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Hydroxy Derivatives of Diamantane, Triamantane, and [121]Tetramantane: Selective Preparation of Bis-Apical Derivatives[‡]

Natalie A. Fokina,[a] Boryslav A. Tkachenko,[a] Anika Merz,[a] Michael Serafin,[b] Jeremy E. P. Dahl,[c] Robert M. K. Carlson,[c] Andrey A. Fokin,*[a,d] and Peter R. Schreiner*[a]

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Functionalizations of diamantane, triamantane, and tetramantane with electrophilic reagents (Br_2, nitric acid) lead to various apical and medial disubstituted products that were separated and characterized individually. The highly desirable and otherwise inaccessible thermodynamically more stable apical bis-derivatives were obtained with high preparative yields through acid catalyzed isomerizations.

Introduction

In recent years considerable research has been focused at the interface between organic chemistry and materials sciences, specifically in the field of nanodiamond applications, ranging from microelectronics[1] to biologically compatible surfaces.[2] Diamond-based materials offer an excellent set of properties, namely hardness, chemical stability, high thermal conductivity, low density, and biocompatibility.[3] Nanometer-sized diamonds (1.4–4.0 nm) are known to be constituents of interstellar dusts and meteorites, carbonaceous residues of detonations, and certain types of diamond films produced by chemical vapor deposition (CVD). These nanodiamond materials are the subject of a growing number of investigations.[4] However, nanodiamonds from these sources cannot be obtained as completely homogeneous materials with definite structures and particle sizes.[5] Their subsequent functionalization produces aggregates with broad size distributions, often with numerous inhomogeneities with respect to surface functionalities.[5]

At the same time, progress in nanotechnology requires functionalized structures assembled with atomic precision. To develop molecule-based electronics it is particularly important to study charge transport across nanometer-scale metal-molecule-metal junctions[6] at various locations of the contact points.[7] Molecules which form assemblies with predictable structures, well-defined attachment points, and highly regular packing are of great value in nanofabrication for the construction of nano-scale devices as well as in polymer chemistry. In the case of self-assembled monolayers,[8,9] chemical and physical properties of the molecular assemblies can lead to numerous applications.

Diamondoids, which resemble parts of the diamond lattice, are very attractive nanoscale building blocks (0.5–2 nm).[10] In contrast to CVD and detonation nanodiamond materials, diamondoids are accessible as individual compounds and allow precise structure-property correlation studies. In particular, electron transport across molecular wire junctions depends on molecular bridge properties and requires analysis of the relationship between transport and properties of the molecular species.[11] Diamondoids possess conformationally rigid structures and their selective functionalizations determine their potential use in nanofabrication techniques as shown recently for adamantane (**1**) (Figure 1).[12] 1-Adamantanethiolate SAMs demonstrated properties useful in "microdisplacement printing", where it was used as a preassembled monolayer being well ordered to protect the surface yet sufficiently labile to enable other molecules to displace it through competitive adsorption. These SAMs are considered as appealing matrices for molecular electronics.[9]

As a whole, the group of lower diamondoids includes also diamantane (**2**) and triamantane (**3**), and higher diamondoids start with tetramantane, which exists in three isomeric forms. Diamondoids are known to be present in nearly all raw petroleum.[13] Adamantane and diamantane

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[a] Institut für Organische Chemie, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany
Fax: +49-641-99-34309
E-mail: prs@org.chemie.uni-giessen.de
Andrey.Fokin@org.chemie.uni-giessen.de
[b] Institut für Anorganische und Analytische Chemie, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany
[c] MolecularDiamond Technologies Chevron Technology Ventures, 100 Chevron Way, Richmond, CA 94802, USA
[d] Department of Organic Chemistry, Kiev Polytechnic Institute, pr. Pobedy 37, 03056 Kiev, Ukraine

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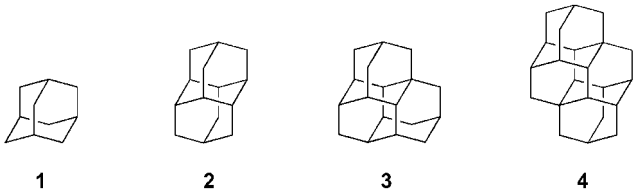


Figure 1. Diamondoids: adamantane (**1**), diamantane (**2**), triamantane (**3**), and [121]tetramantane (**4**).

were the subjects of numerous investigations since their synthesis.[12,14] Diamondoids **3** and **4** also are available synthetically in very small amounts,[15] however, extensive studies became possible only recently. Since they have been found in sizeable quantities in oil, and have been isolated from some deep natural gas condensates,[16] the chemistry of these hydrocarbons received a powerful stimulus.

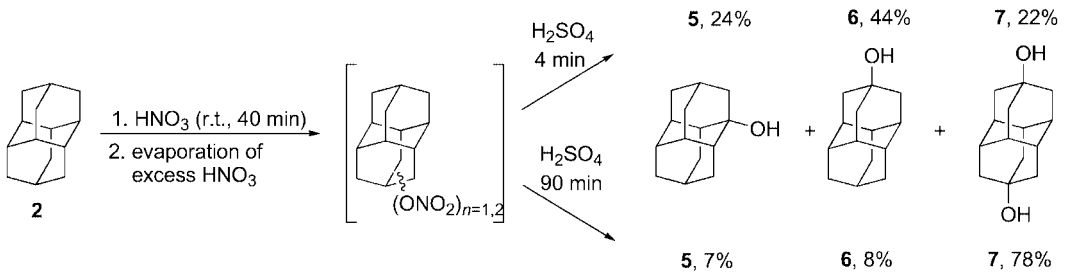
The selective introduction of substituents to diamondoids is a challenging task owing to the large number of similarly reactive tertiary C–H bonds. Previously, based on our computational predictions,[17] we showed experimentally the potential of electrophilic and oxidative transformations of these hydrocarbons.[18,19] The reactions of compounds **2**, **3**, and **4** with electrophilic reagents lead predominantly to medial substitutions[18,20,21] with a selectivity increase in the sequence **2**–**3**–**4**. The utility of these results is emphasized by the fact that free-radical approaches give mixtures of all possible tertiary and even secondary derivatives.[17] Apical derivatives of **3** and **4** can be prepared through photooxidation with triplet diacetyl [$CH_3C(O)$-$C(O)CH_3$].[18,19] The steric hindrance at the medial positions directs the course of these reactions and leads to apical mono- and diacetyl derivatives almost exclusively. However, photoacetylation has poor prospects as a preparative method. Taking into consideration the potential of apical derivatives for various applications, preparative approaches are essential.

Within the broader context of our studies in the field of hydrogen-terminated nanodiamonds (interchangeably used with the term "diamondoids"), we now present approaches that are amenable to the large-scale production of mono- and bis-functionalized diamondoids. These approaches are based on the combination of kinetically and thermodynamically controlled C–H substitutions, and are in agreement with our earlier computational predictions.[17] We studied the oxidations of diamantane (**2**), triamantane (**3**), and [121]-tetramantane (**4**) with 100% nitric acid in order to elaborate the routes to their apical mono- and bis-hydroxy derivatives. The advantages of this derivatization approach are scalability, high yields, and predictable as well as adjustable product compositions. The hydroxy diamondoid products can be converted to a large variety of functionalized diamondoids with well-defined attachment points.[22]

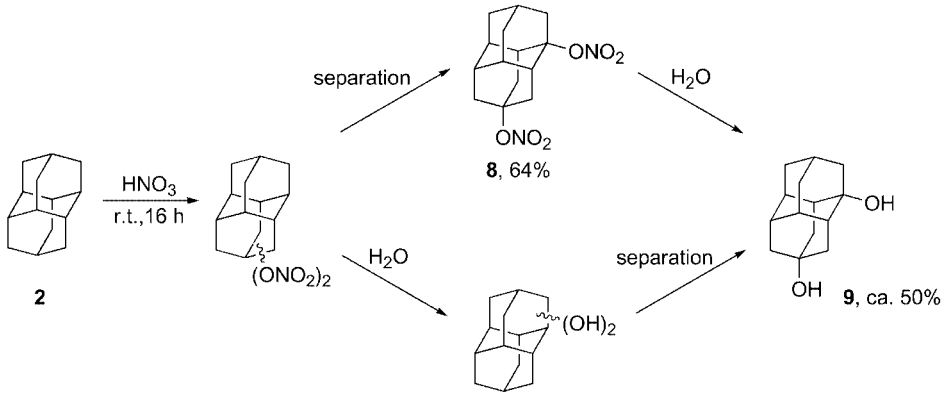
Results and Discussion

The selective preparation of apical derivatives of diamondoids is very challenging. Previously we showed that most C–H functionalizations lead predominantly to substitutions in the medial or "belt" positions.[18] Oxidation of diamondoids with 100% nitric acid affected only tertiary positions, which we preliminarily demonstrated for hydrocarbons **2**, **3**, and **4**.[17,18] Here, we show that their oxidation with 100% nitric acid can be performed in a kinetically controlled way, and that the nitroxy derivatives can be hydrolyzed to the respective hydroxy compounds. The use of 100% nitric acid makes the processes technologically efficient, as the acid can be regenerated by distillation. Moreover, its practical value is reinforced by the fact that the process is metal- and halogen-free. The transformations of hydrocarbons **2**, **3**, and **4** to the alcohols and diols has substantial advantages over bromination because the isomeric hydroxy derivatives are easier to separate.[21,23]

*Hydroxylation of Diamantane (**2**):* En route to apical hydroxy derivatives of diamantane (**2**) we studied the reaction of **2** with 100% nitric acid, which gave a mixture of mono- and dinitroxy derivatives. Subsequent isomerization of this mixture with sulfuric acid followed by hydrolysis gave 4-hydroxydiamantane (**6**) as the major product (Scheme 1). The alcohols **5** and **6** can be separated by column chromatography on silica gel or through recrystallization from cyclohexane or ethyl acetate; pure diol **7** can be filtered from the reaction mixture. Both nitroxy and hydroxy derivatives can be isomerized with sulfuric acid; however, the nitroxy compounds are more soluble in sulfuric acid. Depending on the reaction time, isomerization of the mixture of nitroxy diamantanes can lead either to the mixture of alcohols **5**–**7** enriched with the apical derivative **6**, or to the almost exclusive formation of 4,9-dihydroxydiamantane (**7**, Scheme 1). Oxidation of **2** at longer reaction times allows to obtain the mixture dinitroxydiamantanes, where the 1,4-dinitroxydiamantane (**8**) dominates (Scheme 2).



Scheme 1. Nitroxylation of diamantane (**2**) and subsequent isomerization (all yields are preparative).



Scheme 2. Preparation of 1,4-dihydroxydiamantane (**9**) via nitroxylation and subsequent hydrolysis.

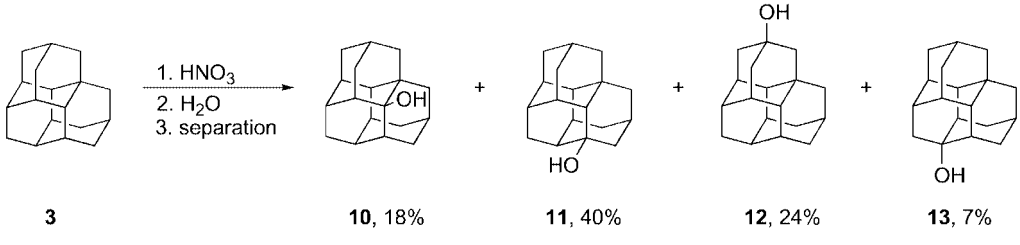
After the reaction with 100% nitric acid, there are two possibilities to isolate the 1,4-diamantane derivatives. The first involves chromatographic separation of 1,4-dinitroxydiamantane (**8**, 64%) from the mixture and its subsequent hydrolysis to the target 1,4-diol (**9**). The second utilizes the hydrolysis of the mixture of dinitroxy derivatives followed by chromatographic separation of diol **9**. We examined both ways and obtained 1,4-dihydroxydiamantane (**9**) in ca. 50% yield.

*Hydroxylation of Triamantane (**3**):* After obtaining satisfactory results with diamantane (**2**), we examined the applicability of this approach to larger diamondoids. The selective functionalization of triamantane (**3**) represents a challenging task as the molecule has four different tertiary C–H bonds. The reactivity of this hydrocarbon has not been studied well, and only some bromo derivatives were obtained earlier.[20,24] Previously, we described the oxidation of **3** with 100% nitric acid leading to three monohydroxytriamantanes with the OH group in the 2- (**10**), 3- (**11**), and 9- (**12**) positions.[18] Here we present a procedure that additionally allows the separation of hitherto unknown 4-hydroxytriamantane (**13**, Scheme 3).

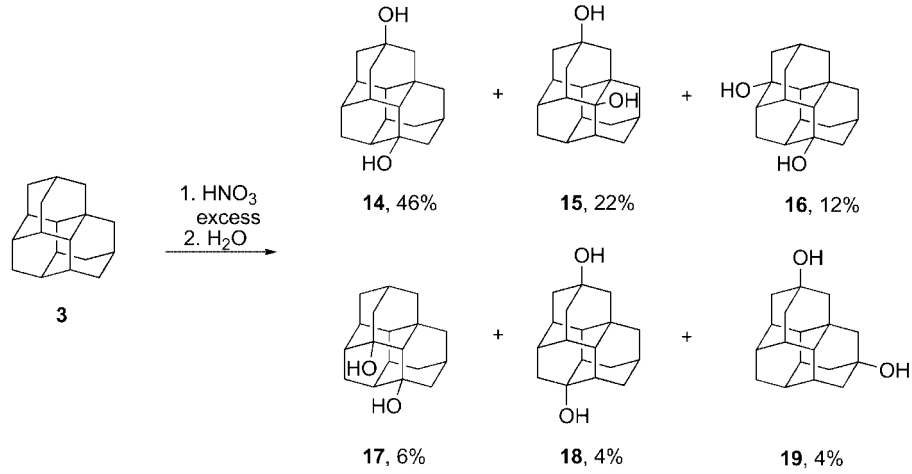
To the best of our knowledge, triamantane derivatives functionalized at C-4 can be obtained only through the protocol presented here. The corresponding 4-bromide is formed only in trace amounts in the reaction of **3** with neat bromine for which the 2-substitution product dominates,[25] while with HNO_3 preferential formation of 3-hydroxytriamantane (**11**) was observed.[18] Thus, we assumed that 3-substituted derivatives must prevail in the disubstitution reaction. Indeed, at elongated reaction times with excess of nitric acid, the hydrolysis gave a mixture of triamantane diols where 3,9-dihydroxy derivative **14** was the main product (46%, Scheme 4). This mixture was separated by column chromatography and diols **14**–**19** were characterized individually.

The structural assignments for diols **14**–**19** were made based on their spectroscopic data. Diol **19** was identical to the standard sample obtained earlier as a result of consecutive transformations, namely, photoacetylation of triamantane (**3**), Baeyer–Villiger oxidation of 9,15-diacetyl triamantane and subsequent hydrolysis.[18] The structure of diol **16** was assigned based on the ^{13}C NMR spectrum considering the fact that this compound is the only one among the tertiary dihydroxy derivatives to have C_2-symmetry. The structures of diols **14**, **15**, **17**, and **18** were determined based on comparison of the experimental and calculated (via increments) ^{13}C NMR spectra. Chemical shifts of each carbon of the diols were calculated via increments obtained from literature data[25] as well as those from the ^{13}C NMR spectrum of 4-hydroxy triamantane (**13**, see above) for the C-4 hydroxy group. Values of the increments of 4-hydroxytriamantane (**13**) in the ^{13}C NMR spectra are provided in the Supporting Information (Figure S1). Additionally, we confirmed the structure of C_s-symmetrical diol **17** by an X-ray analysis (Figure 2).

As expected from the selectivity of the mononitroxylation reaction, the diols with an OH group at C-3 (i.e., diols **14**, **16**, and **17**) dominate in the reaction mixture. However, the kinetically controlled bis-functionalization of **3** is not very selective, although the diol **14** forms as the main product. The most attractive bis-apical C_{2v}-symmetrical diol **19**



Scheme 3. Preparation of monohydroxy derivatives of triamantane (**3**).



Scheme 4. Kinetically controlled bis-substitution of triamantane (**3**) with nitric acid.

was obtained in only 4% yield via the kinetically controlled dinitroxylation of **3**. In order to estimate the possibility of increasing the selectivity through thermodynamically controlled isomerizations we computed the relative stabilities of diols **14**–**19**. We found that diol **17** is the least and diol **19** is the most stable ($\Delta\Delta G_{298}$ = 6 kcal/mol, B3PW91/6-311+G**) among the isomers, and the enthalpy mostly contributes to their energy difference ($\Delta\Delta H_{298}$ = 5.4 kcal/mol, for the relative $\Delta\Delta G_{298}$ values, geometries and *xyz* coordinates of optimized molecules see Supporting Information). As a result, the isomerization of the mixture of hydroxy derivatives in 98% H_2SO_4 led to the selective formation of the most thermodynamically stable diol **19** (Scheme 5). The latter, being highly symmetric, is minimally soluble in or-

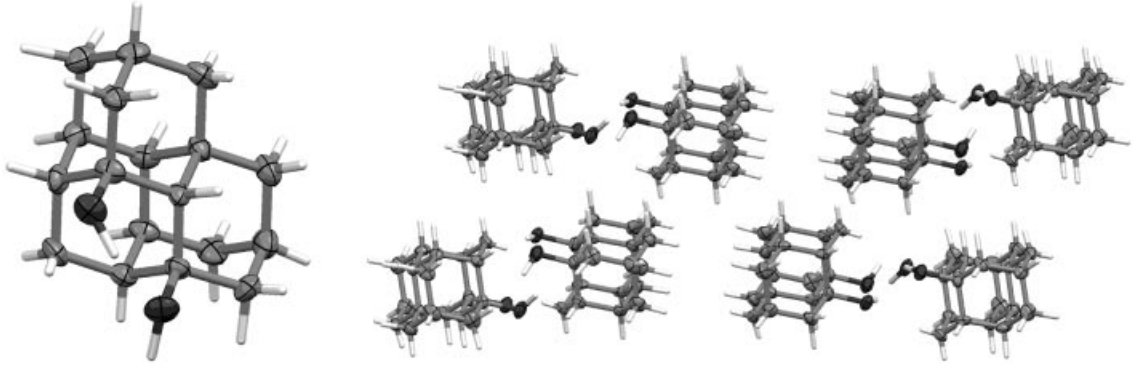
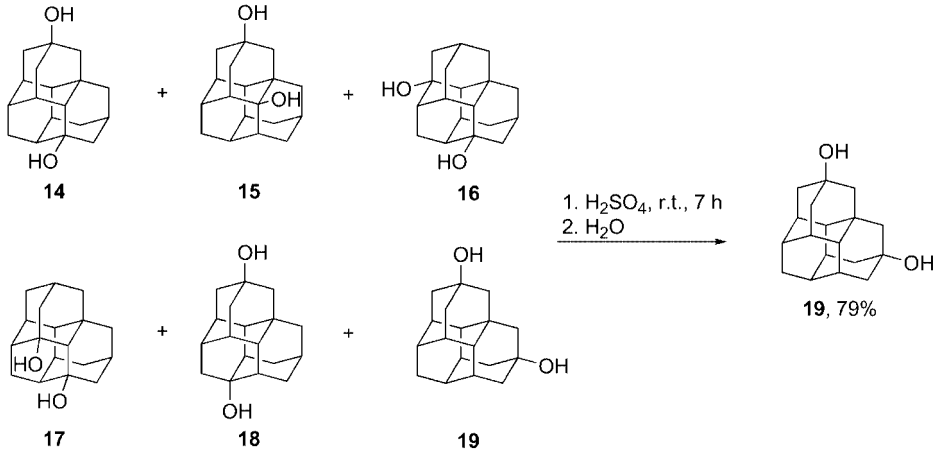


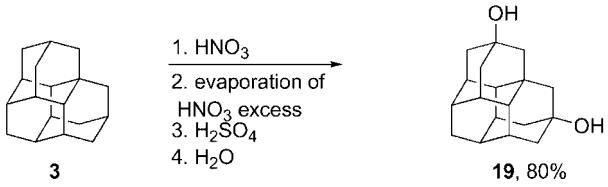
Figure 2. The X-ray structure (50% probability) of diol **17** and its crystal packing.



Scheme 5. Thermodynamically controlled isomerization of triamantane diols.

ganic solvents and was separated by filtration of the reaction mixture in 79% preparative yield (Scheme 5).

Alternatively, we obtained diol **19** directly from **3** (Scheme 6). The mixture of nitroxy derivatives obtained after evaporation of nitric acid was isomerized in presence of sulfuric acid to give diol **19** in 80% preparative yield. This approach may have technological advantages for the preparation of **19** as it avoids photochemical oxidations and treatment with peracids.[17]



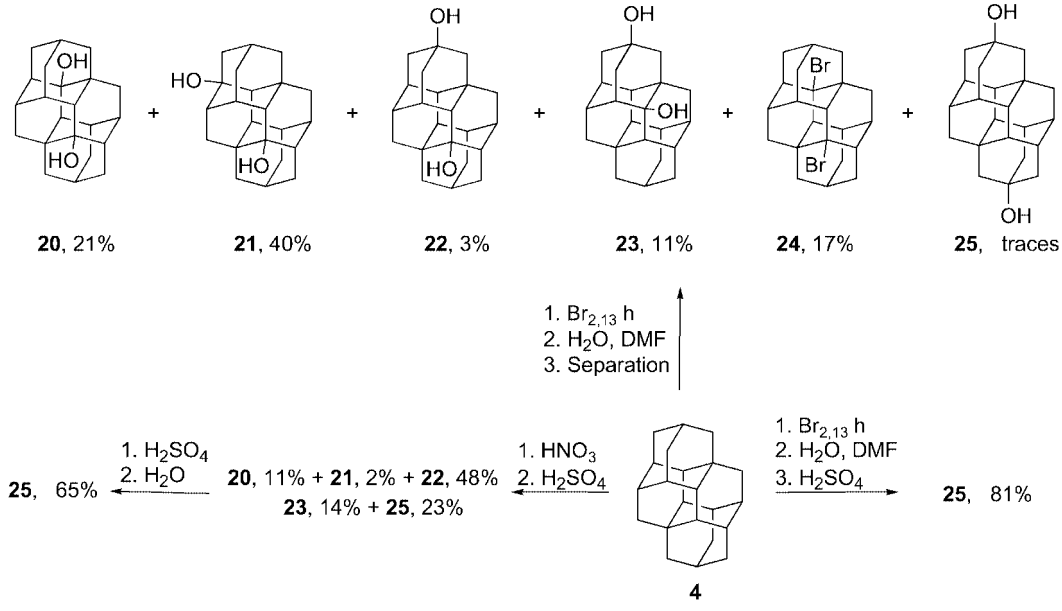
Scheme 6. One-pot preparation of bis-apical diol **19** from triamantane (**3**).

Thus, while the kinetically controlled bis-functionalization with HNO_3 leads to a mixture enriched with belt-substituted triamantanes, the subsequent thermodynamically controlled isomerization allows the selective preparation of bis-apical diol **19**.

*Bis-Functionalization of [121]Tetramantane (**4**):* As we have shown recently, the mono-bromination of [121]tetramantane (**4**) is highly selective and gives 2-bromo derivative in 89% yield; as a consequence, 2-bromo derivatives dominate in the dibromination reaction mixture.[18] After its hydrolysis in DMF/water we obtained a number of diols **20**–**23** as well as dibromide **24** (Scheme 7). The mixture was separated and compounds **20**–**24** were characterized individually. The structures of C_i-symmetric diol **20** and dibromide **24** were confirmed by the ^{13}C NMR spectroscopic data; the structure of dibromide **24** was additionally confirmed by an X-ray analysis (Figure 3). The structures of the asymmetric diols **21**–**23** were assigned by comparing the chemical shifts of C–OH carbon atoms in their ^{13}C NMR spectra with those of 2- and 6-hydroxytetramantanes described previously[18] because the differences in these values for the α-oxygen-substituted C atoms are quite characteristic (73.8 vs. 68.4 ppm for C-2 and C-6 hydroxylated carbon atoms, respectively). Diol **25** was identical to the one obtained earlier via photooxidation of **4** with diacetyl, followed by oxidation and hydrolysis.[18]

As expected from the mononitroxylation reaction, the selectivity of the dinitroxylation is lower than that of the brominations and different selectivities are observed. Thus, in contrast to dibromination/hydrolysis products where medial derivatives **20** and **21** dominate, dinitroxylation followed by hydrolysis gave mostly apical derivatives **22** and **25**. However, substantial amounts of other diols (**20**, **21**, and **23**) were also present in the reaction mixture. The preparative significance of this procedure was substantially improved by subsequent isomerizations. After treatment of the mixture of diols obtained either from bromination or nitroxylation with sulfuric acid, the bis-apical diol **25** was obtained in 81 and 65% yields, respectively. This selectivity is due to the higher thermodynamic stability of the apical derivatives.

The computed $\Delta\Delta G_{298}$ between the least stable diol **20** and the most stable diol **25** is ca 3 kcal/mol at B3PW91/6-311+G**. Thus, thermodynamically controlled transformations clearly favor diapical substitutions in higher diamondoids.



Scheme 7. Bis-functionalizations of [121]tetramantane (**4**).

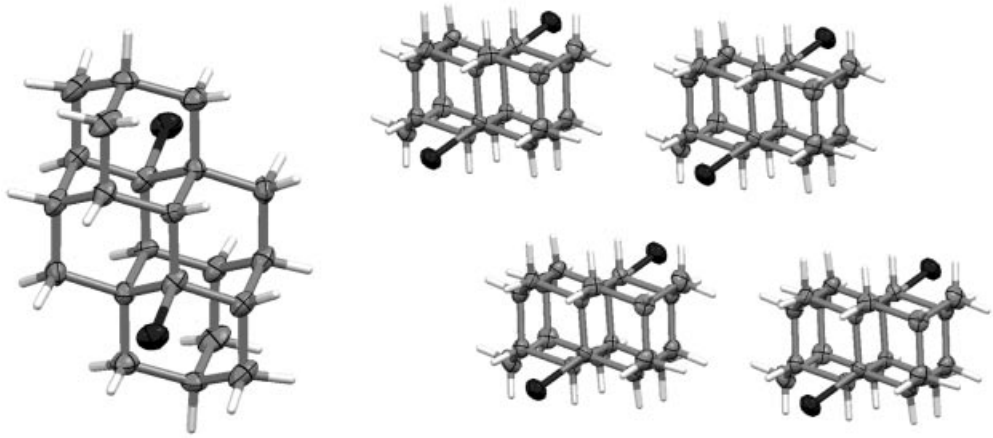


Figure 3. The X-ray structure of dibromide **24** and its crystal packing.

Conclusions

Kinetically controlled dibrominations and dinitroxylations of diamantane, triamantane, and [121]tetramantane show markedly different selectivities. Medial bis-derivatives dominate in the bromination reactions, while apical products predominantly form in the nitroxylations. The apical derivatives thermodynamically are 2–5 kcal/mol more stable then the medial ones. This allows the selective preparation of the bis-apical diamondoid derivatives through acid-catalyzed rearrangements of mixtures of products obtained after the primary functionalizations.

Experimental Section

Computational Details: All computations were performed with the GAUSSIAN03 program suite[26] utilizing analytical first and second energy derivatives. Harmonic vibrational frequencies were computed to ascertain the nature of all stationary points. The computed enthalpies and free energies were not scaled. As several recent studies have questioned the reliability of popular DFT methods for energy evaluations,[27] we used the B3PW91 functional as more trustworthy for large molecules.[28]

General Procedure for Hydroxylation of Diamondoids with Nitric Acid: 100% HNO_3 was added dropwise to a suspension of well triturated diamondoid in CH_2Cl_2 at 0 °C whilst stirring. The reaction mixture was stirred for 0.5 h at 0 °C and then at ambient temperature (for exact times of stirring see Supporting Information). Then the reaction mixture was diluted with water. Excess CH_2Cl_2 was distilled off and the residue was refluxed for 2 h, cooled and extracted with $CHCl_3$. The combined organic extracts were washed with water, aq. satd. $NaHCO_3$, brine, dried with Na_2SO_4. After solvent removal, a mixture was separated by the column chromatography on silica gel.

General Procedure for Hydroxylation of Diamondoids with Subsequent Isomerization: 100% HNO_3 was added dropwise to a solution of diamondoid in CH_2Cl_2 at 0 °C whilst stirring. The reaction mixture was stirred for 0.5 h at 0 °C and then at ambient temperature (for exact times of stirring see Supporting Information). Then the reaction mixture was diluted with water. Excess CH_2Cl_2 was distilled off and the residue was refluxed for 2 h, cooled and extracted with $CHCl_3$. The combined organic extracts were washed with water, aq. satd. $NaHCO_3$, brine, dried with Na_2SO_4 and concentrated under reduced pressure. $CHCl_3$ and 96% H_2SO_4 were added to the residue at 0 °C whilst stirring. The reaction mixture was stirred at 0 °C and then at ambient temperature (for exact times of stirring see the Supporting Information), poured onto ice and filtered. The precipitate was washed with water and chloroform. The filtrate was divided into organic and aqueous parts. The aqueous part of the filtrate was percolated with ether for 24 h. The organic phase of the filtrate was washed with water, aq. satd. $NaHCO_3$, brine, dried with Na_2SO_4. After solvent removal, a mixture was separated by the column chromatography on silica gel.

1,4-Dinitroxydiamantane (8): Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.61 (m, 2 H), 2.41 (m, 1 H), 2.38 (m, 1 H), 2.21 (m, 3 H), 2.12 (m, 4 H), 2.04 (m, 1 H), 1.97 (m, 1 H), 1.94 (m, 1 H), 1.73 (AB, J = 13.4 Hz, 1.68 2 H_A, 1.75 2H_B) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 90.4 (C), 87.0 (C), 41.6 (CH), 39.1 (CH_2), 39.0 (CH), 38.5 (CH), 38.0 (CH_2), 35.3 (CH_2), 34.4 (CH_2), 29.7 (CH) ppm. IR ($\tilde{\nu}$, $CHCl_3$): = 2990 (C–H), 2860 (C–H), 1610 (N=O), 1306 (N=O), 1250 (C–O), 1245 (C–O) cm^{-1}.

1,4-Dihydroxydiamantane (7): Yield 47%. ^{1}H NMR (400 MHz, [D_6]-DMSO, 22 °C): δ = 2.50 (br. s, 2 H), 2.06 (d, J = 11.8 Hz, 2 H), 1.94 (m, 1 H), 1.77 (m, 2 H), 1.69 (m, 1 H), 1.63 (m, 2 H), 1.60–1.50 (m, 6 H) 1.46 (m, 2 H), 1.17 (d, J = 11.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 22 °C): δ = 67.6 (C), 65.2 (C), 45.5 (CH_2), 45.4 (CH_2), 45.3 (CH), 40.0 (CH_2), 38.5 (CH), 38.3 (CH), 36.2 (CH_2), 29.5 (CH) ppm. MS: m/z (%) = 220 (35), 202 (100), 159 (11), 145 (44), 133 (5), 120 (9), 107 (49), 95 (18), 79 (14), 55 (12). Other physico-chemical characteristics of 1,4-dihydroxydiamantane (**7**) are identical to those previously reported.[29]

4-Hydroxytriamantane (13): Was obtained as a colorless solid, yield 7%, m.p. 224–226 °C (*n*-hexane). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.19 (m, 1 H), 2.12 (m, 1 H), 1.85 (m, 3 H), 1.71 (m, 6 H), 1.67 (m, 2 H), 1.61 (d, J = 3 Hz, 2 H), 1.59 (m, 2 H), 1.48 (m, 1 H), 1.42 (m, 1 H), 1.36 (m, 1 H), 1.32 (m, 2 H), 1.26 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 27 °C): δ = 70.1 (C), 49.0 (CH), 46.4 (CH_2), 45.0 (CH_2), 44.4 (CH_2), 43.4 (CH), 39.3 (CH), 37.6 (CH), 37.2 (CH_2), 33.0 (C), 32.5 (CH_2), 27.5 (CH), 27.1 (CH) ppm. MS: m/z (%) = 256 (10), 238 (100), 223 (2), 195 (2), 181 (3), 167 (8), 142 (10), 129 (8), 105 (5), 91 (8). HR-MS (m/z), found 256.1828; calcd. for $C_{18}H_{24}O$: 256.1827. $C_{18}H_{24}O$ (256.38): calcd. C 84.32, H 9.44; found C 84.22, H 9.40.

3,9-Dihydroxytriamantane (14): Was obtained as a colorless solid, yield 46%, m.p. 202–204 °C (chloroform). ^{1}H NMR (400 MHz,

CD_3OD, 23 °C): δ = 2.38 (m, 1 H), 2.25 (dt, J_1 = 12.6, J_2 = 3.3 Hz, 1 H), 2.04 (m, 1 H), 1.91 (m, 1 H), 1.81 (m, 1 H), 1.75–1.55 (m, 11 H), 1.43–1.26 (m, 8 H) ppm. ^{13}C NMR (50 MHz, CD_3OD, 23 °C): δ = 71.8 (C), 68.5 (C), 52.6 (CH_2), 52.0 (CH), 47.2 (CH_2), 46.4 (CH), 45.8 (CH_2), 45.7 (CH_2), 45.6 (CH_2), 41.8 (CH), 41.4 (CH), 40.6 (CH), 39.5 (C), 38.3 (CH_2), 35.8 (CH), 35.1 (CH), 32.9 (CH_2), 31.9 (CH) ppm. MS: *m*/*z* (%) = 272 (5), 254 (100), 197 (7), 183 (3), 148 (9), 145 (17), 131 (7), 106 (10), 91 (5). HR-MS (*m*/*z*), found 272.1754; calcd. for $C_{18}H_{24}O_2$: 272.1776.

2,9-Dihydroxytriamantane (15): Was obtained as a colorless solid, yield 22%, m.p. 246–248 °C (chloroform). ^{1}H NMR (200 MHz, CD_3OD, 22 °C): δ = 2.32–2.15 (m, 2 H), 1.96 (m, 1 H), 1.90 (m, 2 H), 1.85 (m, 1 H), 1.78 (m, 2 H), 1.75–1.62 (m, 10 H), 1.58 (m, 2 H), 1.49–1.33 (m, 2 H), 1.07–0.08 (m, 2 H) ppm. ^{13}C NMR (50 MHz, CD_3OD, 23 °C): δ = 73.3 (C), 68.6 (C), 47.9 (CH), 47.4 (CH_2), 46.2 (CH_2), 44.8 (CH), 41.6 (CH), 41.6 (CH), 40.8 (C), 40.7 (CH), 40.6 (CH_2), 40.1 (CH_2), 39.8 (CH), 39.2 (CH_2), 38.8 (CH), 38.2 (CH_2), 33.4 (CH_2), 28.3 (CH) ppm. MS: *m*/*z* (%) = 272 (24), 254 (100), 196 (13), 158 (7), 145 (97), 129 (5), 107 (5), 91 (8). HR-MS (*m*/*z*), found 272.1772; calcd. for $C_{18}H_{24}O_2$: 272.1776.

3,11-Dihydroxytriamantane (16): Was obtained as a colorless solid, yield 12%, m.p. 278–280 °C (chloroform). ^{1}H NMR (400 MHz, CD_3OD, 24 °C): δ = 2.34 (m, 2 H), 2.03 (m, 2 H), 1.92 (t, J = 2.4 MHz, 2 H), 1.72 (m, 1 H), 1.70–1.60 (m, 6 H), 1.56 (m, 1 H), 1.53 (m, 1 H), 1.50 (m, 2 H), 1.40 (m, 1 H), 1.37 (m, 1 H), 1.28 (m, 4 H), 1.24 (m, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 24 °C): δ = 70.9 (C), 52.4 (CH), 47.1 (CH_2), 45.2 (CH_2), 41.8 (CH), 39.1 (C), 38.1 (CH_2), 34.7 (CH), 31.9 (CH), 27.8 (CH_2) ppm. MS: *m*/*z* (%) = 272 (8), 254 (100), 236 (15), 213 (4), 165 (23), 145 (9), 106 (6), 91 (6). HR-MS (*m*/*z*), found 272.1772; calcd. for $C_{18}H_{24}O_2$: 272.1776.

3,7-Dihydroxytriamantane (17): Was obtained as a colorless solid, yield 6%, m.p. 277–279 °C (chloroform). ^{1}H NMR (400 MHz, CD_3OD, 24 °C): δ = 2.50 (dt, J_1 = 13.9 MHz, J_2 = 3.0 MHz, 1 H), 2.03 (m, 2 H), 1.85 (m, 2 H), 1.72–1.55 (m, 11 H), 1.40 (m, 1 H), 1.37–1.25 (m, 7 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 24 °C): δ = 74.3 (C), 56.2 (CH), 46.5 (CH), 46.3 (CH_2), 45.0 (CH_2), 42.6 (CH), 40.9 (CH), 40.1 (C), 37.9 (CH_2), 31.6 (CH), 29.3 (CH_2) ppm. MS: *m*/*z* (%) = 272 (53), 254 (100), 236 (53), 195 (5), 183 (5), 165 (17), 155 (10), 145 (19), 129 (33), 117 (16), 106 (33), 91 (38). HR-MS (*m*/*z*), found 272.1759; calcd. for $C_{18}H_{24}O_2$: 272.1776. $C_{18}H_{24}O_2$ (272.38): calcd. C 79.37, H 8.88; found C 79.40, H 8.84.

4,9-Dihydroxytriamantane (18): Was obtained as a colorless solid, yield 4%, m.p. 219–221 °C (chloroform). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 2.50 (br. d, J = 12.8 MHz, 2 H), 1.91 (m, 2 H), 1.81 (m, 1 H), 1.77 (m, 1 H), 1.74–1.61 (m, 10 H), 1.59 (m, 2 H), 1.42 (m, 1 H), 1.39 (m, 1 H), 1.35 (m, 2 H), 1.32 (m, 2 H) ppm. ^{13}C NMR (50 MHz, CD_3OD, 24 °C): δ = 74.3 (C), 68.4 (C), 52.6 (CH_2), 49.3 (CH), 46.6 (CH_2), 46.2 (CH_2), 45.4 (CH_2), 43.8 (CH), 41.5 (CH), 39.6 (CH), 36.5 (C), 33.4 (CH_2), 28.1 (CH) ppm. MS: *m*/*z* (%) = 272 (13), 254 (100), 196 (3), 159 (4), 145 (10), 129 (5), 109 (11), 91 (9). HR-MS (*m*/*z*), found 272.1781; calcd. for $C_{18}H_{24}O_2$: 272.1776.

2,17-Dibromo[121]tetramantane (24): Was obtained as a colorless solid, yield 17%, m.p. 230–232 °C (chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.71 (br. s, 2 H), 2.58 (dq, J_1 = 13.1, J_2 = 3.2 Hz, 2 H), 2.24 (t, J = 2.1 Hz, 2 H), 2.16 (m, 2 H), 2.01–1.94 (m, 4 H), 1.94–1.90 (m, 2 H), 1.89–1.83 (m, 2 H), 1.82–1.66 (m, 4 H), 1.60 (dq, J_1 = 13.1, J_2 = 2.7 Hz, 2 H), 1.25–1.15 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 89.51 (CBr), 58.91 (CH), 48.10 (CH), 42.74 (C), 41.26 (CH_2), 40.29 (CH), 40.15 (CH_2), 38.30 (CH_2), 34.86 (CH_2), 34.67 (CH), 26.88 (CH) ppm. MS: *m*/*z* (%) = 371 (99), 369 (100), 325 (4), 307 (3), 289 (16), 233 (2), 193 (2), 155 (6), 141 (15), 129 (14), 105 (11), 91 (18), 79 (6), 67 (5). $C_{22}H_{26}Br_2$ (450.25): calcd. C 58.69, H 5.82; found C 58.54, H 5.63.

[121]Tetramantane-2,17-diol (20): Was obtained as a colorless solid, m.p. 247–248 °C (chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 2.19–2.10 (m, 3 H), 2.10–2.06 (m, 1 H), 1.94–1.87 (m, 2 H), 1.80 (m, 2 H), 1.77 (m, 1 H), 1.75–1.67 (m, 5 H), 1.62–1.58 (m, 1 H), 1.58–1.54 (m, 1 H), 1.50 (m, 2 H), 1.46 (m, 1 H), 1.44–1.38 (m, 3 H), 1.37 (br. s, 2 H), 1.04 (dt, J_1 = 12.5, J_2 = 2.4 Hz, 2 H), 0.98 (dd, J_1 = 13.1, J_2 = 3.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 73.28 (COH), 54.28 (CH), 43.44 (CH), 39.44 (CH_2), 39.17 (CH), 38.47 (C), 38.47 (CH_2), 37.28 (CH_2), 32.20 (CH_2), 31.63 (CH), 26.89 (CH) ppm. MS: *m*/*z* (%) = 324 (31), 306 (100), 289 (18), 193 (2), 179 (5), 144 (22), 129 (15), 105 (12), 91 (21), 79 (12), 55 (7). HR-MS (*m*/*z*), found 324.2082; calcd. for $C_{22}H_{28}O_2$: 324.2089.

[121]Tetramantane-2,18-diol (21): Was obtained as a colorless solid, m.p. 180–182 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ = 2.36–2.30 (m, 1 H), 2.13–2.00 (m, 3 H), 1.92–1.86 (m, 1 H), 1.83–1.77 (m, 1 H), 1.77–1.70 (m, 1 H), 1.69–1.60 (m, 5 H), 1.60–1.47 (m, 7 H), 1.47–1.17 (m, 7 H), 1.15 (br. s, 1 H), 1.06 (dt, J_1 = 12.8, J_2 = 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 72.70 (COH), 70.29 (COH), 52.15 (CH), 51.64 (CH), 45.79 (CH_2), 44.36 (CH_2), 43.66 (CH), 43.31 (CH_2), 42.82 (CH), 42.44 (CH), 39.41 (CH), 38.13 (CH_2), 37.71 (CH_2), 37.40 (C), 37.40 (CH), 36.62 (CH_2), 34.76 (C), 33.77 (CH_2), 33.36 (CH), 32.40 (CH_2), 30.18 (CH), 27.25 (CH) ppm. MS: *m*/*z* (%) = 324 (27), 306 (100), 288 (18), 278 (3), 265 (1), 176 (7), 163 (10), 129 (17), 117 (8), 105 (14), 91 (27), 79 (11), 55 (8). HR-MS (*m*/*z*), found 324.2068; calcd. for $C_{22}H_{28}O_2$: 324.2089.

[121]Tetramantane-2,6-diol (22): Was obtained as a colorless solid, m.p. 213–215 °C (chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.39–2.33 (m, 1 H), 2.14–2.07 (m, 1 H), 1.94–1.89 (m, 1 H), 1.87–1.54 (m, 15 H), 1.54–1.49 (m, 1 H), 1.48–1.41 (m, 1 H), 1.35 (m, 2 H), 1.33 (d, J = 3.2 Hz, 1 H), 1.29–1.21 (m, 2 H), 1.17 (br. s, 1 H), 1.03 (dt, J_1 = 12.7, J_2 = 2.5 Hz, 1 H), 0.98 (dd, J_1 = 12.9, J_2 = 2.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 73.76 (COH), 68.25 (COH), 51.42 (CH), 51.17 (CH_2), 48.71 (CH), 45.70 (CH), 44.83 (CH_2), 44.80 (CH_2), 44.80 (CH_2), 43.95 (CH), 40.08 (CH), 39.52 (CH), 38.84 (CH_2), 38.36 (CH_2), 38.20 (C), 37.83 (CH), 37.68 (CH_2), 35.27 (CH), 35.00 (C), 34.72 (CH), 32.35 (CH_2), 27.28 (CH) ppm. MS: *m*/*z* (%) = 324 (11), 306 (100), 290 (3), 265 (5), 233 (2), 221 (2), 195 (2), 171 (3), 142 (24), 129 (14), 115 (10), 105 (10), 91 (25), 79 (13), 55 (8). HR-MS (*m*/*z*), found 324.2069; calcd. for $C_{22}H_{28}O_2$: 324.2089.

[121]Tetramantane-2,13-diol (23): Was obtained as a colorless solid, m.p. 199–201 °C (chloroform). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.23–2.03 (m, 4 H), 1.92–1.87 (m, 1 H), 1.86–1.76 (m, 3 H), 1.76 (AB, J_{AB} = 12.1 Hz, 1 H), 1.65 (br. s, 3 H), 1.60–1.49 (m, 6 H), 1.48–1.30 (m, 6 H), 1.31 (AB, J_{AB} = 12.8, J_2 = 3.1 Hz, 1 H), 1.24 (AB, J_{AB} = 12.8, J_2 = 3.1 Hz, 1 H), 1.12–1.04 (m, 1 H), 0.96 (AB, J_{AB} = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 73.16 (COH), 70.44 (COH), 54.96 (CH), 49.01 (CH), 48.77 (CH), 47.58 (CH_2), 44.39 (CH_2), 43.63 (CH_2), 43.28 (CH), 42.96 (CH), 39.44 (CH), 39.33 (C), 38.32 (CH_2), 37.74 (CH), 37.64 (CH_2), 37.08 (CH), 34.79 (C), 32.43 (CH_2), 31.90 (CH_2), 31.80 (CH_2), 26.79 (CH), 26.59 (CH) ppm. MS: *m*/*z* (%) = 324 (30), 306 (100), 288 (11), 277 (3), 217 (2), 193 (3), 179 (5), 158 (10), 144 (16), 129 (15), 117 (9), 105 (11), 91 (32), 77 (9), 55 (9). HR-MS (*m*/*z*), found 324.2074; calcd. for $C_{22}H_{28}O_2$: 324.2089.

Supporting Information (see also the footnote on the first page of this article): The exact procedures for functionalization of dia-

mondoids **2**, **3** and **4**, the increments for the NMR ^{13}C chemical shifts of compound **13**, the optimized geometries and computed relative energies of triamantane diols, as well as details of the X-ray structural study are available.

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