calcd for $C_{15}H_{21}Br$: C, 64.06; H, 7.53. Found: C, 64.21; H, 7.34.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The experimental and computational details, the copies of NMR spectra, X-ray crystal structures, as well as *xyz*-coordinates of optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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