ORGANIC
LETTERS

2009
Vol. 11, No. 14
3068−3071

Oxygen-Doped Nanodiamonds: Synthesis and Functionalizations[†]

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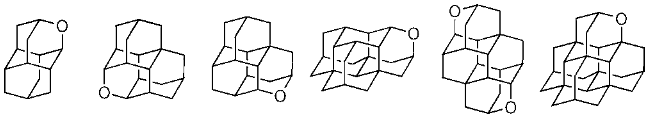
Received May 18, 2009

ABSTRACT



Oxadiamondoids representing a new class of carbon nanoparticles were prepared from the respective diamondoid ketones via an effective two-step procedure involving addition of methyl magnesium iodide and oxidation with trifluoroperacetic acid in trifluoroacetic acid. The reactivities of the oxacages are determined by the position of the dopant and are in good agreement with computational predictions.

The electronic properties of diamond-based materials are determined by the types and amounts of naturally present dopants. For instance, the *p*-semiconductor properties of natural diamond are controlled by trace amounts of boron.[2] Doping also changes the conductivity of artificial CVD diamond dramatically.[3] One of the unique properties of natural hydrogen-terminated diamond is its pronounced negative electron affinity (NEA),[4] which reveals its potential for electronic devices such as field-effect transistors and electron emitters.[5] In contrast to *p*-type diamond, the properties of *n*-type diamond remain almost unexplored, since the preparation of this material doped with donor atoms (O, S, N, P, etc.) is still problematic;[2] *n*-doping enhances the electron-emitting properties of diamond.[6]

Naturally occurring diamondoids represent hydrogen-terminated nanodiamonds with well-defined particle sizes and shapes.[7−9] We recently found that diamondoid derivatives deposited on noble metal surfaces display NEA similar to that of a hydrogen-terminated diamond: a well-ordered self-assembled monolayer of [121]tetramantane-6-thiol deposited on a gold surface behaves as a monochromatic electron emitter with up to 70% electron yield.[10,11] Analogous to bulk diamond, we expect that *n*-doping will enhance the electron-emitting properties of nanodiamonds as well. Our recent theoretical study suggests that replacement of the CH_2 moieties of diamondoid with heteroatoms (internal doping)

[†] Functionalized Nanodiamonds 22. For part 21, see ref 1.

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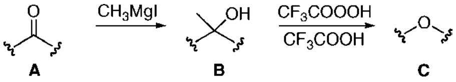
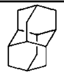
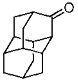
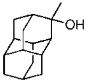
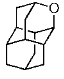
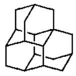
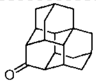
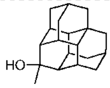
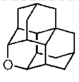
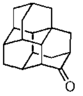
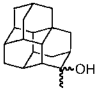
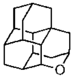
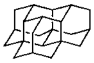
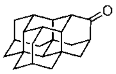
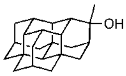
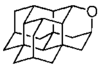
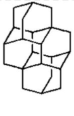
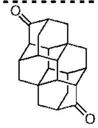
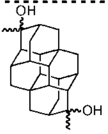
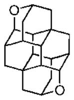
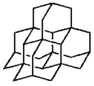
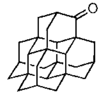
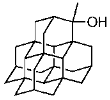
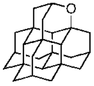
10.1021/ol901089h CCC: $40.75
Published on Web 06/24/2009

significantly changes the electronic properties of these carbon nanoparticles.[12] We now report the preparations and functionalizations of oxygen-doped diamondoids as well as their primary functionalizations. The latter is necessary for attachment of these particles to semiconductor or metal surfaces.

For the preparation of the oxadiamondoids (**C**), we utilized a procedure previously developed by one of us for the preparation of oxaadamantane[13] through the addition of MeMgI to the respective ketone (**A**) and oxidation of thus formed methylhydroxy derivative (**B**) with trifluoroperacetic acid in trifluoroacetic acid (Table 1).

Table 1. Effective Two-Step Carbonyl Group Replacement for Oxygen and the Preparative Yields of Ketones **6**−**11**, Methylhydroxy Derivatives **12**−**17**, and Oxadiamondoids **18**−**23** Obtained from Diamondoids **1**−**5**



no.	Hydrocarbon	**A**, yield	**B**, yield	**C**, yield
1	 **1**	 **6**, 65%	 **12**, 93%	 **18**, 80%
2	 **2**	 **7**, 15%	 **13**, 95%	 **19**, 55%
		 **8**, 45%	 **14**, 95%	 **20**, 90%
3	 **3**	 **9**, 32%	 **15**, 90%	 **21**, 45%
4	 **4**	 **10**, 6%	 **16**, 95%	 **22**, 90%
5	 **5**	 **11**, 55%	 **17**, 95%	 **23**, 90%

Direct oxidation of diamondoids **1**−**5** with sulfuric acid at 75−80 °C led to ketones **6**−**11**. The oxidations of **1** and **5** only gives ketones **6**[14] and **11**, respectively, while oxidation of **2** gives a mixture of ketones **7** and **8**;[15−17] the oxidation of **3** predominantly gives monoketone **9**. Due to the low solubility of [121]tetramantane (**4**) in sulfuric acid, both diketones and hydroxy ketones form.[18] We isolated the most symmetrical ketone **10** (the structure was confirmed by X-ray crystal structure analysis; see the Supporting Information for details) for the preparation of the respective dioxa derivative **22**. The reaction of ketones **6**−**11** with MeMgI almost quantitatively led to the respective adducts **12**−**17**. Adduct **14** forms as a mixture of two and **16** as a mixture of three diastereomers as determined on the basis of the ^{13}C NMR spectral data.

The reaction of alcohols **12**−**17** with trifluoroperacetic at room temperature gave oxaderivatives **18**−**23**. The spectral characteristics of 3-oxadiamantane (**18**) are identical to those of a sample prepared through a cumbersome seven-step literature procedure.[19] The structure of C_{2v}-symmetrical 5-oxatriamantane (**19**) was confirmed by X-ray crystal structure analysis (Figure 1). Deviations of the X-ray experimental geometrical parameters of **19** from those computed at DFT and ab initio levels are small, but the best agreement was found[20] for B3PW91 and MP2 with correlations-consistent basis sets. Notably, the elementary crystal cell of **19** is dominated by the attractive hydrogen−hydrogen van der Waals interactions without involvement of O⋯H contacts (Figure 1).

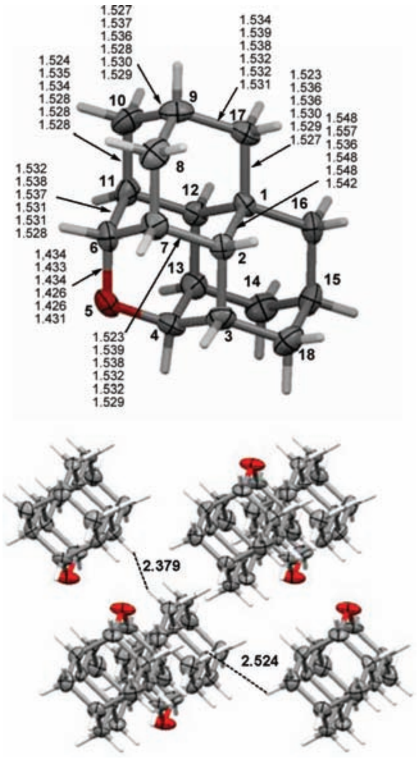


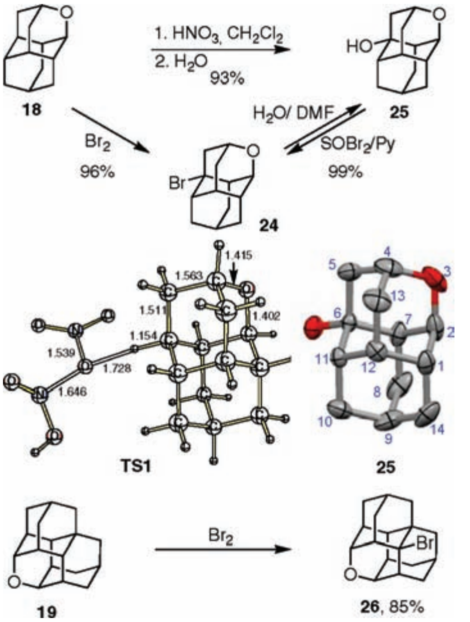
Figure 1. Experimental X-ray crystal structure and the B3LYP/6-311+G(3df,2p)-, B3LYP/cc-pVTZ, B3PW91/cc-pVTZ-, B3PW91/aug-cc-pVTZ-, and MP2/cc-pVTZ-computed geometry of 5-oxatriamantane (**19**) and its crystal packing.

We computed the cell of the C_i-symmetrical hexamer of **19** and found that the experimental values agree well with the HH intermolecular distances of 2.3−2.7 Å computed at B3LYP/6-31G(d) including Grimme's dispersion corrections.[21]

The potential use of *n*-doped nanodiamonds **18**−**23** in the construction of nanoelectronic devices is determined by the ability to deliver the electric charge to the molecule through proper functional groups (OH, SH, COOH, etc.). The available data[22,23] suggest that the presence of a functional group is decisive factor that determines the behavior of diamondoids on metal surfaces. As the attachment of functional groups to diamondoids is most selective with oxidative electrophiles, we tested the reactivity of oxacages **18** and **19** with bromine and with 100% nitric acid as reagents.[24] The bromination of oxadiamantane **18** with neat bromine gave 6-bromo-3-oxadiamantane (**24**) as the only product (Scheme 1). Hydrolysis of **24** with H_2O/DMF gave 6-hydroxy derivative **25** quantitatively. As there are two C_1-isomers possible, the structure of the tertiary monohydroxy derivative **25** was also determined by an X-ray crystal structural analysis (Scheme 1). Structure **25** was also the only product of the reaction of **18** with 100% nitric acid and subsequent hydrolysis of the intermediate nitroxy derivative. Thus, the reaction of **18** with electrophiles where only one out of a possible six tertiary C−H positions is functionalized is in marked contrast to the reaction of parent diamantane for which a mixture of substitution products forms.[24]

We previously suggested that the selectivity of the C−H substitutions with oxidizing electrophiles is determined by the electron transfer from the hydrocarbon to the reagent in the transition structures for hydrogen abstraction (H-coupled ET).[25,26]

Scheme 1. Functionalizations of Oxadiamondoids **18** and **19**, Functional Group Exchange, the Lowest-Lying Transition Structure (**TS1**, B3PW91/cc-pVDZ) for H-Coupled Electron Transfer from **18** (through the C^6-H Position), and the X-ray Crystal Structure of 6-Hydroxy-3-oxadiamantane (**25**) with Numbering of Carbons (Hydrogens Omitted for Clarity)



We computed[27] all possible transition structures for the reaction of **18** with a complex of HNO_3 with the nitronium cation, which is believed to be responsible for the C−H activation.[28] We found that **TS1** (Scheme 1) is indeed the lowest in energy (see the Supporting Information for details).

The selectivity of the bromination of diamondoids correlates well with the stability of the carbocations in the

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corresponding positions.[29] As the most stable 3-oxadiamantyl-6 cation is 1.0 kcal/mol at MP2/cc-pVDZ more stable than the next stable 2-cation (see Figure S1, Supporting Information, for details) the high selectivity of the bromination of **18** is not surprising. We also computed the relative stabilities of the tertiary carbocations of oxatriamantanes **19** and **20**. While the 2-cation is the most stable for 5-oxatriamantane (**19**), three cations are very close in energy in the case of **20** (Figure S1, Supporting Information). As a consequence, the bromination of **19** gave 2-bromo derivative (**26**) as the single product (Scheme 1), whereas **20** resulted in a complex mixture of monobromo derivatives. We conclude that the position of the dopant in the cage is decisive in determining the selectivities of the substitution reactions. While the bromination of triamantane[30] is unselective and gives all four possible monobromides,[31] only one product is formed in the bromination of 5-oxatriamantane **19**. Computations are in good agreement with the selectivities observed experimentally.

We developed a simple and convenient procedure[32] for the preparation of oxygen-doped hydrogen-terminated nanodiamonds (oxadiamondoids) of different sizes, shapes, and dopant positions. The selectivities of their C−H functionalizations are determined by the position of the oxygen in the cage and may be in some cases even higher than that of the parent hydrocarbon. Studying of the electronic properties of *n*-doped nanodiamonds are currently underway.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Ministry of Science and Education of Ukraine, Ukrainian Basic Research Fund, and the Fonds der Chemischen Industrie. We thank the CSC Frankfurt (Germany) and the Institute of Applied System Analysis (Kiev, Ukraine) for computational resources.

Supporting Information Available: Descriptions of the NMR spectra of compounds **6**−**23** as well as copies of the NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) **General Procedure for the Oxidation of Diamondoids 1−5 with H_2SO_4.** A mixture of 1 mmol of the hydrocarbon was stirred in 3 mL of 98% H_2SO_4 for 2 days at 77−80 °C. The reaction mixture was poured onto ice and extracted with $CHCl_3$ (4 × 5 mL), and the 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 pentane/ether (2.5/1). For the yields of the ketones see Table 1 and for the physicochemical characteristics see the Supporting Information. **General Procedure for the Preparation of Hydroxymethyl Derivatives 12−17.** To a solution of the ketone (20 mmol in 50 mL of dry Et_2O) was slowly added an etheral solution of 50 mmol of CH_3MgI, and the mixture was stirred under reflux for 4 h, cooled in an ice−water bath, and quenched with 5% H_2SO_4. The layers were separated, and the aqueous layer was extracted with 3 × 30 mL of diethyl ether. The combined organic layers were washed with a 10% solution of Na_2CO_3 and brine and were dried over anhydrous Na_2SO_4. Evaporation under reduced pressure gave the respective hydroxymethyl derivatives as colorless solids that were used without further purification. For the yields see Table 1 and for the physicochemical characteristics see the Supporting Information. **General Procedure for Preparation of 18−23.** A solution of perfluoroacetic acid in trifluoroacetic acid was prepared as described previously.[13] To 4.5 mL of this solution was added 2.3 mmol of the respective hydroxymethyl derivative (**12**−**17**) as a solid over 10 min at 0 °C, and the mixture was stirred for 30 min at 0 °C and then 1.5 h at room temperature. The reaction mixture was poured into 10 mL of 40% NaOH, 50 mL of water was added, the organic part was extracted with 3 × 10 mL of $CHCl_3$, washed with water (2 × 10 mL), and dried over anhydrous Na_2SO_4, and solvents were distilled off. Column chromatography of the residue on silica gel with pentane/ether = 9/1 gave the respective oxadiamondoids, whose yields are shown in Table 1 and physicochemical characteristics are described in the Supporting Information.