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Simple Preparation of Diamondoid 1,3-Dienes via Oxetane Ring Opening§

Andrey A. Fokin,*,⊥,‡ Ekaterina D. Butova,‡ Lesya V. Chernish,⊥ Natalie A. Fokina,‡ Jeremy E. P. Dahl,|| Robert M. K. Carlson,|| and Peter R. Schreiner*,‡

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

aaf@xtf.ntu-kpi.kiev.ua; prs@org.chemie.uni-giessen.de

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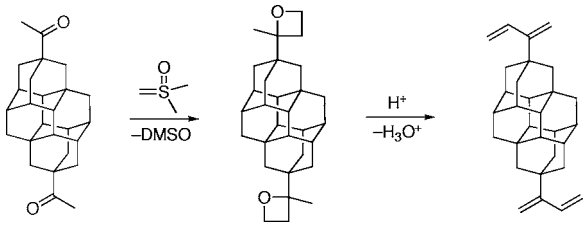
ABSTRACT



The transformations of apical mono- and bisacetyl diamondoids to the respective oxetanes and subsequent acid-catalyzed ring opening/dehydration lead to diamondoidyl mono- and bis-1,3-dienes in high preparative yields.

Functionalized fullerenes, nanotubes, and nanodiamonds are key prospective organic molecules with many potential applications in nanomaterial chemistry and nanoelectronics. Functionalized nanodiamonds[1,2] from CVD or detonation experiments[3] are mostly associated with preparation of new nontoxic[4] drug carriers[5] and biosensors.[6,7] Previously, many functional groups (−COOH, −OH, −F, $-NH_2$, etc.) were attached to the surfaces of nanodiamonds.[1,8] However, surface inhomogeneities and the large deviations in particle sizes make the preparation of selectively functionalized and structurally distinct nanodiamonds unsuitable[9] for many applications. Recently, two of us isolated a number of higher diamondoids from petroleum,[10,11] and these hydrocarbons represent structurally well-defined *monodispersed* hydrogen-terminated nanodiamonds in the 1−2 nm size regime. Various tetramantanes, pentamantanes, and cyclohexamantane are now available in sizable quantities as individual and pure compounds, and some higher representatives, up to undecamantane, are becoming available. This discovery

§ Functionalized Nanodiamonds 7. For part 6, see ref 22.
⊥ Kiev Polytechnic Institute.
‡ Justus-Liebig University.
|| MolecularDiamond Technologies, Chevron Technology Ventures.

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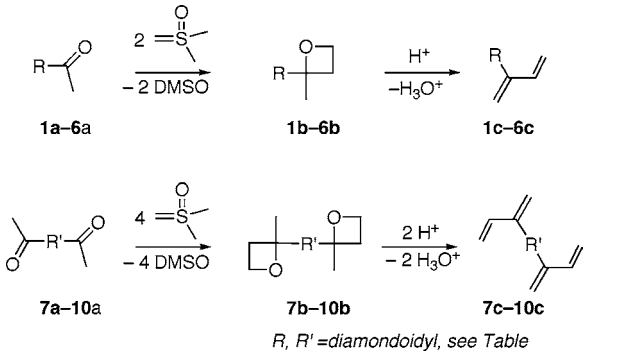
offers a unique opportunity to prepare functionalized nanodiamonds as chemically homogeneous materials. It was theoretically predicted that such diamondoids may be used in optoelectronic and electron-emission devices.[12]

In our previous work, we evaluated theoretically[13] and then found experimentally that selective functionalizations are possible for C_{2h}-tetramantane ([121]tetramantane in Balaban−Schleyer nomenclature)[14] and T_d-pentamantane ([1(2,3)4]-pentamantane)[15] with a number of electrophilic and oxidative reagents, to give pure bromo, hydroxy, carboxylic, and acetyl derivatives. The thiol function (−SH) is of particular interest as it allows the attachment of nanodiamonds onto gold surfaces forming highly ordered self-assembled monolayers (SAMs)[16] as shown for 1-adamantane thiol.[17] Recently, we prepared a selection of diamondoid thiols[18] that are potentially useful for nanoelectronics and nanolithography.[19−22] Another direction of nanoelectronic device development is based on modifying the surfaces of semiconductors (mostly Si) with organic molecules.[23] [2+4] Cycloadditions of 1,3-dienes to the Si═Si bonds of the surface represent the most effective route to such assemblies.

Herein, we describe a simple and convenient preparation of terminal diamondoid 1,3-dienes, the ideal candidates for the formation of nanodiamond SAMs on silicon surfaces. Naturally, these types of structures can also be used for materials and polymer chemistry. Because methyl diamondoidyl ketones (**1a**−**4a**) are now readily available,[15,24] we chose them as the starting materials for the preparation of the respective dienes (Scheme 1). Yet unknown 7-acetyl-T_d-pentamantane (**5a**) and 1-acetyl diadamantane (**6a**) were prepared by photoacetylation of T_d-pentamantane[11] and 1,1′-diadamantyl[25] with diacetyl.

Generally, the preparation of terminal 1,3-dienes from ketones requires many steps and typically involves a sequence of a Mannich reaction, Hofmann degradation, and Wittig olefination.[26] Although the Yurchenko reaction[27] is

Scheme 1. Two-Step Preparation of Diamondoidyl Mono- (**1c**−**6c**) and Bisdienes (**7c**−**10c**) from the Respective Ketones (**1a**−**10a**) via Intermediate Formation of Oxetanes (**1b**−**10b**) (Table 1)



effective for the direct one-step diolefination of ketones, sterically hindered 1-adamantyl methyl ketone gives 1-adamantyl 1,3-diene[28] in only 37% yield. We now describe a simple two-step procedure for the transformation of sterically hindered methyl diamondoidyl ketones to the respective dienes with preparative yields up to 90%. The present methodology is based on the acid-catalyzed ring opening of oxetanes, which are readily available though the reaction of monoketones (**1a**−**6a**) with an excess of dimethylsulfoxonium methylide.[29] We found that this reaction is not very sensitive to steric hindrance and gives diamondoidyl oxetanes (**1b**−**6b**) in high yields at 130 °C in DMSO (Table 1). This transformation was also successfully applied in the preparation of bisoxetanes (**7b**−**10b**) from the bisketones (**7a**−**10a**) when a larger excess of reagents is employed.

Diamondoid oxetanes are quite sensitive toward acids and must be purified by chromatography on basic aluminum oxide. The acid-catalyzed dehydration of mono- as well as dioxetanes in toluene or CH_2Cl_2 in the presence of catalytic amounts of *p*-TSA leads to dienes (**1c**−**6c**). Preparation of bisdienes (**7c**−**10c**) is also effective; these polyenes may possibly be used in the construction of conductive junctions[19] between two semiconductor contacts.

The transformation of oxetanes in the presence of acids with formation of homoallylic alcohols is well documented.[30−33] We have shown that homoallylic alcohols (**1d**−**10d**, Scheme 2) are the key intermediates en route from oxetanes to dienes.

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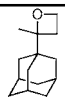
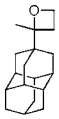
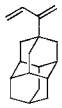
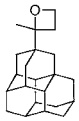
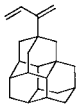
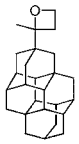
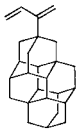
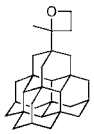
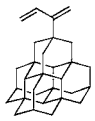
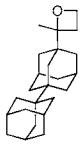
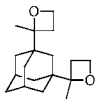
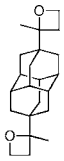
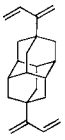
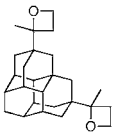
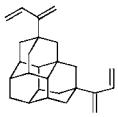
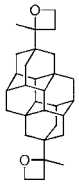
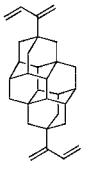
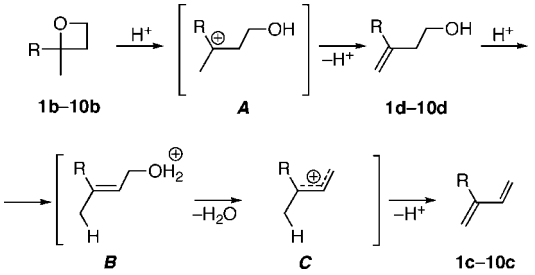
Table 1. Preparative Yields of Oxetanes (**1b**−**10b**) and Dienes (**1c**−**10c**) Obtained from Mono- (**1a**−**6a**) and Diketones (**7a**−**10a**)

#	oxetane	yield [%]	diene	yield [%]
1	 **1b**	96	 **1c**	95
2	 **2b**	98	 **2c**	96
3	 **3b**	96	 **3c**	82
4	 **4b**	89	 **4c**	90
5	 **5b**	93	 **5c**	76
6	 **6b**	79	 **6c**	98
7	 **7b**	57	 **7c**	77
8	 **8b**	60	 **8c**	88
9	 **9b**	86	 **9c**	73
10	 **10b**	89	 **10c**	68

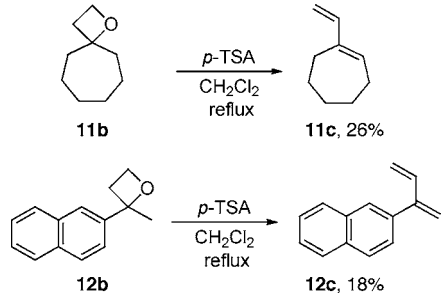
For instance, under the mild reaction conditions, the alcohol (**1d**, R = Ad) was separated; at longer reaction times, it gives diene **1c** presumably through intermediates ***B*** and ***C*** (Scheme 2). The observed transformation of the intermediate homoallylic alcohols (**1d**−**10d**) to dienes (**1c**−**10c**) is selective because only one reaction path exists for the deprotonation from cation ***A***; i.e., the rearrangements and fragmentations do not occur if R = diamondoidyl. When we applied the above reaction conditions to strained oxetanes such as R =

(35) **General Procedure for Preparation of Diamondoid Oxetanes.** To a mixture of 2.8 g (0.12 mol) of sodium hydride in 150 mL of dry DMSO was added 22.2 g (0.1 mol) of trimethylsulfoxonium iodide in portions under stirring at room temperature. The reaction mixture was heated to 130 °C, and 0.017 mol of carbonyl compound was added in 20 mL of dry DMSO. The reaction mixture was stirred at 130 °C for 12 h, cooled, diluted with 200 mL of water, and extracted with 3 × 30 mL of pentane. The combined extracts were washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated. The resulting crude oxetane was filtered through a short column with basic aluminum oxide (pentane/ether 9:1) to give the pure products (see Table 1 for the yields). **General Procedure for the Preparation of Diamondoid Dienes.** To a solution of 1.3 mmol of the respective oxetane in 6 mL of CH_2Cl_2 was added 0.025 g of *p*-TSA. The reaction mixture was refluxed for 1 h, cooled, washed with a solution of $NaHCO_3$, water, and brine, and dried over anhydrous Na_2SO_4. The residue after evaporation of solvent was chromatographed using a silica gel column (pentane) to give the respective diene (see Table 1 for the yields). **Spectral Characterization of Dienes: 2-(Diamantan-4-yl)-butadiene-1,3 (2c).** ^{1}H NMR: 1.60−1.75 (m, 19 H), 4.75 (s, 1 H), 5.0 (dd, 1 H, J^1 = 10.7, J^2 = 2.5 Hz), 5.09 (s, 1 H), 5.38 (dd, 1 H, J^1= 17.1, J^2 = 2.5 Hz), 6.45 (dd, 1 H, J^1= 17.1, J^2 = 10.7 Hz). ^{13}C NMR: 25.8 (CH), 34.9 (C), 36.9 (CH_2), 37.9 (CH), 38.0 (CH_2), 41.9 (CH), 107.3 (CH_2), 114.7 (CH_2), 136.6 (CH), 156.8 (C). HR-MS (*m*/*z*): found, 240.1881; calcd for $C_{18}H_{24}$, 240.1878. **2-(Triamantan-9-yl)butadiene-1,3 (3c).** ^{1}H NMR: 1.10 (s, 2 H), 1.18 (s, 2 H), 1.31 (s, 2 H), 1.50−1.80 (m, 17 H), 4.53 (s, 1 H), 4.85 (dd, 1 H, J^1 = 10.6, J^2 = 2.2 Hz), 5.03 (s, 1 H), 5.32 (dd, 1 H, J^1 = 17.0, J^2 = 2.2 Hz), 6.43 (dd, 1 H, J^1 = 17.0, J^2 = 10.6 Hz). ^{13}C NMR: 27.7 (CH), 33.8 (C), 34.5 (CH), 34.6 (CH), 36.1 (C), 37.8 (CH), 38.6 (CH_2), 38.8 (CH), 41.5 (CH_2), 45.3 (CH_2), 46.8 (CH), 48.9 (CH_2), 107.3 (CH_2), 114.7 (CH_2), 136.5 (CH), 156.6 (C). HR-MS (*m*/*z*): found, 292.2178; calcd for $C_{22}H_{28}$, 292.2191. **2-([121]Tetramantan-6-yl)butadiene-1,3 diene (4c).** ^{1}H NMR: 1.33−1.84 (m, 27 H), 4.67 (s, 1 H), 4.93 (dd, 1 H, J^1 = 10.6, J^2 = 2.2 Hz), 5.02 (s, 1 H), 5.31 (dd, 1 H, J^1 = 17.0, J^2 = 2.2 Hz), 6.37 (dd, 1 H, J^1 = 17.0, J^2 = 10.6 Hz). ^{13}C NMR: 27.9 (CH), 31.3 (CH), 31.6 (CH), 36.2 (C), 36.8 (C), 36.9 (C), 37.9 (CH_2), 38.2 (CH), 38.6 (CH), 41.5 (CH_2), 44.3 (CH_2), 45.3 (CH_2), 45.8 (CH_2), 46.7 (CH), 47.0 (CH), 47.9 (CH_2), 107.5 (CH_2), 114.7 (CH_2), 136.6 (CH), 156.6 (C). HR-MS (*m*/*z*): found, 344.2450; calcd for $C_{26}H_{32}$, 344.2504. **2-([1(2,3)4]Pentamantan-1,1-yl)-butadiene-1,3 (5c)**. ^{1}H NMR: 1.15−1.30 (m, 31 H), 4.62 (s, 1 H), 4.92 (dd, 1 H, J^1 = 10.7, J^2 = 2.2 Hz), 4.99 (s, 1 H), 5.30 (dd, 1 H, J^1 = 17.0, J^2 = 2.2 Hz), 6.35 (dd, 1 H, J^1 = 17.0, J^2 = 10.7 Hz). ^{13}C NMR: 28.5 (CH), 32.8 (C), 33.5 (C), 37.5 (C), 44.90 (CH_2), 44.91 (CH_2), 48.4 (CH_2), 52.9 (CH), 53.05 (CH), 107.1 (CH_2), 114.7 (CH_2), 136.4 (CH), 156.3 (C). HR-MS (*m*/*z*): found, 396.2811; calcd for $C_{30}H_{36}$, 396.2817. **2-(1,1′-Diadamantan-4-yl)butadiene-1,3 (6c).** ^{1}H NMR: 1.41−1.64 (m, 29 H), 4.66 (s, 1 H), 4.93 (dd, 1 H, J^1 = 10.7, J^2 = 2.6 Hz), 5.02 (s, 1 H), 5.31 (dd, 1 H, J^1 = 17.1, J^2 = 2.6 Hz), 6.37 (dd, 1 H, J^1 = 17.1, J^2 = 10.7 Hz). ^{13}C NMR: 29.0 (CH), 29.2 (CH), 34.2 (C), 34.5 (CH_2), 35.4 (CH_2), 36.5 (C), 36.7 (CH_2), 37.2 (C), 37.6 (CH_2), 38.9 (CH_2), 41.0 (CH_2), 107.1 (CH_2), 114.8 (CH_2), 136.5 (CH), 157.5 (C). HR-MS (*m*/*z*): found, 322.2666; calcd for $C_{24}H_{34}$, 322.2661. **1,3-Bis-(1,3-butadien-2-yl)adamantane (7c).** ^{1}H NMR: 1.50−1.67 (m, 12 H), 2.06 (bs, 2 H), 4.68 (s, 2 H), 4.90 (dd, 2 H, J^1 = 10.7, J^2 = 2.2 Hz), 5.03 (s, 2 H), 5.31 (dd, 2 H, J^1 = 16.9, J^2 = 2.2 Hz), 6.36 (dd, 2 H, J^1 = 16.9, J^2 = 10.7 Hz). ^{13}C NMR: 28.9 (CH), 36.2 (CH_2), 37.6 (C), 40.6 (CH_2), 44.6 (CH_2), 107.4 (CH_2), 114.9 (CH_2), 136.3 (CH), 156.7 (C). HR-MS (*m*/*z*): found 240.1795; calcd for $C_{18}H_{24}$, 240.1878. **4,9-Bis(1,3-butadien-2-yl)diamantane (8c).** ^{1}H NMR: 1.60−1.73 (m, 18 H), 4.69 (s, 2 H), 4.95 (dd, 2 H, J^1 = 10.8, J^2 = 2.3 Hz), 5.04 (s, 2 H), 5.32 (dd, 2 H, J^1 = 17.0, J^2 = 2.3 Hz), 6.39 (dd, 2 H, J^1 = 17.0, J^2 = 10.8 Hz). ^{13}C NMR: 34.9 (C), 37.5 (CH), 41.4 (CH_2), 107.5 (CH_2), 114.9 (CH_2), 136.5 (CH), 156.5 (C). HR-MS (*m*/*z*): found, 292.2194; calcd for $C_{22}H_{28}$, 292.2191. IR: 2941, 2870, 1751,1628, 1460, 1440, 1050, 910, 893. **9,15-Bis-(1,3-butadien-2-yl)triamantane (9c).** ^{1}H NMR: 1.10−1.25 (m, 6 H), 1.49 (s, 4 H), 1.50−1.74 (m, 12 H), 4.71 (s, 2 H), 4.87 (dd, 2 H, J^1 = 10.8, J^2 = 2.3 Hz), 5.04 (s, 2 H), 5.41 (dd, 2 H, J^1 = 17.0, J^2 = 2.3 Hz), 6.37 (dd, 2 H, J^1 = 17.0, J^2 = 10.8 Hz). ^{13}C NMR: 33.8 (C), 34.3 (CH), 35.1 (C), 37.5 (CH_2), 38.1 (CH), 41.6 (CH_2), 45.4 (CH), 48.8 (CH_2), 107.3 (CH_2), 114.8 (CH_2), 136.5 (CH), 156.5 (C). HR-MS (*m*/*z*): found, 344.2446; calcd for $C_{26}H_{32}$, 344.2504. **6,13-Bis-(1,3-butadien-2-yl)-[121]tetramantane (10c).** ^{1}H NMR: 1.23−1.74 (m, 26 H), 4.67 (s, 2H), 4.93 (dd, 2 H, J^1 = 10.8, J^2 = 2.3 Hz), 5.02 (s, 2 H), 5.31 (dd, 2 H, J^1 = 17.5, J^2 = 2.3 Hz), 6.38 (dd, 2 H, J^1 = 17.5, J^2 = 10.8 Hz). ^{13}C NMR: 31.6 (C), 36.1 (CH), 36.9 (C), 38.6 (CH), 41.5 (CH_2), 45.3 (CH_2), 46.2 (CH), 47.8 (CH_2), 107.3 (CH_2), 114.7 (CH_2), 136.5 (CH), 156.4 (C). HR-MS (*m*/*z*): found 396.2790; calcd for $C_{30}H_{36}$, 396.2817.

Scheme 2. Acid-Catalyzed Rearrangement of Oxetanes **1b**−**10b** First Giving Homoallylic Alcohols (**1d**−**10d**), Whose Isomerization and Dehydration Lead to Dienes **1c**−**10c**



Scheme 3. Acid-Catalyzed Rearrangement of Spirooxetane (**11b**) and the Naphthalene Derivative **(12b)** to Dienes **11c** and **12c**



cubyl and cyclopropyl, a complex mixture of unsaturated products formed under acidic conditions.

The transformation is not limited to diamondoid ketones. Spirooxetanes and oxetanes with aromatic substituents also form dienes in the presence of acid. For instance, 1-oxaspiro[3,6]decane (**11b**) and 2-methyl-(2-naphthalenyl)-oxetane (**12b**) give dienes **11c** and **12c**, though with low yields owing to polymerization of the labile products (Scheme 3).

Thus, we have developed a simple procedure for the preparation of the diamondoid 1,3-dienes. These molecules represent structurally distinct nanodiamonds with 1,3-diene moieties on their ⟨111⟩ faces.[34] This provides well-defined attachment points on the surfaces of nanodiamonds and thus opens ways to study the electronic properties of these exciting new carbon-rich nanomaterials.[35]

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Supporting Information Available: The descriptions of the NMR spectra of oxetanes **1b**−**10b** as well as the copies of the ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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