A C G publications

organic communications

Towards 3-(2-adamantylidene)diamantane derivatives through the McMurry cross coupling reaction

Ngo Trung Hoc [1,2,*], **Vladimir N. Rodionov,**[1] **and Andrey A. Fokin** [1]

[1]*Igor Sikorsky Kiev Polytechnic Institute*, *pr. Pobedy 37, Kiev, 03056 Ukraine;*
[2] *The Viet Nam University of Firefighting and Prevention, 243 Khuat duy tien, Hanoi 10000, Vietnam*

Abstract: Diamondoid assemblies have a potential in nanoelectronics as the substrates for self-assembled monolayer formation. However, selective functionalization of such molecules is cumbersome. We demonstrate that the McMurry cross-coupling reaction is useful for the preparation of 3-(2-adamantylidene)diamantane derivatives with substituents at the tertiary and secondary positions of the diamantane moiety. This allows to create the surface attachment points in the diamondoid structure.

1. Introduction

Diamondoids (adamantane, diamantane, triamantane, and higher polymantanes) occur in natural petroleum deposits. In most crude oils diamondoid concentrations are in the order of 1–100 ppm and are presented predominantly by adamantane, diamantane and their alkyl derivatives [1]. Only adamantane, diamantane and triamantane exist as a single isomers, higher members of the series can exist in more than one isomeric form and the number of isomers increase with the growing size. Higher diamondoids have a potential as building blocks for nanoelectronic devices. It was shown that tetramantane thiol form well-ordered self-assembled monolayers (SAMs) on gold surface and material [2-6] thus obtained display monochromatic electron emission with low–kinetic energy threshold [3]. Besides, diamondoids and their derivatives serve as a model for hydrogen terminated diamond nanoparticles [7-10]. The availability of diamondoids up to hexamantanes (with 0.6 nm particle size) or pentamantanes (with 0.75 nm particle size) in preparative quantities from oil limited. The larger diamondoid particles are not available despite their potential applications in nanoelectronics [7-12]. This challenge may be addressed by coupling lower diamondoids with various spacers. While the sp^3–sp^3 diamondoid dimers [13] reproduce parts of the hydrogen-terminated diamond lattice, the sp^2-dimers [9] is a model for the presence of unsaturation in diamondoids. This may allow fine tuning the electronic properties of diamond-based materials. The C-H-bond functionalizations of diamondoid oligomers were performed, these provided halogen and hydroxy derivatives with conservation of unsaturation, but with low selectivities[9]. Various alkenes have been produced by the McMurry ketone coupling reaction as a powerful synthetic method [14-16].

---

[*] Corresponding author: E-Mail: trunghoct34@gmail.com

In present study we develop the new synthetic route to the 3-(2-adamantylidene)diamantane derivatives utilizing the McMurry cross-coupling reaction where one of the components already contains the substituent in a certain position of the diamantane cage.

2. Results and Discussion

Hydroxyketal (**1**) was used as a starting compound, whose hydrolyses in the mixture of 10% H_2SO_4 aqueous-THF solution allows to prepare 10-hydroxy-3-diamantanone (**2**) [17]. After the hydroxy-group protection through the reaction with trimethylsilyl chloride 10-trimethysiloxane-3-diamantanone (**3**) [18] was obtained. The later was used as a starting compound for the synthesis of 10-trimethylsiloxane - 3-(2-adamantylidene)diamantane (**4**) through the McMurry cross-coupling with 2-adamantanone under argon atmosphere by adding the mixture of ketones to a freshly prepared titanium reagent (Scheme 1).
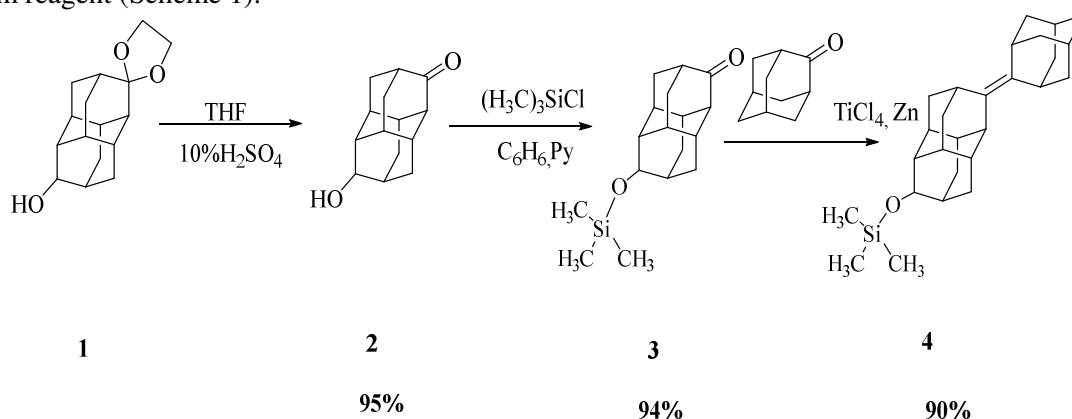
Scheme 1. Synthesis of 10-trimethylsiloxane - 3-(2-adamantylidene) diamantine (**4**)

In a similar way, 9-hydroxy-3-diamantanone (**5**) [19] was used as a starting material for the synthesis of 9-trimethylsiloxane - 3-(2-adamantylidene)diamantane (**7**). After silylation of (**5**) to give (**6**), the McMurry coupling as above gave (**7**) in 92% yield.
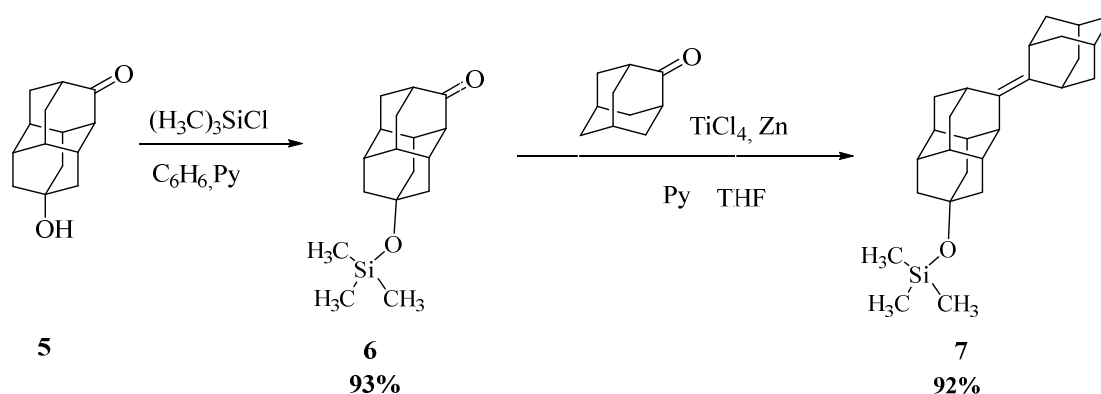
Scheme 2. Synthesis of 9-trimethylsiloxane - 3-(2-adamantylidene) diamantane (**7**)

3. Experimental

3.1. Chemical Material and Apparatus

All reagents and solvents employed were purified and dried or used without further purification as purchased from Fluka, Sigma-Aldrich, and Merck. Elemental analysis were recorded on the VARIO EL III elemental analyzer instrument for C, H, and N. ^{1}H, ^{13}C-NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C, solvent CDCl$_3$.

Column chromatography performed on silica gel 60 (0.063–0.200 mm), purchased from Merck (Darmstadt, Germany). The GLC analysis performed on a capillary column Optima-1 on Shimadzu GC-14B equipped with a flame-ionization detector.

3.2. 10-Hydroxy-3-diamantanone (2)

To a solution of 2 g (76 mmol) of ketal (**1**) in 10 mL of THF 100 mL of 10% solution of sulfuric acid was added, the mixture was maintained at stirring without heating for 5 hours. Excess sulfuric acid was neutralized with solid sodium hydroxide till pH 7 – 8, the reaction product was extracted with dichloromethane, the extract was dried with Na_2SO_4 and the solvent was distilled off in a vacuum.

Yield 1.57 g (95%), mp. 158°C (hexane). ^1H NMR spectrum, δ, ppm: 1.46 – 1.52 s (1H, CH), 1.61 – 1.75 m (8H, CH, CH_2), 1.83 – 1.93 m (5H, CH, CH_2), 2.0 – 2.08 m (3H, CH, CH_2), 3.77 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 30.1 (CH_2), 31.2 (CH), 32.3 CH_2), 33.8 CH_2), 34.3 (CH), 34.5 (CH), 34.6 (CH_2), 36.1 (CH_2), 41.3 (CH_2), 44.6 (CH_2), 74.5 (COH), 217.2 (C=O). Found % C 77.03, H 8.31. $C_{14}H_{18}O_2$. Calculated % C 77.05, H 8.30.

3.3. 10-Trimethysiloxane-3-diamantanone (3)

In a 250 mL vessel equipped with a mechanical stirrer and a reflux condenser, 150 mL of benzene and 5 mL (31.4 mmol) trimethylsilane chloride are placed, then a mixture of 2 g (9.17 mmol) 10-hydroxydiamantan-3-one in 10 mL of pyridine added dropwise and the heating temperature rises to 80 – 85 °C for 2 hours. The benzene layer is separated, washed with 100 mL of distilled water, twice with 100 mL of 5% HCl solution and 100 mL of saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4, the solvent was evaporated on a vacuum rotary evaporator to constant weight, the residue was purified by column chromatography over silica gel, eluent-hexane /diethyl ether 20/1.

Yield 2.5 g (94%), mp. 74°C (hexane). ^1H NMR spectrum, δ, ppm: 0.09 s (9H, CH_3), 1.37 - 1.45 m (1H, CH), 1.7-1.98 m (11H, CH, CH_2), 2.14 s (1H, CH), 2.38 s (2H, CH), 2.42 m (1H, CH), 3.83 s (1H, CH). ^{13}C NMR spectrum, δ, ppm: 0.23 (TMS), 30.2 (CH_2), 30.4 (CH), 32.3 (CH), 34.6 (CH_2), 35.7 (CH), 37.6 (CH_2), 38.1 (CH_2), 38.2 (CH), 39.0 (CH), 43.1 (CH), 44.3 (CH), 55.6 (CH), 74.3 (C-OTMS), 217.5 (C=O). Calculated for $C_{17}H_{26}O_2Si$; % C 70.29, H 9.02. Found, % C 70.26, H 9.03.

3.4. 10-Trimethylsiloxane - 3-(2-Adamantylidene) diamantine (4)

In a 100 mL 2-necked reactor equipped with a magnetic stirrer, septum and an efficient reflux condenser with a device for supplying argon with a bubble counter, 60 mL of THF distilled over sodium in an argon stream was loaded with a syringe. The reactor is cooled with ice water and a 3.75 mL (34 mmol) $TiCl_4$ solution is slowly fed through the septum. The vortex of argon is increased and 4.5 g (70.3 mmol) of zinc dust with intensive mixing is filled with a funnel through the open mouth of the reactor. The reactor is carefully insulated from the external environment, under argon atmosphere and the reaction mixture is boiled for 1 hour with continuous intensive stirring. The reaction mixture is cooled to room temperature and sequentially loaded with a syringe of 1 mL of dry pyridine, 2 g (13 mmol) of 2-adamantanone and 1 g (3.45 mmol) of 10-trimethysiloxane-3-diamantanone (**3**) in 15 mL of THF, distilled over sodium in the current of argon. The reaction mixture was stirred continuously for 20-24 hours in an argon atmosphere, cooled to room temperature, and slowly poured out with vigorous stirring and cooled with ice water to a flat bottom flask, in which 120 mL of a 10% solution of K_2CO_3 were pre-placed. The viscous mass of the resulting dark blue color is stirred for 15 minutes with 200 mL of benzene, then filtered in a Buchner well, and the precipitate was washed three times with 50 mL of benzene on the filter. The benzene layer was separated, washed with 100 mL of distilled water, twice with 100 mL of a 5% solution of HCl and 100 mL of saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4, the solvent is evaporated on a vacuum rotary evaporator to a constant mass, the residue was purified by column chromatography on silica gel, eluent hexane.

Yield 1.26 g (90%), mp. 124 °C (hexane). ^1H NMR spectrum, δ, ppm: 0.12 s (9H, CH_3), 1.2 – 1.26 m (3H, CH), 1.53 s (1H, CH), 1.6 – 1.95 m (23H, CH, CH_2), 2.65 s (1H, CH), 2.79 s (1H, CH), 2.90 s (2H, CH). ^{13}C NMR spectrum, δ, ppm: 2.9 (CH_3), 28.5 (CH), 29.0 (CH), 29.7 (CH_2), 31.9 (CH), 32.2 (CH), 36.5 (CH), 37.3 (CH_2), 38.7 (CH_2), 39.5 (CH), 39.6 (CH_2), 39.7 (CH_2), 40.2 (CH), 41.8

(CH), 46.1 (CH_2), 46.2 (CH_2), 70.6 (C-OTMS), 132.4 – 134.2 (C=C). Found % C 79.35, H 9.87, $C_{27}H_{40}OSi$. Calculated % C 79.32, H 9.91.

9-Trimethysiloxane-3-diamantanone (6): Mp. 78°C (hexane). ^{1}H NMR spectrum, δ, ppm: 0.09 s (9H, CH_3), 1.57 – 1.65 m (2H, CH), 1.68 – 1.9 m (10H, CH, CH_2), 2.04 s (1H, CH), 2.18 s (2H, CH), 2.3 m (2H, CH). ^{13}C NMR spectrum, δ, ppm: 3.07 (TMS), 35.4 (CH), 37.5 (CH), 38.8 (CH_2), 42.4 (CH), 43.4 (CH), 44.7 (CH_2), 45.2 (CH_2), 54.5 (CH), 69.6 (C-OTMS), 217.5 (C=O). Calculated for $C_{17}H_{26}O_2Si$: % C 70.29, H 9.02. Found % C 70.34, H 9.03.

9-Trimethylsiloxane - 3-(2-Adamantylidene) diamantine (7): Mp. 170°C (hexane). ^{1}H NMR spectrum, δ, ppm: 0.14 s (9H, CH_3), 1.64 – 1.7 m (6H, CH, CH_2), 1.71 – 1.8 m (9H, CH, CH_2), 1.8 – 1.9 m (9H, CH, CH_2), 1.891 – 2.0 m (3H, CH, CH_2), 2.65 s (1H, CH), 2.82 s (1H, CH), 2.92 s (2H, CH). ^{13}C NMR spectrum, δ, ppm: 2.94 (CH_3), 28.6 (CH), 29.1 (CH), 29.7 (CH), 31.9 (CH), 32.3 (CH), 36.6 (CH), 37.3 (CH_2), 38.7 (CH_2), 39.5 (CH), 39.6 (CH_2), 39.7 (CH_2), 40.3 (CH), 41.8 (CH), 46.1 (CH_2), 46.2 (CH_2), 70.5 (C-OTMS), 132.4 – 134.2 (C=C). Found % C 79.35, H 9.87. $C_{27}H_{40}OSi$. Calculated % C 79.37, H 9.83.

4. Conclusion

We show that the involvement of substituted diamondoidyl ketones into the McMurry cross coupling reaction allow the preparation of functionalized 3-(2-adamantylidene)diamantanes. Such substituted diamondoid dimers with sp^2 "defects" seem as building blocks for the preparation of respective thiols as surface modifiers with potential in diamond nanoelectronics.

Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/OC

ORCID 🆔
Ngo Trung Hoc : 0000-0001-6571-8345
Andrey A. Fokin: 0000-0002-6381-8948
Vladimir N. Rodionov: 0000-0002-8282-6126

Acknowledgements

References

[1]   Dahl, J. E. P. Moldowan, J. M. Peters, K. E. Claypool, G. E. Rooney, M. A. Michael, G. E. Mello, M. R. Kohnen, M. L. Diamondoid hydrocarbons as indicators of natural oil cracking. *Nature* **1999**, 399, 54 – 57. doi:10.1038/19953

[2]   Willey, T. M.; Fabbri, J. D.; Lee, J. R. I.; Schreiner, P. R.; Fokin, A. A.; Fokina, N. A; Dahl, J. E. P.; Carlson, R. M. K.; Vance, A. L.; Yang, W.; Terminello, L. J.; van Buuren, T.; Melosh, N. A. Near-edge X-ray absorption fine structure spectroscopy of diamondoid thiol monolayers on gold. *J. Am. Chem. Soc.* **2008**, *130*, 10536. DOI**:** 10.1021/ja711131e

[3]   Yang, W. L.; Fabbri J. D.; Willey, T. M.; Lee, J. R. I.; Dahl, J. E.; Carlson, R. M. K.; Schreiner, P. R.; Fokin, A. A.; Tkachenko, B. A.; Fokina, N. A.; Meevasana, W.; Mannella, N.; Tanaka, K.; Zhou, X. J.; van Buuren, T.; Kelly, M. A.; Hussain, Z.; Melosh, N. A.; Shen, Z.-X. Monochromatic electron photoemission from diamondoid monolayers. *Science* **2007**, *316*, 1460. DOI: 10.1126/science.1141811

[4]   Roth, S.; Leuenberger, D.; Osterwalder, J.; Tkachenko, B. A.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R.; Hengsberger, M. Negative-electron-affinity diamondoid monolayers as high-brilliance

source for ultrashort electron pulses. *Chem. Phys. Lett.* **2010**, 495, 102. https://doi.org/10.1016/j.cplett.2010.06.063

[5]   Thimmavajjula, K. Ge, C. Fabbri, J. Clay, W. Tkachenko, B. Fokin, A. Schreiner, P. Dahl, J.Carlson, R. Shen, Z.-X. Melosh, N. Ultra-low effective work function surfaces using diamondoid monolayers. *Nature Nanotech.* **2016**, *11*, 267–273. doi:10.1038/nnano.2015.277

[6]   Clay, W. A.; Maldonado, J. R.; Pianetta, P.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R.; Fokin, A. A.;Tkachenko, B. A.; Melosh, N.; Shen, Z.-X. Photocathode device using diamondoid and cesium bromide films *Appl. Phys. Lett*. **2012**, *101*, 241605. https://doi.org/10.1063/1.4769043

[7]   Fokin, A. A.; Tkachenko, B. A.; Gunchenko, P. A.; Gusev, D. V.; Schreiner. P. R. Functionalized Nanodiamonds Part I. An experimental assessment of diamantane and computational predictions for higher diamondoids *Chem. Eur. J.* **2005**, 11, 7091. https://doi.org/10.1002/chem.200500031

[8]   Fokin, A. A.; Zhuk, T. S.; Pashenko, A. E.; Dral, P. O.; Gunchenko, P. A.; Dahl, J. E. P.; Carlson, R. M. K.; Koso, T. V.; Serafin, M.; Schreiner, P. R.Oxygen-doped nanodiamonds: Synthesis and functionalizations. *Org. Lett*. **2009**, 11, 3068. DOI: 10.1021/ol901089h

[9]   Zhuk, T.S.; Koso, T.; Pashenko, A.E.; Trung Hoc, N.; Rodionov, V.N.; Serafin, M.; Schreiner, P.R.; Fokin, A.A. Toward an Understanding of Diamond sp^2-Defects with Unsaturated Diamondoid Oligomer Models. *J. Am. Chem. Soc*. **2015**, *137*, 6577–6586, doi**:**10.1021/jacs.5b01555.

 [10]   Fokin, A. A.; Zhuk, T. S.; Pashenko, A. E., et. al. Functionalization of Homodiamantane: Oxygen insertion reactions without rearrangement with dimethyldioxirane *J. Org. Chem.* **2014**, 79, 1861. DOI**:** 10.1021/jo4026594

[11]   Fokin, A.A.; Yurchenko, R.I.; Tkachenko, B.A.; Fokina, N. A.; Gunawan, M. A.; Poinsot, D.; Dahl, J. E. P.; Carlson, R. M. K.;Serafin, M.; Cattey, H.; Hierso, J.-C.; Schreiner, P. R. Selective preparation of diamondoid phosphonates. *J. Org. Chem.***2014**, *79*, 5369–5373.

[12]   Banerjee, S.; Saalfrank, P. Vibrationally resolved absorption, emission and resonance Raman spectra of diamondoids: a study based on time-dependent correlation functions. *Phys. Chem. Chem. Phys*. **2014**, 16, 144−158. DOI: 10.1039/C3CP53535E

[13]   Fokin, A. A.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R. Stable alkanes containing very long carbon–carbon bonds *J. Am. Chem. Soc*. **2012**, 134, 13641−13650. DOI:10.1021/ja302258q

[14]   McMurry, J. E.; Felming, M .P. New method for the reductive coupling of carbonyls to olefins. Synthesis of. beta.-carotene. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709, doi**:**10.1021/ja00821a076.

[15]   M M Krayushkin, M A Kalik, V A Migin. McMurry reaction in the synthesis of photochromic dihetarylethenes.*Russ.Chem.Rev*.**2009**,78 329. https://doi.org/10.1070/RC2009v078n04ABEH004018

[16]   Tanpure, R.P., Harkrider, A.R., Strecker, T.E., Hamel, E., Trawick, M.L., and Pinney, K.G. Application of the McMurry Coupling Reaction in the Synthesis of Tri- and Tetra-arylethylene Analogues as Potential Cancer Chemotherapeutic Agents. *Bioorg. Med. Chem.* **2009**, 17, 6993-7001. DOI :10.1016/j.bmc.2009.08.011

[17]   Ngo Trung Hoc; Fokin, A.A.; Rodionov, V.N Synthesis of 10-methoxydiamantan-3-one.   *Molbank*. **2018**. 2018, M990; doi:10.3390/M990

[18]   T. Morita, S. Yoshida, Y. Okamoto, H. Sakurai,Chlorotrimethysilane/Sodium iodide : A new reagent for conversion of ancohols into iodides *Synthesis*, **1979**, 379. DOI: 10.1055/s-1979-28689

[19]   Hoc, N.T.; Kusko, A.O.; Fokin, A.A.; Rodionov, V.N. Functional derivatives of diamantanone. *Russ. J. Org. Chem.* **2016**, *52*, 1209–1211, doi:10.1134/S1070428016080212.