

Towards the Rational Synthesis of Norfullerenes. Controlled Deletion of One Carbon Atom from C₆₀ and Preparation of 2,5,9-Trioxo-1-nor(C₆₀-I_h)-[5,6]fullerene C₅₉(O)₃ Derivatives

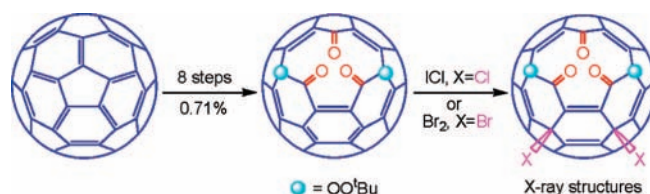
Jiayao Yao,[†] Zuo Xiao,[†] Liangbing Gan,^{*,†,‡} Dazhi Yang,[†] and Zheming Wang^{*,†}

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

gan@pku.edu.cn; zmw@pku.edu.cn

Received March 17, 2008

ABSTRACT



Norfullerenes are fullerene-like compounds (fulleroids) resulting from partial deletion of fullerene skeleton carbons. The one carbon less norfullerene C₅₉(O)₃ derivatives having three carbonyl groups on the rim of the orifice are prepared through peroxide-mediated reactions. A key step involves a novel PCI₅ initiated rearrangement of a hydroxyl amine adduct. Decarboxylation serves as the carbon removal step.

Modification of the fullerene skeleton has attracted much attention. Various fullerene-like compounds (fulleroids) have been studied both theoretically and experimentally.¹ There are four major types of fulleroids: heterofullerene, seco-

fullerene, homofullerene, and norfullerene (Scheme 1).² The azafullerenes C₅₉N(R) and C₆₉N(R) remain the only heterofullerenes available in synthetic scale.^{1c,e,3} Well-established examples have been reported for homofullerene,^{1,4} azahomofullerene,⁵ oxahomofullerene,⁶ and cobaltahomofullerene.⁷

[†] College of Chemistry and Molecular Engineering, Peking University.

[‡] Shanghai Institute of Organic Chemistry.

(1) (a) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317. (b) Rubin, Y. *Top. Curr. Chem.* **1999**, *199*, 67. (c) Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 93. (d) Chen, Z.; King, R. B. *Chem. Rev.* **2005**, *105*, 3613. (e) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191. (f) Komatsu, K. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2285.

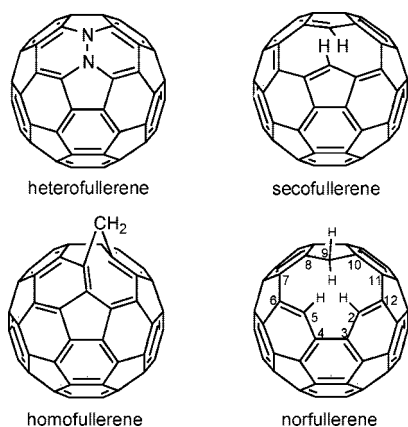
(2) For classification and IUPAC nomenclature, see: Well, W. H.; Cozzi, F.; Moss, G. P.; Thilgen, C.; Hwu, R. J.-R.; Yerin, A. *Pure Appl. Chem.* **2002**, *74*, 629.

(3) (a) Averdung, J.; Luftmann, H.; Schlachter, I.; Mattay, J. *Tetrahedron* **1995**, *51*, 6977. (b) Lamparth, I.; Nuber, B.; Schick, G.; Skieba, A.; Grosser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257. (c) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554.

(4) (a) Suzuki, T.; Li, Q. C.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301. (b) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231. (c) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492. (d) Kiely, A. F.; Haddon, R. C.; Meier, M. S.; Selegue, J. P.; Brock, C. P.; Patrick, B. O.; Wang, G. W.; Chen, Y. S. *J. Am. Chem. Soc.* **1999**, *121*, 7971.

(5) (a) Prato, M.; Li, Q. C.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148. (b) Lamparth, I.; Nuber, B.; Schick, G.; Skieba, A.; Grosser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257. (c) Kanakamma, P. P.; Huang, S.-L.; Juo, C.-G.; Her, G.-R.; Luh, T.-Y. *Chem.—Eur. J.* **1998**, *4*, 2037. (d) Casas, M.; Duran, M.; Mestres, J.; Martin, N.; Sola, M. *J. Org. Chem.* **2001**, *66*, 433. (e) Ulmer, L.; Mattay, J. *Eur. J. Org. Chem.* **2003**, 2933.

Scheme 1. Structures of Representative Fulleroids



Remarkable progress has been made in secofullerene (cage-opened fullerene).^{1b,f} A number of compounds have been reported with different orifice sizes.⁸

Norfullerene results from partial deletion of fullerene carbon atoms. Bonds attached to the atom removed are not reconnected according to the IUPAC definition of norfullerene.² Thus, norfullerenes are cage-opened compounds different from those cage-closed nonclassical fullerenes (called smaller fullerenes) such as C₂₀H₁₀,⁹ C₃₆H_x,¹⁰ C₅₀Cl₁₀,¹¹ and C₅₈F₁₈.¹² Various fullerene fragments resulting from skeleton carbon atom deletion have been observed via the mass spectra.^{13–18} Electron-impact dissociation/ionization of C₆₀ generated various C_n⁺ (*n* = 50, 52, 54, 56, and 58).¹³ Signals corresponding to odd-numbered fullerene fragments C_n[–] (*n* = 53, 55, 57, 59) were observed in the mass spectrum of C₆₀(O).¹⁴ Fragmented fullerenes C_{54–59}H_x have been observed on the mass spectra of hydrogenated fullerene derivatives.¹⁵ Electrochemical reduction of C₆₀ led to disruption of the cage and formation of C₅₀H₁₀O, as detected by

(6) (a) Weisman, R. B.; Heymann, D.; Bachilo, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 9720. (b) Boltalina, O. V.; Vaissière, B. de L.; Fowler, P. W.; Lukonin, A. Y.; Abdul-Sada, A. K.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2212. (c) Huang, S. H.; Xiao, Z.; Wang, F. D.; Zhou, J.; Yuan, G.; Zhang, S. W.; Chen, Z. F.; Thiel, W.; Schleyer, P. von R.; Zhang, X.; Hu, X. Q.; Chen, B. C.; Gan, L. B. *Chem.–Eur. J.* **2005**, *11*, 5449.

(7) Arce, M. J.; Viado, A. L.; An, Y. Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775.

(8) (a) Rubin, Y. *Chem.–Eur. J.* **1997**, *3*, 1009. (b) Rubin, Y.; Jarrosson, T.; Wang, G. W.; Bartberger, M. D.; Houk, K. N.; Schick, G.; Saunders, M.; Cross, R. *J. Angew. Chem., Int. Ed.* **2001**, *40*, 1543. (c) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238. (d) Iwamatsu, S.-I.; Murata, S. *Synlett* **2005**, *14*, 2117. (e) Chuang, S. C.; Murata, Y.; Murata, M.; Komatsu, K. *J. Org. Chem.* **2007**, *72*, 6447. (f) Roubelakis, M. M.; Vougioukalakis, G. C.; Orfanopoulos, M. *J. Org. Chem.* **2007**, *72*, 6526. (g) Roubelakis, M. M.; Murata, Y.; Komatsu, K.; Orfanopoulos, M. *J. Org. Chem.* **2007**, *72*, 7042. (h) Xiao, Z.; Yao, J. Y.; Yang, D. Z.; Wang, F. D.; Huang, S. H.; Gan, L. B.; Jia, Z. S.; Jiang, Z. P.; Yang, X. B.; Zheng, B.; Yuan, G.; Zhang, S. W.; Wang, Z. M. *J. Am. Chem. Soc.* **2007**, *129*, 16149.

(9) Prinzbach, H.; Weller, A.; Landenberger, P.; Wahl, F.; Worth, J.; Scott, L. T.; Gelmont, M.; Olevano, D.; Issendorff, B. *Nature* **2000**, *407*, 60.

(10) Piskoti, C.; Yarger, J.; Zettl, A. *Nature* **1998**, *393*, 771.

(11) Xie, S. Y.; Gao, F.; Lu, X.; Huang, R.-B.; Wang, C.-R.; Zhang, X.; Liu, M.-L.; Deng, S.-L.; Zheng, L. S. *Science* **2004**, *304*, 699.

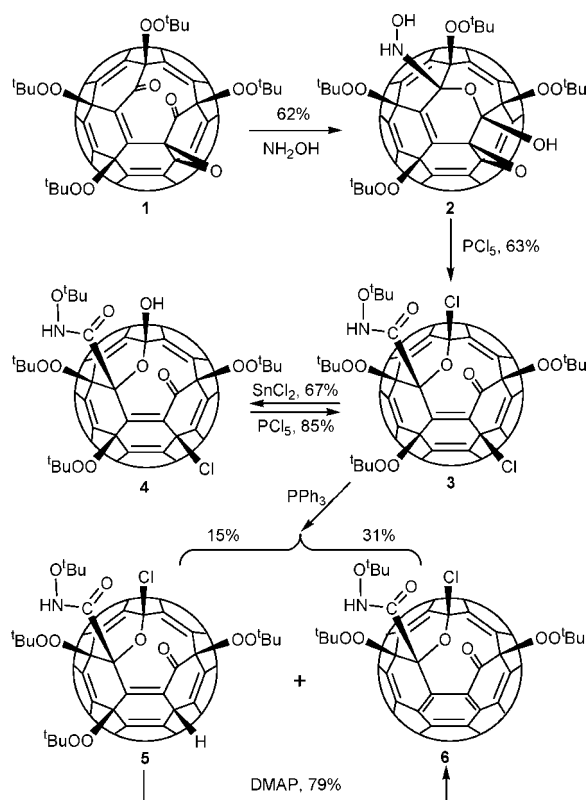
(12) Troshin, P. A.; Avent, A. G.; Darwish, A. D.; Martsinovich, N.; Abdul-Sada, A. K.; Street, J. M.; Taylor, R. *Science* **2005**, *309*, 278.

mass spectra.¹⁶ MALDI-TOF spectra of fullerene-mixed peroxides C₆₀(O)(OO*t*Bu)₄ showed signals due to C₅₈(O)_{1–3} and C₅₉(O)_{2–4}.¹⁷ But little is known about the structural information of these novel compounds. Theoretical calculations have been carried out for some norfullerenes.^{1e,18}

We have prepared a number of fullerene-mixed peroxides.^{6c,8h,17,19} In an effort to make skeleton-modified fullerene derivatives, we explored the chemistry of compound **1** as part of our continuous work on fullerene peroxide chemistry. Due to the unique spherical structure of fullerenes, fullerene peroxides exhibit different reaction patterns from those of classical organic peroxides. We have recently reported several open-cage C₅₉ derivatives,^{8h} which may be classified as seco-norfullerenes. Here we report the removal of one carbon atom from C₆₀ through peroxide-mediated stepwise reactions.

The cage-opened fullerene derivative **1** was prepared in 14% yield from C₆₀, as previously reported.^{8h} To test the reactivity of the fullerene carbonyl groups, we treated compound **1** with hydroxylamine (Scheme 2). Instead of the

Scheme 2. Reactions of Fullerenes



expected oxime derivative, the oxahomofullerene derivative **2** with a hydroxylaminoketal moiety was obtained. The addition pattern is analogous to the reaction between aromatic amines and fullerene peroxides similar to **1**.^{8h} Inspired by the PCl₅ promoted rearrangement of hydroxylamine derivatives (Stieglitz rearrangement),²⁰ we then treated **2** with PCl₅ and obtained compound **3**. The structure of **3** has one

fullerene carbon moved out of the cage skeleton and a *t*-butoxyl group migrated onto the nitrogen. To assign the structure of **3**, various methods were tested to grow suitable crystals for X-ray diffraction analysis, but all failed. After the chlorine atom on the oxygen-bound carbon was converted to the hydroxyl group in compound **4**, a single crystal was obtained from the slow evaporation of compound **4** in a mixture of CS₂/EtOH. The mild Lewis acid SnCl₂ gave the best yield for the conversion of **3** to **4**. Other acids, such as FeCl₃, FeBr₃, CF₃COOH, and H₂SO₄, could also induce the hydroxylation, but with lower yields. Treatment of **4** with PCl₅ gave back the dichloroderivative **3** in good yield (85%). Reduction of **3** with PPh₃ led to the replacement of one Cl into H and the formation of product **5**. The major product was compound **6**, with one OO*t*Bu group and one Cl atom removed, both of which are on the same hexagon. Compound **5** could be converted to **6** by a base such as *N,N*-dimethylaminopyridine (DMAP).

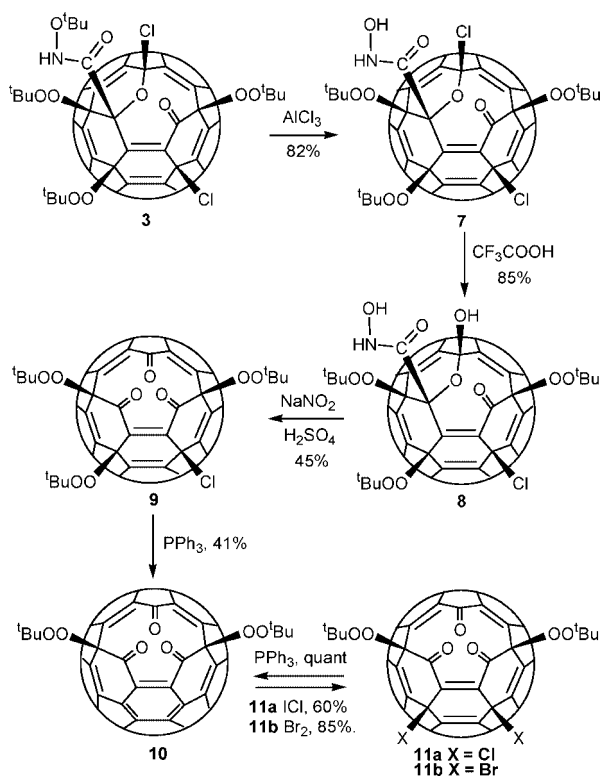
To remove the amide group from the cage and make a norfullerene, we then tried a sequential hydrolysis and decarboxylation process (Scheme 3). Mineral acids gave a

nated the chlorine atom and one OO*t*Bu group to form the C_s symmetric compound **10**. Both ICl and Br₂ add readily to the newly formed benzene ring in compound **10** to form **11a** and **11b**, respectively.

Unambiguous structure assignment of **4** by spectroscopic data and single crystal X-ray diffraction analysis played a key role for the structure elucidation of compounds **3**, **5**, **6**, and **7**. The spectroscopic data of **4** revealed all the functional groups present in the molecule. The crystal structure confirmed the presence of these groups and most importantly showed their relative locations on the cage. Compounds **4**, **5**, and **7** were all derived from **3**. Their NMR spectra in particular the ¹³C NMR spectra showed the same pattern, indicating analogous structures for these four compounds. The conversion of **4** back to **3** (Scheme 2) further confirmed the structure assignment for **3**. Single crystal structures of **11a** and **11b** also provided convincing evidence for the structure assignments of their precursors **9** and **10**. NMR spectra confirmed the C_s symmetry of compounds **10** and **11**.

X-ray structures of compounds **4**, **11a**, and **11b** are shown in Figure 1. The *N*-butoxyl amide is clearly shown in the structure of compound **4**. The amino hydrogen atom forms hydrogen bond with one of the adjacent peroxy oxygen atoms. The pyran ring is almost planar, but the six-membered ring containing the carbonyl group takes a twisted chair conformation with the carbonyl group pointing out of the cage surface.

Scheme 3. Formation of Norfullerenes



complex mixture of products. Aluminum chloride removed the *t*-butyl group selectively to form the hydroxylamine amide **7**. Similar to compound **3**, the chlorine atom on the oxygen-bound carbon of **7** could be converted into the hydroxyl analog **8**. Oxidation of **8** with nitrous acid removed the amide group successfully to give the norfullerene derivative **9**. Reduction of **9** with triphenylphosphine elimi-

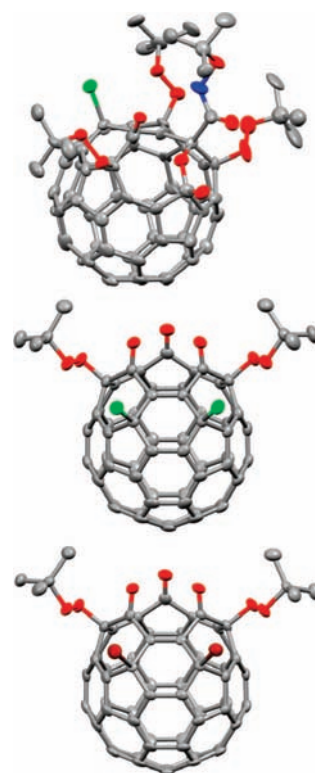
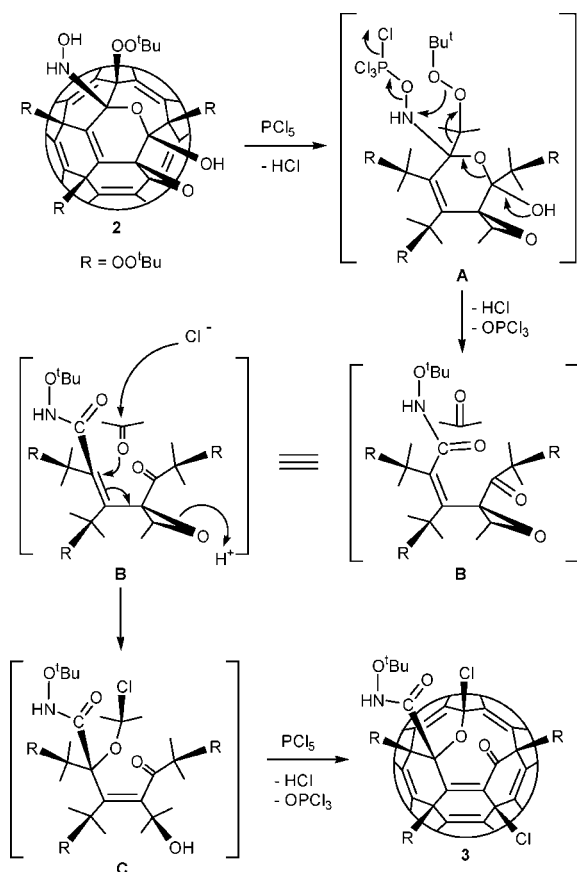


Figure 1. X-ray structure of **4** (top), **11a** (middle), and **11b** (bottom). For clarity, hydrogen atoms were not drawn. Ellipsoids were at 50%. Color scheme: grey = C, blue = N, red = O, green = Cl, wine-red = Br.

The conversion of **2** to **3**, promoted by PCl_5 , is unprecedented. A possible pathway is proposed in Scheme 4. The

Scheme 4. Possible Mechanism for the Reaction of **2** with PCl_5



first step is the interaction of PCl_5 with the hydroxyl group of the hydroxyamino carbonyl moiety to form intermediate **A**. Cleavage of the N–O bond in **A** initiates a multi bond cleavage process leading to intermediate **B**. A concerted process is drawn in Scheme 4 for this step, but the present data cannot rule out a stepwise process involving nitrogen,

oxygen, and carbon cations. A five-membered ring transition state probably facilitates the rearrangement of the *t*-butoxyl group onto the nitrogen atom. Addition of chloride to intermediate **B** in the third step is analogous to a $\text{S}_{\text{N}}2''$ process. Unlike the classical 1,4-addition of unsaturated ketone compounds, steric strain results in the carbonyl oxygen attacking the α -position of the unsaturated amide moiety. Conjugation between the amide and the double bond in the center is limited due to severe steric hindrance. Replacement of the hydroxyl group by chlorine in the final step should follow a $\text{S}_{\text{N}}1$ mechanism. The carbocation formed in this step may be stabilized by double bonds around it.

In summary, the first C_{59} norfullerene derivative is prepared through deletion of one carbon atom from the C_{60} cage. Stability of the norfullerene derivatives prepared here are comparable with those fullerene adducts with an intact cage. Work is in progress to prepare other norfullerenes.

Acknowledgment. Financial support is provided by NNSFC (Grants 20632010, 20521202, and 20472003), and MOST (2006CB806201).

Supporting Information Available: Selected spectra for new compounds and crystallographic data in CIF format for compounds **4**, **11a**, and **11b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL800611R

(13) Löffler, D.; Jester, S. S.; Weis, P.; Böttcher, A.; Kappes, M. M. *J. Chem. Phys.* **2006**, *124*, 054705.

(14) Deng, J. P.; Ju, D. D.; Her, G. R.; Mou, C. Y.; Chen, C. J.; Lin, Y. Y.; Han, C. C. *J. Phys. Chem.* **1993**, *97*, 11575.

(15) Talyzin, A. V.; Tsybin, Y. O.; Purcell, J. M.; Schaub, T. M.; Shulga, Y. M.; Noreus, D.; Sato, T.; Dzwilewski, A.; Sundqvist, B.; Marshall, A. G. *J. Phys. Chem. A* **2006**, *110*, 8528.

(16) Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* **1991**, *314*, 363.

(17) Gan, L. B.; Huang, S. H.; Zhang, X. A.; Zhang, A. X.; Cheng, B. C.; Cheng, H.; Li, X. L.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384.

(18) Cyranski, M. K.; Howard, S. T.; Chodkiewicz, M. L. *Chem. Commun.* **2004**, 2458.

(19) (a) Gan, L. B. *Pure Appl. Chem.* **2006**, *78*, 841. (b) Gan, L. B. *C. R. Chim.* **2006**, *9*, 1001.

(20) Hoffman, R. V.; Poelker, D. J. *J. Org. Chem.* **1979**, *44*, 2364.