molbank

MDPI

Communication

Synthesis of 10-Methoxydiamantan-3-One

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

[1] Kiev Polytechnical Institute, National Technical University of Ukraine, pr. Pobedy 37, 03056 Kiev, Ukraine; aaf@xtf.kpi.ua (A.A.F.); vnr@xtf.kpi.ua (V.N.R.)
[2] The Viet Nam University of Firefighting and Prevention, 243 Khuat duy tien, Hanoi 10000, Vietnam
* Correspondence: trunghocngo@yahoo.com; Tel.: +84-934567183

Received: 21 March 2018; Accepted: 4 April 2018; Published: 9 April 2018

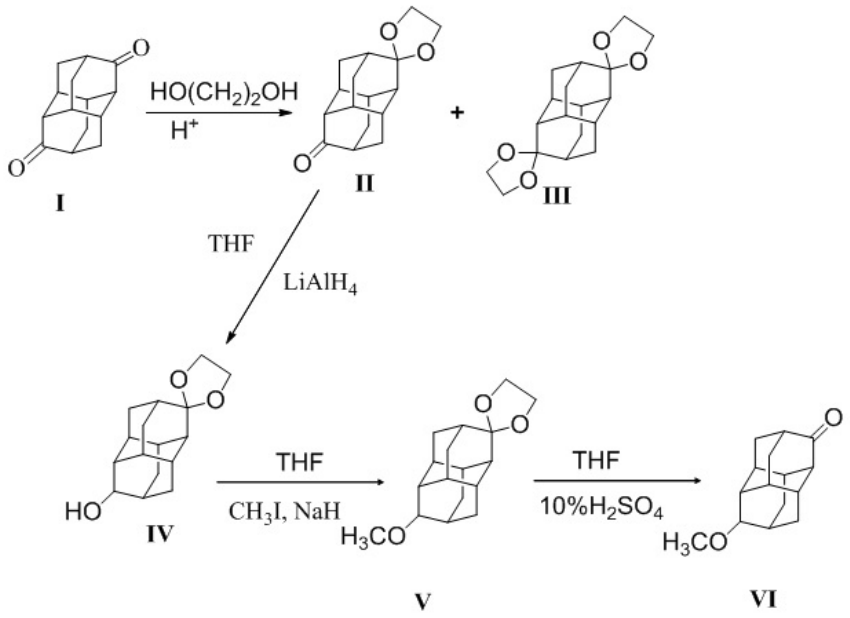
Abstract: The synthesis of diamondoids particles up to 1–5 nm, in order to detect the nanostructure in the construction of nanoelectronic devices, for which the present of quantum limitation effects are theoretically presaged, is at the present time problematic. Diamondoids have many important physical characteristics, including rigidity, lipophilicity, low strain energy, etc. Diamantane and their derivatives are also interesting for the study of nanoparticles. The present study deals with the development of the new synthetic route and diamantine-containing precursor for McMurry coupling reactions.

Keywords: McMurry coupling reaction; diamondoids; nanoelectronics; diamantane

1. Introduction

Nanotechnology is currently developing new materials such as carbon-based structures (darbon nanotubes, carbon nanofibers, fullerenes, graphene, and nanodiamonds). Thanks to its wide range of electronic properties with high chemical stability, diamond maybe the most interesting material in nanoelectronics, optics, and other material sciences fields. In fact, the diamondoid only exists as hexamantanes and pentamantanes (particle size of 0.6–0.75 nm) for the rod-shaped isomer in limited quantities from oil. Therefore, diamondoids with the desired size larger than 1 nm, in order to explore applications in nanoelectronics [1–4], for which the present of quantum limitation effects are theoretically presaged, remains problematic at the present time. This can be solved by a coupling reaction using lower diamondoids with various spacers. That was successfully done by fullerene, where the particles are about 10 nm.

The diamondoids assemblies will affect the electronic and optical properties by various spacers. One promising way to combine unsaturation with structure is coupling reactions to give the corresponding diamondoid dimer. The functionalization of diamondoid dimers is considered as the key to their flexible application [5–7]. The present study deals with the development of the new synthetic route to produce the diamantane-containing precursor for McMurry coupling reaction [8] (Scheme 1).



Scheme 1. Synthesis of 10-methoxydiamantan-3-one.

2. Results and Discussion

Diamantane-3,10-dione (**I**) was used as a starting material [9]. After carbonyl group protection, ketoketal (**II**) was prepared and instead of hydroxyketal (**III**), in presence of $LiAlH_4$ in THF, gave ethylene ketal (**IV**). The reaction of ethylene ketal (**IV**) with methyl iodide in the presence of NaH furnished ethylene ketal of 10- methoxydiamantan-3-one (**V**), whose hydrolysis with a mixture of 10% sulfuric acid and THF, 10:1, led to the formation of 10-methoxydiamantan-3-one (**VI**) in a virtually quantitative yield. Methoxyketone (**VI**) may be utilized for the synthesis of diamond-like materials suitable for modification of surface of metals and semiconductors.

Synthesis of 10-methoxydiamantan-3-one from diamantanedione-3,10, to prepare reactor McMurry coupling of these ketones, was studied. The functionalization of diamondoid dimers was performed in order to create new building blocks for potential nanoelectronic devices.

3. Materials and Methods

3.1. General Information

All chemicals were purchased from Aldrich, Acros and used without further purification. All solvents employed were purified and dried prior to use. Spectra ^{1}H and ^{13}C-NMR were registered on a Bruker DPX-400 spectrometer (operating frequencies: ^{1}H, 400.13. MHz; ^{13}C, 100.61 MHz, Bruker BioSpin GmbH, Karlsruhe, Germany) respectively, solvent $CDCl_3$. Melting points are uncorrected, and were taken with a Gallenkamp melting point apparatus (Sanyo GallenkampPLC, Loughborough, UK). The separations and purifications were performed Silica gel 60 (0.063–0.200 mm) for column chromatography (70–230 mesh ASTM), Merck, Darmstadt, Germany. The reported results are based on the integration of ^{1}H and ^{13}C-NMR spectra GLC analysis were performed on a capillary chromatograph Shimadzu GC-14B (Shimadzu, Tokyo, Japan) equipped with a flame-ionization detector, column Optima-1, vaporizer temperature 275 °C, ramp 80–250 °C, heating rate 20 °C/min. The results of elemental analysis were performed on the VARIO EL III Elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) for C, H, and N.

3.2. 10-Ethylene Ketal Diamantan-3-One (**II**)

The mixture of 10 g (0.046 mol) of diketone (**I**), 8.7 g (0.14 mol) of ethylene glycol, and 0.5 g of *p*-toluenesulfonic acid monohydrate in 250 mL of anhydrous benzene was refluxed with a Dean–Stark trap for 2 h. The benzene solution was washed in succession with water, 10% water solution of sodium carbonate, and with brine, dried with Na_2SO_4, the solvent was distilled off in a vacuum. The pure ketoketal (II) can be isolated by column chromatography of hexane/7% ethyl acetate.

Yield 7.7 g (64.4%), m.p. 69 °C (hexane). ^{1}H-NMR spectrum, δ, ppm: 1.58–1.66 m (2H, CH), 1.81 s (1H, CH), 1.85 s (1H, CH), 1.92–12.03 m (6H, CH, CH_2), 2.05–2.12 (2H, CH), 2.15 s (2H, CH_2), 2.38 s (1H, CH), 2.45 s (1H, CH) 3.95 s (4H, CH_2). ^{13}C-NMR spectrum, δ, ppm: 33.1 (CH_2), 33.6 (CH), 33.8 (CH), 37.4 (CH_2), 38.1 (CH), 43.9 (CH), 44.3 (CH), 54.8 (CH), 64.3 (CH_2), 111.7 (C), 216.9 (C=O). Found % C 73.82, H 7.74, $C_{16}H_{20}O_3$. Calculated % C 73.80, H 7.75.

3.3. 3,10 Diethylene Ketal Diamantan (**III**)

m.p. 165 °C (hexane). ^{1}H-NMR spectrum, δ, ppm: 1.45–1.55 m (6H, CH, CH_2), 1.65 s (2H, CH), 1.86 s (4H, CH_2), 1.92 s (2H, CH), 1.94 s (2H, CH) 3.85 s (8H, CH_2). ^{13}C-NMR spectrum, δ, ppm: 33.5 (CH), 33.8 (CH_2), 34.1 (CH), 44.4 (CH), 54.8 (CH), 64.0 (CH_2), 111.3 (C). Found % C 71.03, H 7.95 $C_{18}H_{24}O_4$. Calculated % C 71.04, H 7.96.

3.4. Ethylene Ketal of 10-Hydroxydiamantan-3-One (**IV**)

$LiAlH_4$ (1.6 g (42 mmol)) in 70 mL of dry diethyl ether is charged into a three-necked 1 L reactor equipped with a magnetic stirrer, reflux condenser, and dropping funnel, and a solution of 5 g (0.019 mol) of ketoketal (**II**) in 100 mL of dry diethyl ether. The reaction mixture is refluxed for 2–3 h, after which, with stirring and cooling, 50 mL of saturated ammonium chloride solution is decomposed with ice water. The organic layer was separated and the aqueous layer was extracted three times with 50 mL of diethyl ether. The combined ether extracts are washed 3 times with 50 mL of brine and dried over anhydrous sodium sulfate. After evaporation of the solvent on a vacuum rotary evaporator of a colorless viscous oil crystallizing on standing are obtained.

Yield 4.5 g (90%), m.p. 154 °C (hexane). ^{1}H-NMR spectrum, δ, ppm: 1.45–1.53 m (1H, CH), 1.57–1.77 m (8H, CH, CH_2), 1.8–1.96 m (5H, CH, CH_2), 1.97–2.1 m (3H, CH), 3.77 s (1H, OH), 3.93 s (4H, CH_2). ^{13}C-NMR spectrum, δ, ppm: 30.1 (CH), 31.2 (CH_2), 32.3 (CH), 33.8 CH), 34.3 (CH_2), 34.5 (CH_2), 34.6 (CH), 35.5 (CH_2), 36.0 (CH), 36.1 (CH), 41.3 (CH), 44.6 (CH), 64.1 (CH_2), 74.5 (COH), 111.2 (C). Found % C 73.25, H 8.45 $C_{16}H_{22}O_3$. Calculated % C 73.26, H 8.44.

3.5. Ethylene Ketal of 10-Methoxydiamantan-3-One (**V**)

The mixture of 4 g (0.015 mol) of ethylene ketal (**IV**) and 1.1 g (0.045 mol) of NaH in 80 mL of anhydrous THF was added dropwise at stirring a solution of 4.2 g (0.029 mol) of methyl iodide in 20 mL of THF. The reaction mixture was refluxed for 4 h, cooled, poured on ice, the reaction product was extracted with dichloromethane. The organic layer was washed with water and brine, dried with Na_2SO_4, the solvent was distilled off in a vacuum.

Yield 3.8 g (91%), m.p. 96–97 °C (hexane). ^{1}H-NMR spectrum, δ, ppm: 1.58–1.62 m (7H, CH, CH_2), 1.7 s (3H, CH), 1.75–1.85 m (2H, CH), 1.88 s (1H, CH), 1.93–2.0 s (2H, CH), 2.2 s (2H, CH), 3.2 s (3H, CH_3), 3.93 s (4H, CH_2). ^{13}C-NMR spectrum, δ, ppm: 33.7 (CH), 33.9 (CH_2), 35.4 (CH), 37.1 (CH), 38.8 (CH), 40.2 (CH_2), 40.6 (CH_2), 44.5 (CH), 48.1 (CH), 64.1 (CH_2), 71.1 (OCH_3), 111.5 (C). Found % C 73.88, H 8.75. $C_{17}H_{24}O_3$. Calculated % C 73.89, H 8.77.

3.6. 10-Methoxydiamantan-3-One (**VI**)

To a solution of 3 g (0.01 mol) of ketal (**V**) in 10 mL of THF was added 100 mL of 10% solution of sulfuric acid, the obtained mixture was maintained at stirring without heating for 5 h. Excess sulfuric

acid was neutralized with solid sodium hydroxide till pH 7–8, the reaction product was extracted with CH_2C_{l2}, and was dried with Na_2SO_4, the solvent was removed in a vacuum.

Yield 2.17 g (94%), m.p. 95–96 °C (hexane). ^{1}H-NMR spectrum, δ, ppm: 1.66–1.72 m (2H, CH_2), 1.79–1.88 m (6H, CH, CH_2), 1.93–2.03 m (4H, CH_2), 2.14 s (1H, CH), 2.28 s (2H, CH), 2.36 s (1H, CH), 2.42 s (1H, CH), 3.93 s (3H, CH_3). ^{13}C-NMR spectrum, δ, ppm: 35.7 (CH), 37.5 (CH_2), 38.4 (CH), 39.8 CH_2), 40.4 (CH_2), 41.9 (CH), 43.4 (CH), 48.3 (CH), 54.6 (CH), 70.3 (OCH_3), 217.2 (C=O). Found % C 77.55, H 8.68 $C_{15}H_{20}O_2$. Calculated % C 77.57, H 8.67.

4. Conclusions

In summary, we propose a simple procedure for the synthesis of 10-methoxydiamantan-3-one (**VI**) may be utilized for the synthesis of diamond-like materials suitable for modification of surface of metals and semiconductors.

Supplementary Materials: The following are available online, Scheme 1. Synthesis of 10-methoxydiamantan-3-one, Spectra ^{1}H and ^{13}C-NMR for compounds **II**, **III**, **IV**, **V** and **VI** are available in the supplementary information.

Acknowledgments: The authors thank Justus Liebig University of Giessen (Giessen, Germany) for ^{1}H and ^{13}C-NMR spectra.

Author Contributions: V. N. Rodionov and Ngo Trung Hoc conceived and designed the experiments; A. A. Fokin performed and interpreted the NMR experiments and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. 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. [CrossRef] [PubMed]
2. Randel, J.C.; Niestemski, F.C.; Botello-Mendez, A.R.; Mar, W.; Ndabashimiye, G.; Melinte, S.; Dahl, J.E.P.; Carlson, R.M.K.; Butova, E.D.; Fokin, A.A.; et al. Unconventional molecule-resolved current rectification in diamondoid–fullerene hybrids. *Nat. Commun.* **2014**, *5*, 4877. [CrossRef] [PubMed]
3. Shiwata, H.; Acremann, Y.; Scholl, A.; Rotenberg, E.; Hellwig, O.; Dobisz, E.; Doran, A.; Tkachenko, B.A.; Fokin, A.A.; Schreiner, P.R.; et al. Diamondoid coating enables disruptive approach for chemical and magnetic imaging with 10 nm spatial resolution. *Appl. Phys. Lett.* **2012**, *101*, 163101. [CrossRef]
4. 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.A.; Shen, Z.X. Photocathode device using diamondoid and cesium bromide films. *Appl. Phys. Lett.* **2012**, *101*, 241605. [CrossRef]
5. Roth, S.; Leuenberger, D.; Osterwalder, J.; Dahl, J.E.P.; Carlson, R.M.K.; Tkachenko, B.A.; 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*, 102–108. [CrossRef]
6. 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*, 3068–3071. [CrossRef] [PubMed]
7. Yang, W.L.; Fabbri, J.D.; Willey, T.M.; Lee, J.R.I.; Dahl, J.E.P.; Carlson, R.M.K.; Schreiner, P.R.; Fokin, A.A.; Tkachenko, B.A.; Fokina, N.A.; et al. Monochromatic electron photoemission from diamondoid monolayers. *Science* **2007**, *316*, 1460–1462. [CrossRef] [PubMed]
8. 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. [CrossRef]
9. Hoc, N.T.; Kusko, A.O.; Fokin, A.A.; Rodionov, V.N. Functional derivatives of diamantanone. *Russ. J. Org. Chem.* **2016**, *52*, 1209–1211. [CrossRef]