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Functionalized Nanodiamonds: Triamantane and [121]Tetramantane†

Peter R. Schreiner,*,‡ Natalie A. Fokina,‡ Boryslav A. Tkachenko,‡ Heike Hausmann,‡ Michael Serafin,§ Jeremy E. P. Dahl,|| Shenggao Liu,|| Robert M. K. Carlson,|| and Andrey A. Fokin*,‡,⊥

Institut für Organische Chemie and Institut für Anorganische und Analytische Chemie, Justus-Liebig University, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany, MolecularDiamond Technologies, Chevron Technology Ventures, 100 Chevron Way, Richmond, California 94802, and Department of Organic Chemistry, Kiev Polytechnic Institute, pr. Pobedy 37, 03056 Kiev, Ukraine

prs@org.chemie.uni-giessen.de; andrey.fokin@org.chemie.uni-giessen.de

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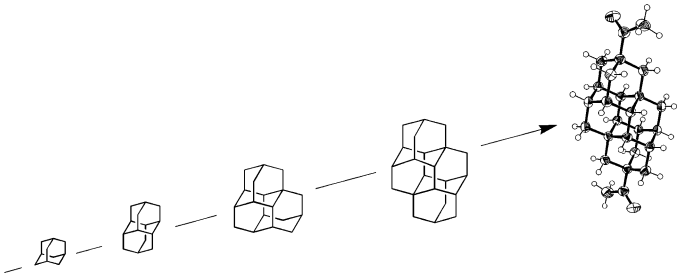

The selective functionalizations of the fundamental hydrogen-terminated nanodiamonds triamantane **1**, as well as the most symmetrical representative of the tetramantanes (C_{2h}-[121]tetramantane **2**) were elaborated. Electrophilic reagents (Br_2, HNO_3) predominantly attack the medial C−H positions of the cages; bromination of **2** gave the medial 2-bromo derivative almost exclusively. Highly selective apical substitution in **1** and **2** is possible either under single-electron-transfer oxidations via hydrocarbon radical cations or through photoacetylation with diacetyl. The mono- and the bis-acetyl derivatives of **1** and **2** were converted through Bayer−Villiger oxidation and subsequent hydrolysis to the respective apical mono- and dihydroxy derivatives. This exceptional synthetic specificity facilitates the transformation of **2**, and perhaps larger nanodiamond molecules, into functionalized building blocks needed for a wide range of applications such as nanotechnology.

Introduction

Modern nanotechnology continuously reduces the size of its building blocks and currently targets the 1−5 nm scale, which is already the domain of large single molecules.[1] However, in the nanotechnology community, the physical and mechanical properties of nanomaterials quite often are not expressed in terms of singular molecular structures even when operating at the single-molecule level.[2] Nanodiamonds, which are nanometer-sized single-molecule hydrocarbons,[3] close the gap between chemistry, physics,[4] and the material sciences in terms of their

† Functionalized Nanodiamonds. Part 2. For part 1, see ref 36.
‡ Institut für Organische Chemie, Justus-Liebig University.
§ Institut für Anorganische und Analytische Chemie, Justus-Liebig University.
|| MolecularDiamond Technologies, Chevron Technology Ventures.
⊥ Department of Organic Chemistry, Kiev Polytechnic Institute.

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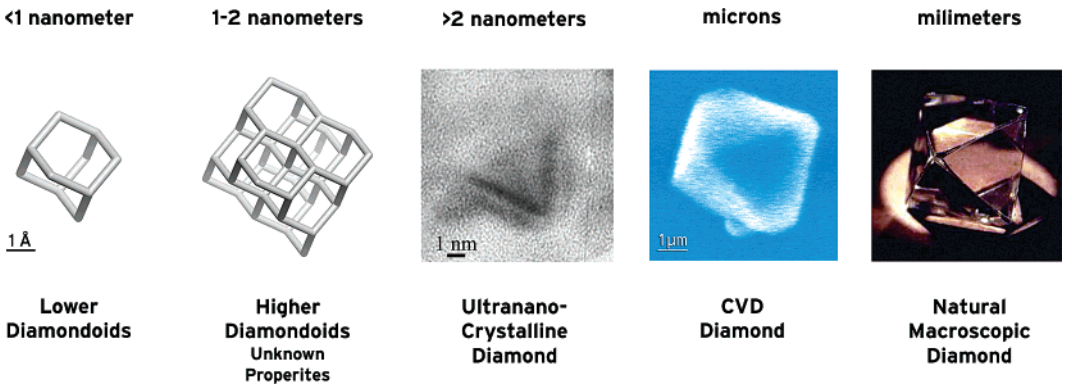

FIGURE 1. Dimensions of diamondoid and nanodiamond materials. The middle image (UNCD) is reprinted with permission from S. Prawer, J. L. Peng, J. O. Orwa, J. C. McCallum, D. N. Jamieson, L. A. Bursill, *Phys. Rev. B 62*, 16360 (2000), copyright (2000) by the American Physical Society.

size and properties.[5] Indeed, the size of microcrystalline hydrogen-terminated[6] nanodiamonds approaches 2 nm (Figure 1),[7,8] which is very close to the dimensions of medium-sized diamondoid hydrocarbons (1−2 nm). The physics community uses the term "nanodiamonds" for the constituents of diverse systems including interstellar dusts and meteorites, carbonaceous residues of detonations, and diamond-like films.[9] As the grain sizes of diamond nanoparticles in carbonaceous chondrites vary from 1.4 to 4.0 nm,[10] it is clear that discrete diamondoid structures (several of which are the targets of the present paper) are at the lower end (around 1 nm) of this size domain. Recent studies suggest that reducing the size of diamond[11] to the nanoscale may have stronger effects on its optical gap than, e.g., in the case of Si and Ge;[8,12] nanodiamonds are therefore very attractive objects for studying molecular semiconductors, especially in combination with the powers of organic chemistry to functionalize and assemble these hydrocarbon materials.[13] The most important and most difficult step is the selective functionalization of nanodiamonds that typically display several sets of similarly reactive secondary and tertiary C−H bonds.

The chemistry of diamondoids, which resemble parts of the diamond lattice, for a long time was associated with adamantane $C_{10}H_{16}$,[14] whose derivatives have found quite a number of highly practical applications.[15] The chemistry of lower $C_{4n+6}H_{4n+12}$ diamondoids, which are characterized as having only one geometrical isomer, has been mostly represented by diamantane ($C_{14}H_{20}$), which became available[16] at the end of 1960s both synthetically and from Nature.[17] The chemistry of higher diamondoids (starting with tetramantane), which occur in isomeric and some chiral forms and whose molecular sizes already stretch from 0.6 to 1 nm, still remains largely unexplored as sizable quantities of these hydrocarbons became readily available from natural sources only recently.[18,19] Diamondoids are present in nearly all raw petroleum in traces but were found in more substantial amounts (starting with triamantane[20] (**1**) up to at least undecamantane) in some deep natural gas condensates from the Norphlet Formation, U.S. Gulf of Mexico, and the Western Canada Basin.[18,21] Currently **1**, as well as the most symmetrical representatives (Figure 2) of the tetramantanes (C_{2h}-tetramantane, [121][22] tetramantane **2**[23]), are available in sizable quantities through pyrolytic, chromatographic, and crystallization procedures. Pentamantanes (e. g., T_d-pentamantane, [1(2,3)4]pen-

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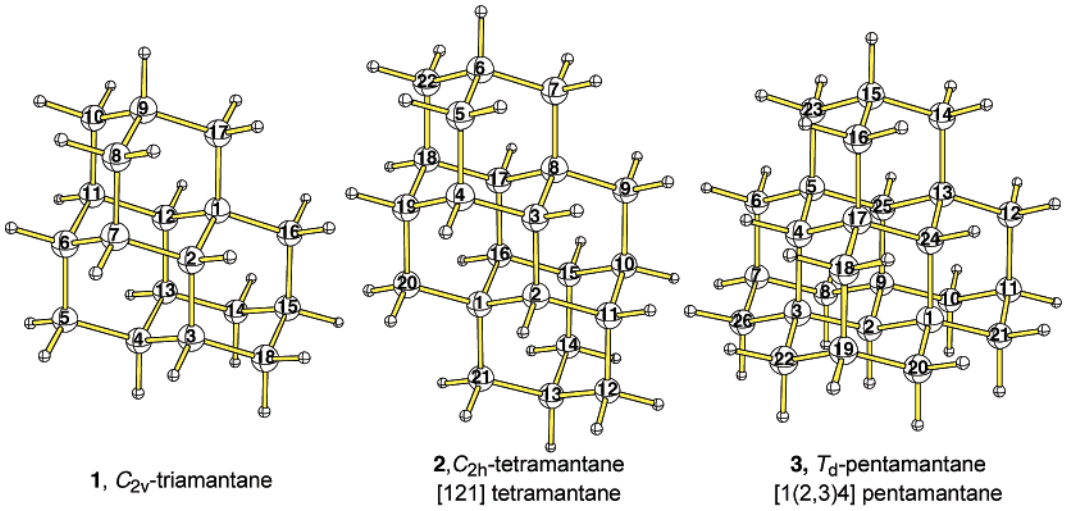
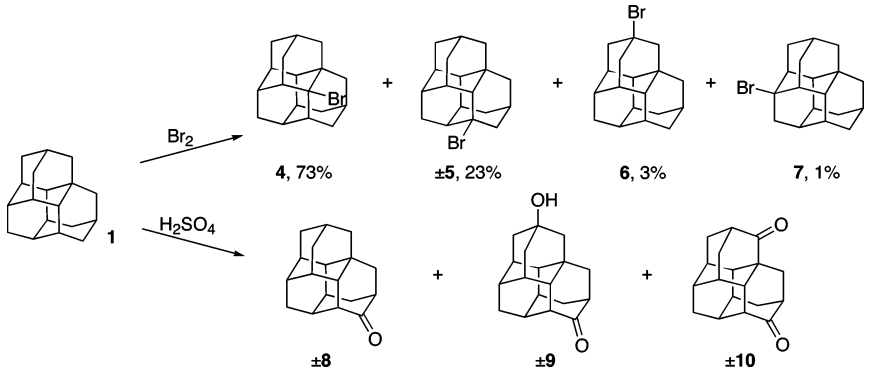


FIGURE 2. Selected most symmetrical diamondoids with numbering of carbon atoms.

SCHEME 1. Direct Functionalizations of Triamantane (1) from the Literature Data (% Product Distribution)[a]



[a] For racemic compounds, only one enantiomer is shown.

tamantane **3**) also are isolable but currently at very low quantities; the structure of **3** is included in Figure 1 for comparison. The inaccessibility of higher diamondoids was the main reason the chemistry of these fascinating cage hydrocarbons is virtually undeveloped.

It is generally assumed that graphite is more stable than diamond at atmospheric pressures, but this is apparently not true for the phase stability of diamond in the nanometer size regime. The transformations of nanodiamonds to carbon-onions has been observed experimentally at the temperatures that are particle-size dependent;[24] the reverse transformations of carbon-onions to nanocrystalline diamond has also been observed experimentally.[25] Furthermore, size dependence of the structural stability of nanocrystalline diamond has also been reported in the nm range.[26]

Hence, at least up to a size of about 6 nm, low molecular weight sp^3 carbon compounds are considerably more stable than those composed of sp and sp^2 carbons. The crossover point between diamondoid and graphite-like structures (so-called graphenes) occurs approximately at a number of approximately 10^5 carbon atoms and a diamondoid diameter of about 5−6 nm.[9,26,27] That is, in terms of thermodynamic stability up to this number of carbon atoms and, as a consequence for (mechanical) applications in nanotechnology, diamondoids are at least as important and interesting as graphenes, fullerenes, or even nanotubes. For chemists, the next crucial step is the ability to modify diamondoids selectively to make them applicable to nanoscale manufacturing.

Functional derivatives of hydrocarbons **1** and **2** almost certainly will have applications in pharmacology, surface and polymer chemistry, as well as in nanotechnology.[28] In contrast to other alkanes, diamondoids are quite reactive toward radicals and, especially, electrophilic reagents.[29−31] However, owing to the large number of different C−H bonds, the *selective*

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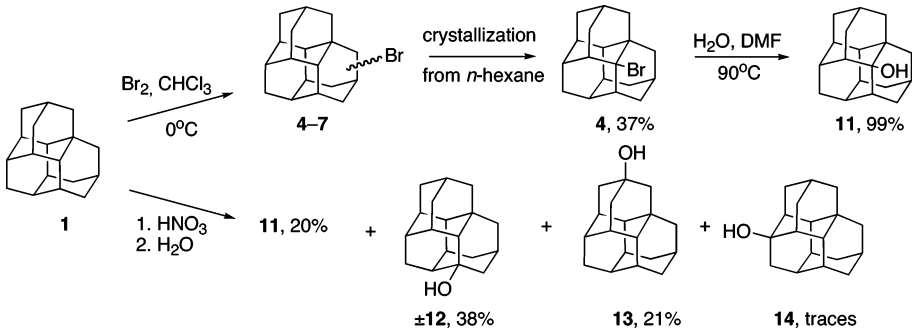
SCHEME 2. Functionalizations of Triamantane 1 with Electrophiles (All Yields Are Preparative)[a]



[a] For chiral **12**, only one enantiomer is shown.

functionalization of diamondoids, in contrast to adamantane,[32] is rather difficult. This conclusion is supported by the existing data on the reactivity of **1**, where all possible tertiary bromo derivatives were obtained in the reaction with neat bromine;[33,34] a mixture of oxygenated products forms in the reaction with sulfuric acid (Scheme 1).[35] The reactivity of hydrocarbon **2** has not been studied thus far.

Recently,[36] we proposed new approaches for the selective functionalization of diamantane; several of these should also be applicable to the next higher diamondoids. We will utilize traditional oxidizing electrophiles (Br_2, HNO_3) as well as single-electron-transfer oxidizers, which, in agreement with our earlier computational assessment,[36] are expected to react more selectively. Most radical species are not expected to show satisfactory selectivities as also found for adamantane;[30,37] however, some exceptionally selective radical-like reagents, e.g., triplet diacetyl, also will be presented. We will demonstrate that the selectivities in the functionalizations of higher diamondoids with these and other reagents go beyond common expectations, making these beautiful molecules suitably functionalized building blocks for a large variety of applications.

Results and Discussion

Functionalization of Triamantane (1). The literature procedure[33] for the bromination of **1** leads to a mixture of bromides **4**−**7** (Scheme 2). We were able to isolate *medial* 2-bromotriamantane (**4**) in only 37% preparative yield after two crystallizations of a mixture of bromides **4**−**7** from *n*-hexane. Hydrolysis of **4** in H_2O/DMF gave triamantyl-2-ol (**11**) cleanly. However, the more attractive *apical* 9-derivatives are not available through this method since bromide **6** is only a minor product. As in the case of diamantane,[36] the selectivities in the C−H substitution of **1** slightly change with 100% nitric acid[38] relative to the reaction with bromine. The nitroxylation of **1** and subsequent hydrolysis gave hydroxy triamantanes **11**, **12**, and **13** in a 25:48:27 ratio; the 4-hydroxy derivative **14** was identified only in trace amounts. Although alcohols **11**−**13** were isolated in pure form by column chromatography in 20, 38, and 21% yields, respectively, the selectivity of the nitroxylation reaction, and especially the yield of the apical derivative **13**, is unsatisfactory.

The selective preparation of the apical derivatives (such as **13**) of triamantane was achieved through photooxidation with diacetyl ($CH_3C(O)C(O)CH_3$) that usually gives acetyl derivatives directly.[39] We found that triplet diacetyl preferentially abstracts a hydrogen atom from the least sterically hindered apical position of **1**. The selectivity of this reaction is much higher than that for diamantane[39] for which a 5:1 ratio of apical to medial product was observed. In the case of **1**, for which the medial ("belt") positions are more hindered sterically, photoacetylation leads to 9-acetyltriamantane **15** almost exclusively (selectivity >95%). The second C−H substitution also occurs predominantly at the next available apical position to give 9,15-diacetyl triamantane **16** (Scheme 3). Three other diacetyl derivatives of **1** were identified only by GC/MS, but were not isolated (total amount is less than 5% in the reaction mixture). Compounds **15** and **16** were separated by column chromatography and characterized separately; the X-ray structure of **15** is shown in Figure 3. The Bayer−Villiger oxidation of **15** and **16** leads to acetates **17** and **18**, and after hydrolysis to alcohols **13** and **19**. Ketones **15** and **16** are highly useful synthons for other apical derivatives of **1**. For example, subsequent oxidation of ketone **15** with sodium nitrite in acidic media[40] and esterification with diazomethane gave the methyl ester of triamantane 9-carboxilic acid **20**. The 9-carboxy derivatives of **1** will be unavailable in sizable quantities via the Koch−Haaf reaction because of the higher stability of the medial triamantyl cations;[36] electrophilic aromatic substitution with apical diamantane cations generated in *t*-BuBr + HBr mixtures (sludge catalyst) and benzene have been reported.[41] Thus, photoacetylation is a key step in the selective preparation of mono- and bis-apical derivatives of **1**.

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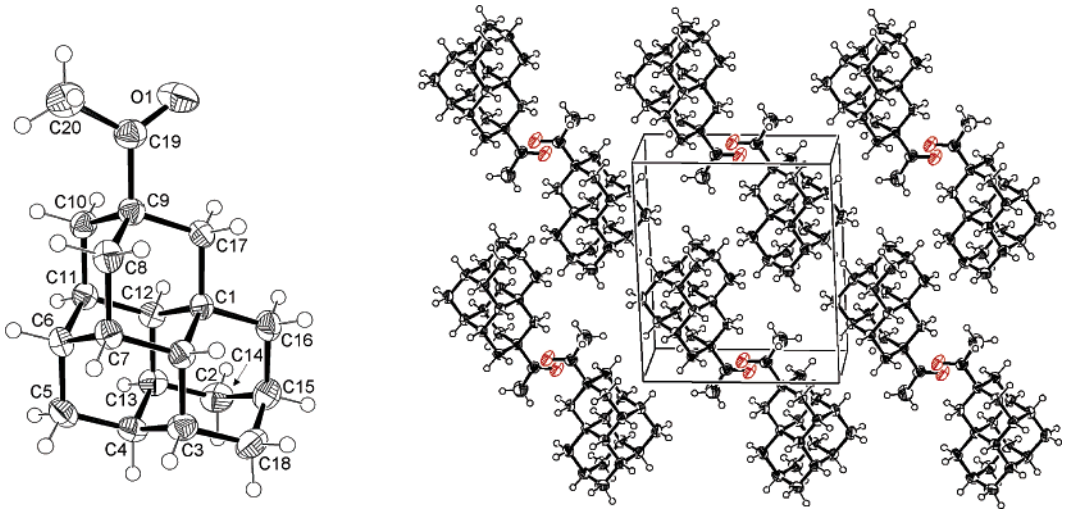
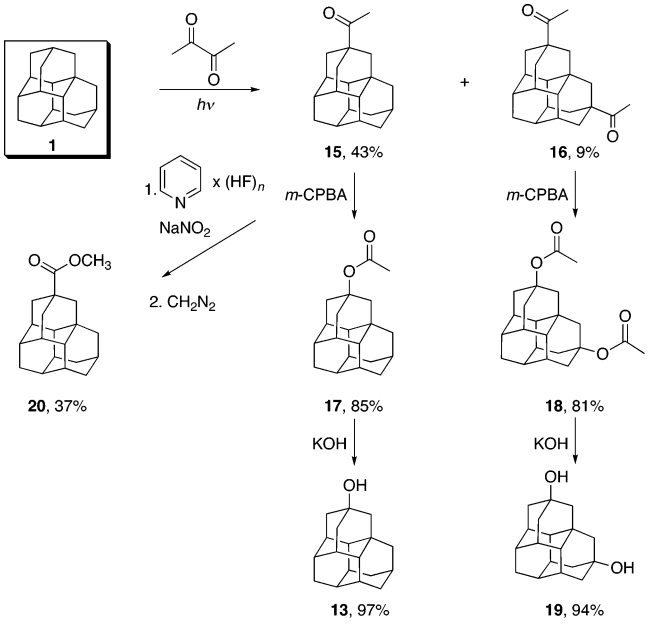


FIGURE 3. X-ray structure of **15** and its packing in the crystal.

SCHEME 3. Preparation of Apical Derivatives of Triamantane (1) via Photoacetylation (All Yields Are Preparative)



In accordance with our recent computational predictions, another way for the selective preparation of the apical derivatives of **1** involves single-electron oxidation of **1** to the radical cation $\mathbf{1}^{\cdot+}$. This was rationalized with the finding that **1** forms a radical cation with an elongated (electron-depleted) apical C−H bond, from which deprotonation occurs (Scheme 4). The experimental SET-oxidation of **1** was performed under photoirradiation with a low-pressure UV lamp in acetonitrile in the presence of 1,2,4,5-tetracyanobenzene (TCB).[42] To avoid overoxidation by photoexcited TCB, which is one of the most powerful organic oxidants,[43] the reaction was carried out with an excess of **1**. The apical aryl derivative **21** and unreacted **1** were the only cage products found in the reaction mixture (Scheme 4).

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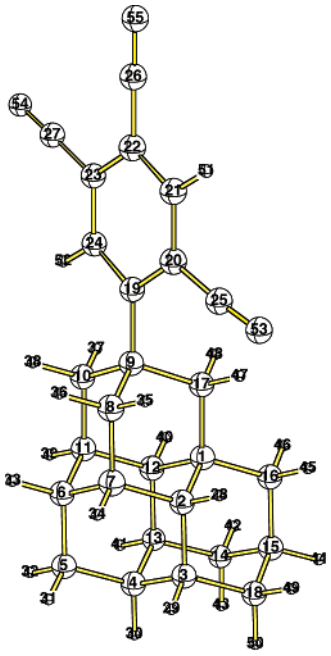


FIGURE 4. Numbering of atoms in **21** for the NMR assignments.

Structure Elucidation: Assignment of NMR Spectra. Obviously, the assignment of the exact substitution patterns in the higher diamondoids becomes increasingly difficult as there are many nearly equivalent methylene and methine resonances that often cannot be interpreted in terms of first-order NMR spectra. Using structure **21** as an example (Figure 4), we will outline in the following our strategy for assigning the substitution patterns utilizing a variety of NMR techniques that will be helpful for future structural assignments of diamondoid derivatives; other examples can be found in the Supporting Information.

The substitution pattern in the position "9" of **21** (Figure 5) was unequivocally confirmed by means of one-dimensional (^{1}H NMR, ^{13}C NMR, ^{13}C DEPT NMR, and ^{1}H DPFGNOE) and two-dimensional (^{1}H,^{1}H DQF-COSY, ^{1}H,^{13}C HSQC, and ^{1}H,^{13}C HBMC) spectral techniques. The ^{1}H NMR spectrum is characterized by an AB spin system at δ = 2.16−2.07 ppm that

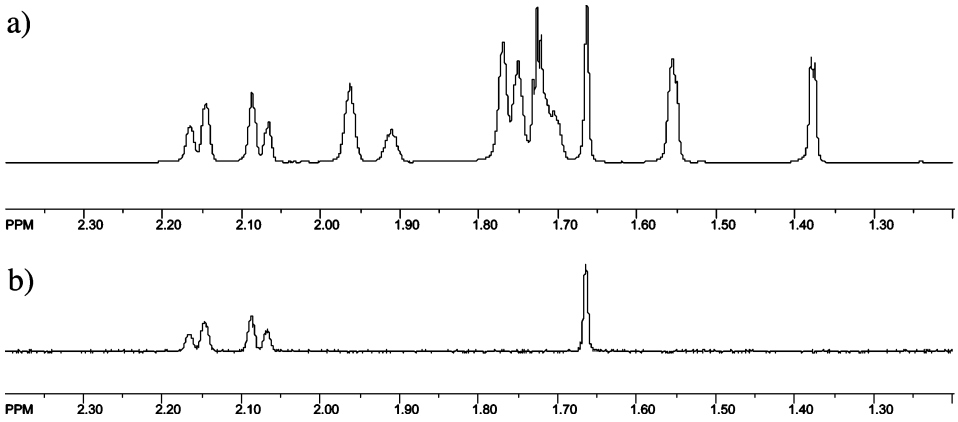


FIGURE 5. Expansions from the ^{1}H NMR spectrum (a) und DPFGNOE spectrum (b) of **21** acquired on a Varian Unity plus 600 instrument; selective irradiation at $\delta = 7.87$ ppm.

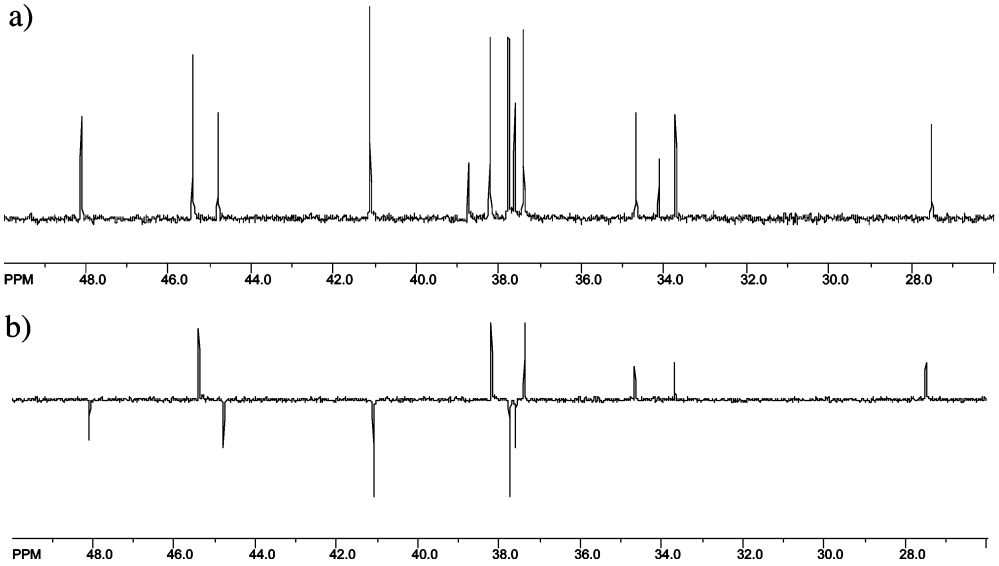
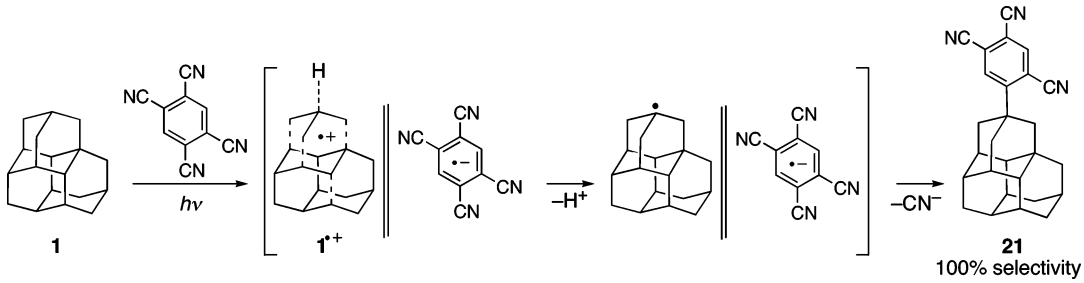


FIGURE 6. High-field part of ^{13}C NMR (a) and DEPT 135 (b) spectra of **21** (Bruker AM 400).

SCHEME 4. SET-Oxidation of Triamantane (1) Forming the Apical Derivative 21 Exclusively



could be assigned to the methylene hydrogens (geminal on the carbon atoms 8 and 10). The singlet at $\delta = 1.66$ ppm is assigned to the two methylene hydrogens associated with carbon atom 17; the doublet at $\delta = 1.38$ ppm is caused by the methylene hydrogens attached to carbon atom 16. The sequential assignments of CH and CH_2 hydrogens were verified by analysis of the connectivities in the DQF-COSY spectrum (not shown). A noteworthy ^{1}H NMR feature is the long-range (^4J) "W-coupling" between the CH_2 hydrogens on C-8/10 and C-17. 1D nuclear Overhauser (NOE) spectroscopy indicated the linkage of the substituent with carbon atom 9. As shown in Figure 5b, the selective pulse was adjusted to the signal of the aromatic proton in the *ortho* position ($\delta = 7.87$ ppm), NOE effects are observed for the AB spin system at $\delta = 2.16-2.07$ ppm and for the singlet of the CH_2 hydrogens at $\delta = 1.66$ ppm. The experimental ^{1}H and ^{13}C NMR spectra are also in good agreement with the computed GIAO-B3LYP/6-311+G*//B3LYP/6-31G* spectra. The ^{1}H-decoupled ^{13}C NMR spectrum of **21** (Figure 6a) consists of 13 resolved signals for the triamantyl skeletal framework. A comparative analysis of ^{13}C NMR and DEPT spectra was used to identify all signals corresponding to seven methine, four methylene, and two quaternary carbon atoms. The identification of the carbon types was particularly helpful for the application of the HSQC and HMBC techniques which were successfully

TABLE 1. ^{1}H NMR (600 MHz) and ^{13}C (150 MHz) NMR for 21: Chemical Shifts (δ, ppm)

		HSQC		HMBC−$^n J$(C,H)	
C	DEPT assignment	δ_C	δ_H	^2J(C,H)	^3J(C,H)
1	C-q	34.1		H-45/46, H-47/48	
2, 12	CH	45.4	1.55 m (2H)		H45/46, H-47/48
3, 13	CH	37.4	1.77 s (2H)		
4	CH	34.7	1.71 m (1H)		
5	CH_2	37.6	1.73 m (2H)		
6	CH	33.7	1.75 m (1H)		
7, 11	CH	38.2	1.96 m (2H)		
8, 10	CH_2	41.1	2.16−2.07 (4H) AB spin system		H-47/48
9	C-q	38.7		H-47/48, H-35/36, H-37/38	H-52
14, 18	CH_2	37.7	1.73 m (4H)		
15	CH	27.5	1.91 s (1H)	H-45/46	
16	CH_2	44.7	1.36 d (2H)		
17	CH_2	48.1	1.67 bs (2H)		H-45/46
19	C−q	159.0			H-51
24	CH	132.4	7.87 s (1H)		
21	CH	139.5	8.04 s (1H)		

used to assign the chemical shifts of all carbons as represented in Table 1.

The ^{13}C NMR spectrum shows the expected two signals δ = 34.1 ppm and δ = 38.7 ppm for the quaternary carbon atoms (atoms 1 and 9). The carbon having the substituent attached can be deduced from the HMBC spectrum. Since this carbon (δ = 38.7 ppm) is correlated to an aromatic proton at 7.87 ppm, the substituent *must* be situated at position 9. The CH_2 resonance at δ = 41.1 ppm can be assigned to the two equivalent methylene carbons (atoms 8 and 10) and that at δ = 48.1 ppm for the CH_2 carbon atom 17.

Functionalizations of C_{2h}-[121]Tetramantane (2). In accordance with our recent computational assessments,[36] the C−H substitution in **2** with electrophiles is expected to be more selective because of the exceptionally high stability of the 2-C_{2h}-tetramantyl cation relative to isomeric C_{2h}-[121]tetramantyl cations. Furthermore, while the difference in the stabilities of triamantyl cations varies within 3 kcal/mol (B3LYP/6-31G*),[36] the stabilities of C_{2h}-[121]tetramantyl cations differ even more: the C_{2h}-[121]tetramantyl 2-cation is ca. 5 kcal/mol more stable than the least stable cation in the apical position "6" (Figure 2). While this makes the electrophilic substitution at the medial position more favorable, it is even more difficult to obtain apical derivatives of **2**. The bromination of **2** with elementary bromine gave 2-bromo-C_{2h}-tetramantane (**22**) almost exclusively (we identified only traces of other bromides in the reaction mixture); 2-hydroxy-C_{2h}-tetramantane (**23**) forms in high yield after hydrolysis of **22** (Scheme 5).

Oxidation of **2** with 100% nitric acid followed by hydrolysis gave a mixture of all possible tertiary hydroxy derivatives **23**−**26**. The medial alcohol **23** is still the dominant product in this reaction mixture; the yield of the apical derivative **26** is very low (4% after column chromatography). For the selective preparation of apical hydroxy derivatives of **2** we used the photoacetylation reaction, which is even more selective than for triamantane **1** (vide supra). The apical ketone **27** was separated in 57% preparative yield from 11% of the apical diacetyl derivative **28**, whose crystal structure is shown in Figure 7. Ketones **27** and **28** were oxidized with *m*-chloroperbenzoic acid to the respective acetates **29** and **30**; subsequent hydrolysis gave apical mono- (**26**) and dihydroxy (**31**) derivatives in high preparative yields. As we have shown previously,[36] hydrocarbon **2** forms a single radical cation C_{2h}-symmetrical structure with two elongated apical C−H bonds. As a result, the single-electron-transfer oxidation of **2** with TCB exclusively leads to the apical substitution product **32**.

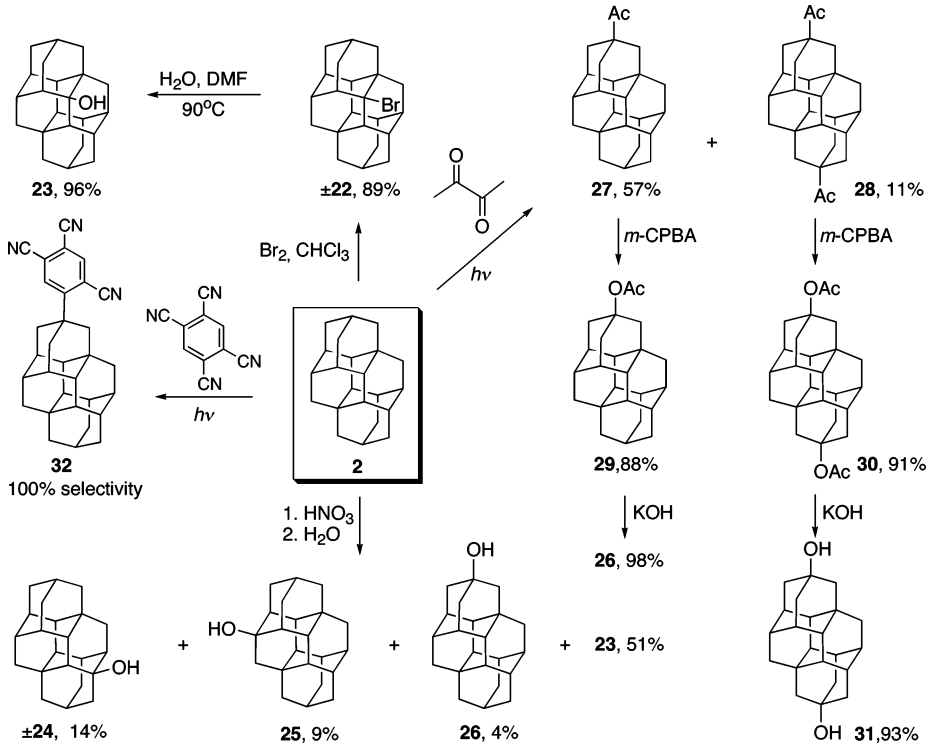
We also studied some other transformations of **2** in electrophilic media, e.g., with concentrated sulfuric acid (Scheme 6). The oxidation in 98% H_2SO_4 at 78 °C led to a mixture of [121]tetramantane-7,12-dione **33** and hydroxy ketone **34** in 61% and 18% preparative yields, respectively. The diamondoid ketones form in sulfuric acid via intermolecular H-transfer between tertiary cation intermediates and the secondary C−H bonds of the neutrals. The B3LYP/6-31G* computations indeed show that **33** is the most thermodynamically stable diketone in the C_{2h}-tetramantane series (all computational details can be found in the Supporting Information). The same explanation applies to the predominant formation of apical alcohol **34**; the B3LYP/6-31G* computations show that the apical hydroxy derivatives of **2** are thermodynamically more stable than the medial ones. This situation is similar to that found for hydroxy diamantanes where the apical derivative is 0.9 kcal/mol more stable than the medial one ($\Delta_{298}H$, B3LYP/6-31G*, the experimental value[44] is 1.1 kcal/mol). An even more pronounced difference ($\Delta\Delta_{298}H$ = 2.7 kcal/mol) was computed for the bis-medial dihydroxy (positions "2" and "17") C_{2h}-tetramantane and bis-apical derivative **31** (Scheme 5). The higher stability of diamantane axial derivatives had been previously explained[44] by symmetry considerations (different symmetry numbers for 1- and 4-hydroxy diamantane (C_s and C_{3v} symmetries, respectively)).

Direct oxidation of **2** to the mono ketone is difficult because of the low solubility of **2** in sulfuric acid; the hydroxy derivatives are more soluble. Alcohol **23** oxidizes to tetramantan-5-one (**35**) rapidly, but **33** and **34** form as byproducts. Interestingly, **35** is 0.2 kcal/mol ($\Delta_{298}G$, B3LYP/6-31G*) *less* stable than tetramantan-7-one. Moreover, the 5-tetramantyl cation also is less stable than the 7-cation ($\Delta\Delta_{298}G$ = 1.6 kcal/mol).

Generally, the transition structures for the hydrogen transfer from the hydrocarbon C−H bond to carbocations are elusive and are difficult to locate computationally (exceptions are rare).[31] We estimated the most favorable proton-transfer path by comparing the energies of the complexes between **2** and the

(44) Johnston, D. E.; Rooney, J. J.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1972**, 29−30.

SCHEME 5. Tertiary C−H Functionalizations of 2[a]



[a] For racemic compounds, only one enantiomer is shown.

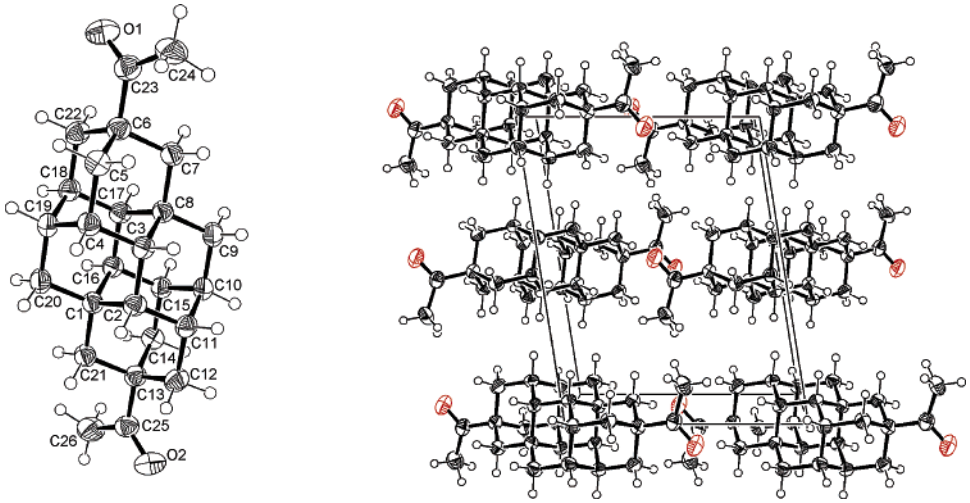


FIGURE 7. X-ray structure of **28** and its packing in the crystal.

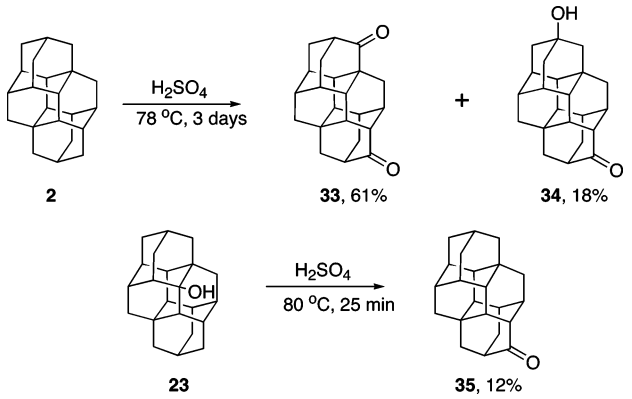
1-adamantyl cation as a model. Indeed, the complex of **2** involving the C-5-H bond is tighter and more stable than the one resulting from the H-abstraction from the C-7-H fragment ($\Delta\Delta_{298}G = 1.7$ kcal/mol). Thus, the predominant formation of **35** in sulfuric acid is not due to the higher stability of the intermediate secondary cations or products but rather is determined kinetically by a less sterically hindered approach of the abstracting carbocation onto the C-5-H bond of **2**.

Conclusions

The selectivities for the tertiary C−H bond substitutions significantly *increase* from triamantane (**1**) to C_{2h}-tetramantane (**2**), and a large number of their derivatives substituted with key functional groups amenable to further transformations can be prepared in high yields. The current study reports more than 20 new diamondoid derivatives mono- and difunctionalized with OH, $COCH_3$, $COOCH_3$, and Br groups.

In contrast to **1**, whose functionalizations in the presence of electrophiles gave mixtures of all possible tertiary substitution products, the functionalizations of **2** are rather selective and lead to medial substitution products in high yields. Since the medial positions of these diamondoids are sterically hindered, the selective apical substitution is possible through photoacetylation with triplet diacetyl, which is highly sensitive to steric effects. In full agreement with our earlier computational predictions, single-electron transfer oxidations involving diamondoid radical cations are even more selective and exclusively lead to the apical substitution products.

SCHEME 6. Oxidations of C_{2h}-Tetramantane (2) with Sulfuric Acid



Hence, the way is paved for utilizing diamondoids in many applications such as surface attachment (with, e.g., hydroxy and thiol derivatives;[45] acids, available through the haloform reaction of the acetyl derivatives), polymers (with, e.g., diols, diacids), medicinal applications (e.g., amines from Curtius rearrangements of the acids), and many others.

Experimental Section

Bromination of Triamantane 1. To a mixture of 6 g (0.025 mol) of triamantane (**1**) in 10 mL of $CHCl_3$ was added 15 mL (0.3 mol) of neat bromine (distilled) dropwise during 5 min at 0 °C. The reaction mixture was stirred for 15 min at 0 °C, quenched with $NaHSO_3$ solution, and extracted 4 × 20 mL of $CHCl_3$. Combined extracts were washed with brine and dried over Na_2SO_4. Evaporation gave 6.8 g of a mixture of monobromides **4**−**7** that was recrystallized two times from *n*-hexane to give 3.4 g (43%) of 2-bromotriamantane (**4**) as a white solid (98% purity, GC/MS). This bromide was dissolved in 47 mL of DMFA, and 18 mL of water was added. The reaction mixture was stirred at 90°C overnight, solvents were evaporated in vacuo, and the residue was dissolved in 50 mL of $CHCl_3$, washed with brine, and dried over Na_2SO_4. Evaporation gave 3.1 g of the crude alcohol, whose recrystallization from ethyl acetate gave 2.4 g (37%) of analytically pure 2-hydroxy triamantane (**11**) identical the material described earlier.[46]

Oxidation of Triamantane 1 with TCB. A mixture of 350 mg (1.45 mmol) of triamantane **1** and 130 mg (0.73 mmol) of 1,2,4,5-tetracyanobenzene in 220 mL of CH_3CN ("far UV") was irradiated with a low-pressure 300 W Hg lamp for 1 h under argon. The reaction mixture was diluted with 30 mL of brine, 30 mL of CH_2Cl_2 was added, and the organic part was separated, dried with Na_2SO_4, and evaporated. The GC/MS, as well as the ^{1}H NMR, spectra of the reaction mixture show the presence of a single adduct. The residue was separated by column chromatography on silica gel. Elution with cyclohexane gave 210 mg of unreacted triamantane **1**; changing the eluant to cyclohexane/EtOAc (5/1) gave 98 mg (43%) of the slightly brownish adduct, from which recrystallization from EtOAc gave a pure sample of 9-(2,4,5-tricyanobenzyl)-triamantane (**21**) as colorless solid. Mp = 275−276 °C dec. ^{1}H NMR: 8.04 (s, 1H), 7.87 (s, 1H), 2.13 (*AB*-system, Δ=0.09 ppm, J = 7.5 Hz, 4H), 1.97 (m, 2H), 1.92 (s, 1H), 1.80−1.70 (m, 10H), 1.67 (bs, 2H), 1.51 (m, 2H), 1.38 (m, 2H). ^{13}C NMR: 159.0 (C), 139.5 (CH), 132.4 (CH), 119.3 (C), 116.7 (C), 116.0 (C), 114.5 (C), 113.9 (C), 113.6 (C), 48.1 (CH_2), 45.4 (CH), 44.8 (CH_2), 41.1 (CH_2), 38.7 (C), 38.2 (CH), 37.7 (CH_2), 37.6 (CH_2), 37.4 (CH), 34.7 (CH), 34.1 (C), 33.7 (CH), 27.5 (CH). MS (*m*/*z*): 391 (100), 376 (3), 280 (11), 239 (22), 149 (16), 105 (12), 91 (23), 84 (84), 47 (27). HR-MS (*m*/*z*): found 391.2040, calcd for $C_{27}H_{25}N_3$ 391.2048.

Nitroxylation of Triamantane (1) and Subsequent Hydrolysis. HNO_3 (100%, 3 mL) was added to a solution of triamantane (**1**) (3 g, 12.48 mmol) in CH_2Cl_2 (15 mL) at 0 °C under stirring. The reaction mixture was stirred for 1 h at 0 °C and was diluted with water (13 mL). Excess CH_2Cl_2 was distilled off, and the residue was refluxed for 1.5 h, cooled, and extracted with CH_2Cl_2 (5 × 7 mL). The combined organic extracts were washed with water, aq satd $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Separation of the residue by column chromatography on silica gel (pentane/ethyl acetate gradient elution 5:1, 3:1, 1.5:1) gave 0.64 g (20%) of 2-hydroxytriamantane (**11**), 1.22 g (38%) of 3-hydroxytriamantane (**12**), and 0.67 g (21%) of 9-hydroxytriamantane (**13**) as a colorless solid whose physicochemical properties were identical to those previously reported.[46]

Photoacetylation of Triamantane (1). A solution of triamantane (**1**) (2.63 g, 10.94 mmol) and diacetyl (26 mL, 297.5 mmol) in CH_2Cl_2 (74 mL) was irradiated in a quartz vessel with a high-pressure 150 W mercury lamp for 80 h under argon. The mixture was concentrated under reduced pressure, and the residue was separated by column chromatography on silica gel (pentane/ether 6:1, pentane/ethyl acetate 3.5:1) to give 1.33 g (43%) of 9-acetyltriamantane (**15**) as a colorless solid. Mp: 88−90 °C (hexane). ^{1}H NMR: 2.08 (s, 3H), 1.86 (m, 1H), 1.80 (m, 2H), 1.76 (m, 2H), 1.74 (m, 2H), 1.71 (m, 4H), 1.67 (m, 5H), 1.61 (m, 1H), 1.43 (m, 2H), 1.32 (m, 2H), 1.30 (m, 2H). ^{13}C NMR: 213.9 (C), 46.7 (C), 46.0 (CH), 45.8 (CH_2), 45.0 (CH_2), 38.9 (CH_2), 38.0 (CH_2), 37.9 (CH_2), 37.8 (CH), 37.7 (CH), 34.9 (CH), 34.3 (CH), 33.5 (C), 27.6 (CH), 24.5 (CH_3). MS (*m*/*z*) 282 (5), 240 (20), 239 (100), 91 (12). HR-MS (*m*/*z*): found 282.1998, calcd for $C_{20}H_{26}O$ 282.1984. Anal. Calcd for $C_{20}H_{26}O$ (282.42): C, 85.06; H, 9.28. Found: C, 85.20; H, 9.78. Separately, 0.32 g (9%) of 9,15-diacetyltriamantane (**16**) as a colorless solid was obtained. Mp: 113−115 °C (hexane). ^{1}H NMR: 1.36 (m, 3H), 1.39 (m, 3H), 1.62 (m, 2H), 1.69 (m, 3H), 1.73 (m, 3H), 1.77 (m, 3H), 1.80 (m, 2H), 1.84 (m, 3H), 2.07 (s, 6H). ^{13}C NMR: 213.3 (C), 46.5 (C), 45.4 (CH_2), 44.9 (CH), 38.6 (CH_2), 37.3 (CH), 37.2 (CH_2), 33.8 (CH), 33.5 (C), 24.4 (CH_3). MS (*m*/*z*): 324 (7), 281 (100), 238 (2), 91 (6). HR-MS (*m*/*z*): found 324.2113, calcd for $C_{22}H_{28}O_2$ 324.2089. Anal. Calcd for $C_{22}H_{28}O_2$ (324.46): C, 81.44; H, 8.70. Found: C, 81.64; H, 8.87.

Oxidation of 9-Acetyltriamantane (15). Dry *m*-CPBA (1.83 g, 10.62 mmol) was added to a solution of 1.00 g, (3.54 mmol) of ketone (**15**) in 15 mL CH_2Cl_2 under stirring. The reaction mixture was stirred for 21 h and quenched with aq satd $NaHCO_3$ and $NaHSO_3$ solution under stirring. The mixture was extracted with CH_2Cl_2 (3 × 6 mL), washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (pentane/ether 20:1) gave 0.89 g (85%) of 9-acetoxytriamantane (**17**) as a colorless solid. Mp: 85−88 °C (hexane). ^{1}H NMR: 2.04 (m, 4H), 1.94 (s, 3H), 1.88 (m, 2H), 1.83 (m, 1H), 1.67 (m, 12H), 1.45 (m, 2H), 1.33 (m, 2H). ^{13}C NMR: 170.3 (C), 80.1 (C), 48.3 (CH_2), 45.6 (CH), 44.8 (CH_2), 41.5 (CH_2), 40.3 (CH), 37.8 (CH_2), 37.4 (CH_2), 37.2 (CH), 35.9 (C), 34.8 (CH), 34.0 (CH), 27.0 (CH), 22.7 (CH_3). MS (*m*/*z*) 298 (1), 238 (100), 142 (51), 91 (14). HR-MS (*m*/*z*): found 298.1935, calcd for $C_{20}H_{26}O_2$ 298.1933. Anal. Calcd for for $C_{20}H_{26}O_2$ (298.42): C, 80.50; H, 8.78. Found: C, 80.76; H, 9.00.

Hydrolysis of 9-Acetoxytriamantane (17). A mixture of 10% KOH/ethanol solution (6 mL) and 9-acetoxytriamantane (**17**) (450 mg, 1.51 mmol) was stirred for 20 h, and ethanol was evaporated under reduced pressure. The residue was dissolved in water and extracted with CH_2Cl_2 (5 × 10 mL). The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give 0.37 g (97%) of 9-hydroxytriamantane (**13**) as a colorless solid, whose physicochemical properties were identical to those previously reported.[46]

(45) Tkachenko, B. A.; Liu, S.; Fokina, N. A.; Chernish, L. V.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R. *Org. Lett.* **2006**, in press.

(46) Duddeck, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 360−365.

Oxidation of 9,15-Diacetyltriamantane (16). Dry *m*-CPBA (0.24 g, 1.39 mmol) was added to a solution of ketone (**16**) (0.10 g, 0.32 mmol) in CH_2Cl_2 (3.5 mL) under stirring. The reaction mixture was stirred for 45 h, quenched with aq satd $NaHCO_3$ and $NaHSO_3$ solution under stirring, and extracted with CH_2Cl_2 (3 × 4 mL). Combined extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (pentane/ether 10:1, pentane/ether 5:1, pentane/ethyl acetate 10:1) gave 90 mg (81%) of 9,15-diacetoxytriamantane (**18**) as colorless solid. Mp = 133−136 °C. ^{1}H NMR: 2.04 (*AB*-system, Δ=0.06 ppm, J_{AB} = 12 Hz, 8H), 1.98 (s, 6H), 1.95 (m, 4H), 1.76 (m, 4H), 1.69 (m, 4H), 1.50 (m, 2H). ^{13}C NMR: 170.3 (C), 79.6 (C), 47.7 (CH_2), 44.5 (CH), 41.3 (CH_2), 39.4 (CH), 38.6 (C), 36.3 (CH_2), 33.7 (CH), 22.6 (CH_3). MS (*m*/*z*): 296 (13), 236 (100), 156 (12), 91 (6). HR-MS (*m*/*z*): found 356.1935, calcd for $C_{22}H_{28}O_4$ 356.1988.

Hydrolysis of 9,15-Diacetoxytriamantane (18). A mixture of 6 mL of 10% KOH/ethanol solution and 450 mg (1.51 mmol) of 9,15-diacetoxytriamantane (**18**) was stirred at ambient temperature for 20 h, and ethanol was evaporated under reduced pressure. The residue was dissolved in H_2O and extracted with CH_2Cl_2 (5 × 5 mL). The combined organic extracts were washed with brine (2 × 5 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give 0.38 g (94%) of 9,15-dihydroxytriamantane (**19**) as a colorless solid. Mp = 243−246 °C. ^{1}H NMR (CD_3OD): 1.93 (bs, 4H), 1.78−1.68 (m, 7H), 1.68−1.58 (m, 6H), 1.39−1.26 (m, 7H). ^{13}C NMR (CD_3OD): 68.4 (C), 53.0 (CH_2), 46.1 (CH), 46.1 (CH_2), 41.1 (CH), 39.6 (C), 37.7 (CH_2), 35.4 (CH). MS (*m*/*z*): 272 (100), 255 (23), 161 (25), 145 (10), 107 (11), 91 (8), 77 (4). MS (*m*/*z*): 296 (13), 236 (100), 156 (12), 91 (6). HR-MS (*m*/*z*): found 272.1775, calcd for $C_{18}H_{24}O_2$ 272.1776.

Oxidation of Ketone 15. To a suspension of 280 mg (0.99 mmol) of 9-acetyltriamantane (**15**) stirred in a polyethylene bottle with 4 mL of HF/pyridine complex (the Olah reagent) was added 280 mg (4 mmol) of $NaNO_2$ in one portion. The reaction mixture was stirred for 30 h at room temperature, poured onto ice, and extracted with 4 × 5 mL of chloroform. The combined extracts were washed with brine, dried over Na_2SO_4, evaporated, and dissolved in 1 mL of 10% methanolic NaOH. The residue after the evaporation was dissolved in 250 mL of hot water, cooled to room temperature, and washed with 5 × 4 mL of chloroform. The water solution was acidified to pH = 2 with concentrated HCl. Extraction (4 × 4 mL of chloroform), washing combined extracts with brine, drying over Na_2SO_4, and evaporation gave 230 mg of the mixture of acids, from which methylation with an etheral solution of CH_2N_2 and further column chromatography on silica (pentane/ether 10/1) gave 109 mg (37%) of methyl triamantane-9-carboxylate (**20**) as colorless crystals. Mp = 59−60 °C (*n*-hexane). ^{1}H NMR: 3.61 (s, 3H), 1.82 (m, 5H), 1.78 (m, 3H), 1.70−1.60 (m, 9H), 1.44 (m, 4H), 1.29 (m, 2H). ^{13}C NMR: 178.0 (C), 51.5 (CH_3), 46.3 (CH_2), 45.9 (CH), 44.9 (CH_2), 40.8 (C), 39.4 (CH_2), 38.0 (CH_2), 37.9 (CH_2), 37.8 (CH), 37.7 (CH), 34.9 (CH), 34.2 (CH), 33.4 (C), 27.6 (CH). MS (*m*/*z*): 298 (19), 239 (100), 197 (1), 183 (2), 157 (5), 143 (10), 129 (11), 105 (10), 91 (27), 79 (14), 59 (5). HR-MS (*m*/*z*): found 298.1949, calcd for $C_{20}H_{26}O_2$ 298.1933. Anal. Calcd for $C_{20}H_{26}O_2$ (298.42): C, 80.49; H, 8.78. Found: C, 80.00; H, 8.77.

Nitroxylation of C_{2h}-[121]Tetramantane (2) and Subsequent Hydrolysis. HNO_3 (100%, 1.7 mL) was added to a solution of C_{2h}-tetramantane (**2**) (2.00 g, 6.84 mmol) in CH_2Cl_2 (13 mL) at 0 °C under stirring. The reaction mixture was stirred for 30 min at 0 °C and diluted with water (7.5 mL) under stirring, CH_2Cl_2 was distilled off, and the residual water solution was refluxed for 1.5 h. The cooled mixture was extracted with CH_2Cl_2 (5 × 7 mL), and the combined organic layers were washed with aq satd $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Separation of the residue by column chromatography on silica gel (pentane/ether 1:1, pentane/ethyl acetate 2:1) gave 1.07 g (51%) of 2-hydroxytetramantane (**23**) as a colorless solid. Mp: 186−189 °C (*n*-hexane). ^{1}H NMR: 2.15 (m, 2H), 1.91 (m, 1H), 1.64 (m, 17H), 1.34 (m, 3H), 1.23 (m, 3H), 1.02 (m, 1H), 0.94 (m, 1H). ^{13}C NMR: 73.7 (C), 52.6 (CH), 49.3 (CH), 47.0 (CH), 45.3 (CH_2), 44.0 (CH_2), 43.9 (CH), 39.9 (CH_2), 39.7 (CH), 38.6 (CH_2), 37.9 (CH), 37.8 (CH_2), 37.6 (CH), 37.5 (CH_2), 37.4 (CH_2), 36.5 (CH), 35.4 (C), 35.1 (C), 32.5 (CH_2), 32.0 (CH), 27.4 (CH), 27.3 (CH). MS (*m*/*z*): 308 (22), 290 (100), 148 (20), 129 (7), 105 (7), 91 (13). HR-MS (*m*/*z*): found 308.2142, calcd for $C_{22}H_{28}O$ 308.2140. Anal. Calcd for $C_{22}H_{28}O$ (308.46): C, 85.36; H, 9.38. Found: C, 85.54; H, 9.37. Separately, 0.48 g of a mixture of 4-hydroxytetramantane (**24**) (14%) and 10-hydroxytetramantane (**25**) (9%) as a colorless solid and 0.08 g (4%) of 6-hydroxytetramantane [**26**, mp = 172−174 °C (*n*-hexane)] as a colorless solid was isolated. ^{1}H NMR of compound **26**: 1.87 (m, 3H), 1.67 (m, 12H), 1.46 (m, 2H), 1.39 (m, 1H), 1.31 (m, 10H). ^{13}C NMR of compound **26**: 68.4 (C), 51.6 (CH_2), 46.6 (CH), 46.1 (CH), 45.4 (CH_2), 45.3 (CH_2), 44.8 (CH_2), 44.2 (CH_2), 40.5 (CH), 38.1 (CH), 37.8 (CH_2), 36.3 (CH), 35.7 (CH), 33.8 (C), 31.2 (C), 27.8 (CH). MS (*m*/*z*): 308 (100), 291 (12), 129 (4), 105 (5), 91 (9). HR-MS (*m*/*z*): found 308.2152, calcd for $C_{22}H_{28}O$ 308.2140. Anal. Calcd for $C_{22}H_{28}O$ (308.46): C, 85.36; H, 9.38. Found: C, 85.66; H, 9.30.

Bromination of C_{2h}-[121]Tetramantane 2. To a solution of 200 mg (0.7 mmol) of C_{2h}-tetramantane **(2)** in 0.8 mL of $CHCl_3$ was added 0.8 mL (16 mmol) of bromine dropwise under intense stirring at 12 °C during 30 s; the reaction mixture was stirred for 10 min at 12 °C, quenched with $NaHSO_3$ solution, and extracted 3 × 7 mL of $CHCl_3$. Combined extracts were washed with brine and dried over Na_2SO_4. Evaporation gave 252 mg of the crude product as a white solid, which was recrystallized from *n*-hexane to give 225 mg (89%) of 2-bromo-C_{2h}-tetramantane (**22**) as a white solid. Mp: 128−129 °C (*n*-hexane). ^{1}H NMR: 2.65 (m, 2H), 2.17 (bs, 1H), 2.0−1.75 (m, 7H), 1.70−1.60 (m, 8H), 1.55 (d, *J* = 6.2 Hz, 1H), 1.38−1.15 (m, 6H), 1.10 (d, *J* = 6.2 Hz, 1H), 1.00 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR: 93.6 (C), 56.4 (CH), 51.3 (CH), 48.0 (CH), 47.2 (CH), 45.0 (CH_2), 43.9 (CH_2), 41.3 (CH_2), 41.2 (CH), 40.4 (CH_2), 38.4 (CH_2), 38.3 (CH), 38.2 (CH), 37.8 (C), 37.4 (C), 37.3 (CH_2), 37.2 (CH_2), 36.5 (CH), 35.3 (CH_2), 34.6 (CH), 27.4 (CH), 27.3 (CH). MS (*m*/*z*): 372/370 (<1), 291 (100), 155 (7), 141 (3), 129 (2), 91 (4). HR-MS (*m*/*z*): found 370.1300, calcd for $C_{22}H_{27}Br$ 370.1296. Anal. Calcd for $C_{22}H_{27}Br$ (371.35): C, 71.15; H, 7.33. Found: C, 71.17; H, 7.44.

Bromination of C_{2h}-[121]Tetramantane 2 and Hydrolysis of Bromide 22. To a solution of 300 mg (1.03 mmol) of C_{2h}-tetramantane in 1.2 mL of $CHCl_3$ was added 0.8 mL (16 mmol) of bromine dropwise under intense stirring at 5 °C during 30 s; the reaction mixture was stirred for 15 min at 12 °C, quenched with $NaHSO_3$ solution, and extracted 3 × 7 mL of $CHCl_3$. Combined extracts were washed with brine and dried with Na_2SO_4. Evaporation gave 360 mg of white solid, which was dissolved in a mixture of 6 mL of DMFA and 2 mL of water and heated at 90 °C with stirring for 3 h. Evaporation of the reaction mixture in vacuo, dissolving in 10 mL of $CHCl_3$, washing with brine, drying over Na_2SO_4, and evaporation gave 305 mg (96%) of 2-hydroxy-C_{2h}-tetramantane (**23**) as a white solid. The material after recrystallization from *n*-hexane was identical to the sample of **23** described above.

Photoacetylation of C_{2h}-[121]Tetramantane (2). A solution of C_{2h}-tetramantane (**2**) (2.30 g, 7.86 mmol) and biacetyl (18.5 mL, 213.9 mmol) in CH_2Cl_2 (75 mL) was irradiated in a quartz vessel with a high-pressure 150 W mercury lamp for 98 h under argon, and the mixture was concentrated under reduced pressure. The residue was separated by column chromatography on silica gel (pentane/ether 7:1, pentane/ether 3:1, pentane/ethyl acetate 3.5:1) to give 1.49 g (57%) of 6-acetyl-C_{2h}-tetramantane (**27**) as a colorless solid. Mp: 121−124 °C (*n*-hexane). ^{1}H NMR: 2.08 (s, 3H), 1.85 (m, 1H), 1.79 (m, 2H), 1.74 (m, 4H), 1.67 (m, 8H), 1.43 (m, 2H), 1.36 (m, 4H), 1.30 (m, 2H), 1.26 (m, 4H). ^{13}C NMR: 213.8 (C), 46.8 (CH), 46.7 (C), 46.4 (CH), 45.5 (CH_2), 45.2 (CH_2), 44.9 (CH_2), 44.2 (CH_2), 38.7 (CH_2), 38.0 (CH), 37.9 (CH), 37.8 (CH_2), 36.9 (CH), 36.0 (CH), 31.4 (C), 31.1 (C), 27.8 (CH), 24.4 (CH_3). MS

(*m*/*z*): 334 (6), 291 (100), 155 (11), 129 (11), 117 (6), 91 (19). HR-MS (*m*/*z*): found 334.2325, calcd for $C_{24}H_{30}O$ 324.2297. Anal. Calcd for $C_{24}H_{30}O$ (334.49): C, 86.18; H, 9.04. Found: C, 86.34; H, 8.89. Separately, 0.32 g (11%) of 6,13-diacetyl-C_{2h}-tetramantane (**28**) as a colorless solid with mp 198−200 °C (*n*-hexane) was obtained. ^{1}H NMR: 2.09 (s, 6H), 1.82 (m, 4H), 1.76 (m, 8H), 1.69 (m, 2H), 1.42 (m, 4H), 1.38 (m, 4H), 1.33 (m, 4H); ^{13}C NMR: 213.6 (C), 46.6 (C), 45.9 (CH), 44.8 (CH_2), 44.6 (CH_2), 38.5 (CH_2), 37.8 (CH), 35.9 (CH), 31.2 (C), 24.5 (CH_3). MS (*m*/*z*): 376 (5), 333 (100), 290 (6), 155 (10), 129 (10), 91 (18), 79 (10). HR-MS (*m*/*z*): found 376.2380, calcd for $C_{26}H_{32}O_2$ 376.2402. Anal. Calcd for $C_{26}H_{32}O_2$ (376.53): C, 82.94; H, 8.57. Found: C, 82.64; H, 8.55.

Oxidation of 6-Acetyl[121]tetramantane (27). The dry *m*-CPBA (1.00 g, 5.83 mmol) was added to a solution of ketone (**27**) (0.65 g, 1.94 mmol) in CH_2Cl_2 (9 mL) under stirring. The reaction mixture was stirred for 22 h and quenched with aq satd $NaHCO_3$ and $NaHSO_3$ solution under stirring. The mixture was extracted with CH_2Cl_2 (3 × 8 mL), washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (pentane/ether 20:1) gave 0.60 g (88%) of 6-acetoxy-C_{2h}-triamantane (**29**) as a colorless solid. Mp: 120−123 °C (*n*-hexane). ^{1}H NMR: 2.04 (m, 4H), 1.94 (s, 3H), 1.86 (m, 3H), 1.68 (m, 10H), 1.44 (m, 2H), 1.38 (m, 2H), 1.29 (m, 4H), 1.25 (m, 2H). ^{13}C NMR: 170.3 (C), 80.3 (C), 47.3 (CH_2), 46.5 (CH), 46.1 (CH), 45.2 (CH_2), 44.6 (CH_2), 44.1 (CH_2), 41.3 (CH_2), 40.3 (CH), 38.0 (CH), 37.7 (CH_2), 36.2 (CH), 35.8 (CH), 33.9 (C), 31.1 (C), 27.8 (CH), 22.7 (CH_3). MS (*m*/*z*): 350 (4), 290 (100), 156 (22), 154 (54), 129 (20), 91 (32). HR-MS (*m*/*z*): found 350.2281, calcd for $C_{24}H_{30}O_2$ 350.2246. Anal. Calcd for for $C_{24}H_{30}O_2$ (350.49): C, 82.24; H, 8.63. Found: C, 81.83; H, 8.64.

Oxidation of 6,13-Diacetyl[121]tetramantane (28). Dry *m*-CPBA (0.84 g, 4.87 mmol) was added to a solution of diketone (**28**) (0.30 g, 0.80 mmol) in CH_2Cl_2 (9 mL) under stirring. The reaction mixture was stirred for 22 h and quenched with aq satd $NaHCO_3$ and $NaHSO_3$ solution under stirring. The mixture was extracted with CH_2Cl_2 (3 × 8 mL), washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Separation by column chromatography (pentane/ethyl acetate 10:1) gave 0.29 g (91%) of 6,13-diacetoxy-C_{2h}-tetramantane (**30**) as a colorless solid. Mp: 229−233 °C (*n*-hexane). ^{1}H NMR: 2.04 (m, 8H), 1.94 (s, 6H), 1.88 (m, 4H), 1.72 (m, 6H), 1.44 (m, 4H), 1.34 (m, 4H). ^{13}C NMR: 170.2 (C), 80.0 (C), 47.0 (CH_2), 45.2 (CH), 44.0 (CH_2), 41.1 (CH_2), 40.0 (CH), 35.0 (CH), 33.6 (C), 22.6 (CH_3). MS (*m*/*z*): 408 (1), 348 (100), 288 (34), 154 (42), 142 (33), 105 (26), 91 (39). HR-MS (*m*/*z*): found 408.5281, calcd for $C_{26}H_{32}O_4$ 408.5299.

Hydrolysis of 6,13-Diacetoxy-C_{2h}-[121]tetramantane (30). A mixture of 1.2 mL of 10% KOH/ethanol solution and 120 mg (0.29 mmol) of 6,13-diacetoxy-C_{2h}-[121]tetramantane (**30**) was stirred at ambient temperature for 20 h, after which time ethanol was evaporated under reduced pressure. The residue was dissolved in H_2O and extracted with CH_2Cl_2 (5 × 2 mL). The combined organic extracts were washed with brine (2 × 1 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give 0.088 g (93%) of 6,13-dihydroxy[121]tetramantane (**31**) as a white solid. Mp: 119−120 °C. ^{1}H NMR: 1.89 (bs, 4H), 1.74−1.65 (m, 10H), 1.56 (bs, 2H), 1.44−1.25 (m, 12H). ^{13}C NMR: 68.3 (C), 51.5 (CH_2), 45.3 (CH), 45.1 (CH_2), 44.2 (CH_2), 40.3 (CH), 35.0 (CH), 33.6 (C). MS (*m*/*z*): 324 (100), 307 (30), 181 (10), 157 (30), 145 (13), 107 (16), 91 (33). HR-MS (*m*/*z*): found 324.2085, calcd for $C_{18}H_{24}O_2$ 324.2089.

Oxidation of C_{2h}-[121]Tetramantane 2 with TCB. A mixture of 220 mg (0.75 mmol) of C_{2h}-tetramantane (**2**) and 85 mg (0.48 mmol) of 1,2,4,5-tetracyanobenzene in 160 mL of CH_3CN ("far UV") was irradiated with a low-pressure 300 W Hg lamp for 1 h under argon. The reaction mixture was diluted with 20 mL of brine, 20 mL of CH_2Cl_2 was added, and the organic part was separated, dried with Na_2SO_4, and evaporated. The GC/MS as well as the ^{1}H NMR of the reaction mixture show the presence of a single adduct. The residue was separated by column chromatography on silica gel. Elution with cyclohexane gave 110 mg of unreacted starting hydrocarbon **2**; changing of the eluant to cyclohexane/EtOAc (6/1) gave 65 mg (40%) of the slightly yellowish adduct, from which recrystallization from EtOAc gave pure sample. Mp: 275−276 °C dec of 6-(2,4,5-tricyanobenzyl)-C_{2h}-tetramantane (**32**). ^{1}H NMR: 8.05 (s, 1H), 7.95 (s, 1H), 2.04 (*AB*-system, $\Delta = 0.01$ ppm, $J =$ 7.5 Hz, 4H), 1.97 (m, 2H), 1.89 (bs, 1H), 1.80 (bs, 1H), 1.75 (bs, 1H), 1.73−1.69 (m, 8H), 1.50 (bs, 4H), 1.33 (m, 6H). ^{13}C NMR: 159.1 (C), 139.5 (CH), 132.4 (CH), 119.3 (C), 116.7 (C), 116.6 (C), 114.5 (C), 113.7 (C), 112.3 (C), 47.2 (CH_2), 46.6 (CH), 45.9 (CH), 45.3 (CH_2), 44.8 (CH_2), 44.0 (CH_2), 40.9 (CH_2), 38.9 (C), 38.2 (CH), 37.9 (CH), 37.7 (CH_2), 36.7 (CH), 35.4 (CH), 32.1 (C), 31.1 (C), 27.2 (CH). MS (*m*/*z*): 443 (100), 428 (2), 291 (13), 222 (3), 105 (4), 91 (11). HR-MS (*m*/*z*): found 443.2342, calcd for $C_{31}H_{29}N_3$ 443.2361.

Oxidation of C_{2h}-[121]Tetramantane (2) with Sulfuric Acid. A 200 mg (0.68 mmol) portion of C_{2h}-tetramantane (**2**) was stirred in 2.2 mL of 98% H_2SO_4 for 3 days at 77 °C. The reaction mixture was poured onto ice and extracted with $CHCl_3$ (4 × 5 mL), and combined extracts were washed with water and brine and dried over Na_2SO_4. The residue after the evaporation was separated by column chromatography on silica gel. With *n*-hexane, 15 mg of starting hydrocarbon **2** was isolated. By changing the eluant to hexane/EtOAc (2/1) 134 mg (0.41 mmol, 61%) of C_{2h}-tetramantane-7,12-dione (**33**) was obtained. Mp: 182−183 °C (*n*-hexane). ^{1}H NMR: 2.49 (bs, 2H), 2.45 (bs, 1H), 2.08 (bs, 2H), 2.10−1.86 (m, 5H), 1.81−1.76 (m, 3H), 1.71−1.53 (m, 7H), 1.45−1.32 (m, 3H), 1.26−1.20 (m, 1H).^{13}C NMR (δ, ppm, $CDCl_3$): 216.2 (C), 216.1 (C), 55.1 (CH), 54.5 (CH), 47.1 (CH), 46.8 (CH), 45.3 (CH), 45.2 (CH), 45.1 (CH), 45.0 (CH), 44.4 (CH_2), 44.3 (CH_2), 42.0 (CH_2), 41.9 (CH_2), 38.6 (CH), 38.4 (CH), 37.7 (CH_2), 37.6 (CH_2), 36.6 (CH), 36.0 (CH), 31.1 (C), 31.0 (C). MS (*m*/*z*): 320 (100), 292 (9), 264 (2), 167 (2), 129 (8), 115 (6), 91 (15), 77 (7). HR-MS (*m*/*z*): found 320.1770, calcd for $C_{22}H_{24}O_2$ 320.1776. Anal. Calcd for $C_{22}H_{24}O_2$ (320.42): C, 82.46; H, 7.55. Found: C, 82.27; H, 7.65.

Elution with hexane/EtOAc (1/1) gave 38 mg (0.12 mmol, 18%) of 6-hydroxy-C_{2h}-tetramantane-12-one (**34**). Mp: 161−162 °C (*n*-hexane). ^{1}H NMR: 2.47 (bs, 1H), 2.36 (bs, 1H), 2.1 (bs, 1H), 1.96−1.91 (m, 3H), 1.85−1.79 (m, 2H), 1.75−1.66 (m, 8H), 1.57 (m, 2H), 1.44 (m, 4H), 1.37−1.35 (m, 2H), 1.30−1.22 (m, 2H). ^{13}C NMR: 217.2 (C), 68.0 (C), 55.6 (CH), 51.3 (CH_2), 47.4 (CH), 45.5 (CH), 45.4 (CH), 45.3 (CH), 45.2 (CH), 45.0 (CH_2), 44.9 (CH_2), 44.7 (CH_2), 43.4 (CH_2), 42.9 (CH_2), 40.1 (CH), 39.5 (CH), 38.4 (CH), 38.0 (CH_2), 37.0 (CH), 35.3 (CH), 33.7 (C), 31.1 (C). MS (*m*/*z*): 322 (100), 294 (9), 145 (8), 105 (4), 91 (12), 77 (4). HR-MS (*m*/*z*): found 320.1931, calcd for $C_{22}H_{26}O_2$ 322.1933. Anal. Calcd for $C_{22}H_{26}O_2$ (322.44): C, 81.95; H, 8.13. Found: C, 81.90; H, 8.17.

Oxidation of Alcohol 23 with Sulfuric Acid. A solution of 250 mg of 2-hydroxy-C_{2h}-tetramantane (**23**) in 2.5 mL of 97% H_2SO_4 was stirred at 80 °C for 25 min. The reaction mixture was poured onto ice and extracted with $CHCl_3$ (4 × 4 mL), and the combined extracts were washed with water and brine and dried over Na_2SO_4. The residue after the evaporation of the solvent was separated by column chromatography on silica gel. With pentane, 155 mg of C_{2h}-tetramantane (**2**) was separated. By changing the eluant to pentane/ether (3/2) 29 mg (12%) of C_{2h}-tetramantane-5-one (**35**) was obtained as a white solid. Mp = 134−135 °C (*n*-hexane). ^{1}H NMR: 2.49 (bs, 1H), 2.40 (bs, 1H), 2.06 (bs, 1H), 1.96 (m, 1H), 1.92 (m, 1H), 1.89 (m, 1H), 1.81 (bs, 1H), 1.78−1.70 (m, 7H), 1.69−1.59 (m, 5H), 1.55 (bs, 1H), 1.46 (bs, 1H), 1.40−1.30 (m, 3H), 1.28−1.20 (m, 2H). ^{13}C NMR: 217.7 (C), 55.8 (CH), 48.1 (CH), 46.6 (CH), 46.5 (CH), 46.2 (CH), 45.5 (CH), 44.9 (CH_2), 44.1 (CH_2), 44.9 (CH_2), 43.7 (CH_2), 39.0 (CH), 38.2 (CH_2), 37.8 (CH), 37.6 (CH_2), 37.5 (CH_2), 37.1 (CH), 37.0 (CH), 36.5 (CH), 31.3 (C), 31.2 (C), 27.6 (CH). MS (*m*/*z*): 306 (100), 278 (31), 263 (3), 237 (4), 141 (16), 128 (22). HR-MS (*m*/*z*): found

306.1998, calcd for $C_{22}H_{26}O$ 306.1984. Anal. Calcd for $C_{22}H_{26}O_2$ (306.44): C, 86.23; H, 8.55. Found: C, 85.53; H, 8.60.

X-ray Structure Determination. Crystals were obtained as described above. The X-ray crystallographic data for **15** were collected on a STOE IPDS at room temperature; data for **28** were collected at 83 K on the same diffractometer equipped with a low-temperature system. Mo Kα radiation (λ = 0.71069 Å) and a graphite monochromator were used. Cell parameters were refined by using up to 5000 reflections. A sphere of data (190 frames) was collected with the φ-oscillation mode (1° frame width; irradiation times/frame: 14, 65, and 8 min for **15** and **28**). No absorption corrections were applied. The structures were solved by direct methods in SHELXS97 and were refined by using full-matrix least-squares methods in SHELXL97.[47] For **15** and **28**, the non-hydrogen atoms were treated anisotropically. The methyl hydrogen atoms of the acetyl groups were calculated in ideal positions and were riding on their respective carbon atoms; all other hydrogen atoms were treated isotropically. The structure of **15** was solved in space group $P\bar{1}$; a total of 284 parameters were refined $R_1 = 4.1\%$ (2063 reflections with $F_o > 4\,\sigma(F_o)$) and w$R_2 = 12.4\%$ (all 3243 reflections). For compound **28** (space group $P2_1/c$) a total of 182 parameters were refined to $R_1 = 6.3\%$ (1185 reflections with $F_o > 4\,\sigma(F_o)$) and w$R_2 = 18.5\%$ (all 2081 reflections). Refinement was done with F^2. The crystal structure data for **15** and **28** have been deposited at the Cambridge Database: CCDC nos. 293485 and 293486. Data are available, on request, from the Director of the Cambridge Crystallographic Data Center, University Chemical laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

(47) Sheldrick, G. M. SHELXL-93/97, Programm für die Kristallstrukturverfeinerung, Universität Göttingen, 1997.

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Supporting Information Available: CIF files containing X-ray structural data for compounds **15** and **28** and additional NMR data. Details of the computations (energies, *xyz* coordinates). This material is available free of charge via the Internet at http://pubs.acs.org.

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