Pergamon

TETRAHEDRON
LETTERS

Tetrahedron Letters 42 (2001) 895–897

Photooxygenative partial ring cleavage of bis(fulleroid): synthesis of a novel fullerene derivative with a 12-membered ring

Hirofumi Inoue,[a] Hiroshi Yamaguchi,[a] Sho-ichi Iwamatsu,[b] Takeshi Uozaki,[a] Toshiyasu Suzuki,[c] Takeshi Akasaka,[d] Shigeru Nagase[e] and Shizuaki Murata[a,b,*]

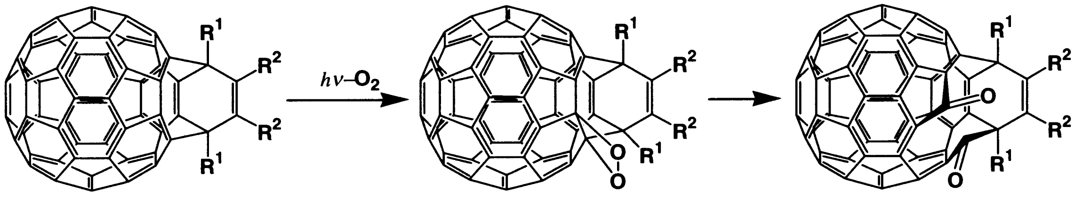
[a]*Graduate School of Human Informatics, Nagoya University, Nagoya 464-8601, Japan*
[b]*CREST, JST (Japan Science and Technology), Japan*
[c]*Institute for Molecular Sciences, Okazaki 444-8585, Japan*
[d]*Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan*
[e]*Department of Chemistry, Tokyo Metropolitan University, Hachiouji 192-0397, Japan*

Received 3 August 2000; revised 30 October 2000; accepted 17 November 2000

Abstract—Photooxidation of tetrasubstituted bis(fulleroid) derivatives gives novel diketone derivatives with 12-membered rings on the surface of fullerene in high yields. © 2001 Elsevier Science Ltd. All rights reserved.

It has been investigated for a long time to insert atoms or small molecules inside the carbon cages of fullerenes in the development of new materials with useful physical properties. For example, endohedral complexes of fullerenes (such as $La_2@C_{80}$, $Sc@C_{82}$ and $Y@C_{82}$) have been synthesized using high temperature arc-discharge methods or high pressure reactions.[1,2] Consequently, it is impossible to employ these known methods for preparation of well designed endohedral fullerenes with fine organic molecules. A stepwise (tailor-made) method consisting of usual organic operations, such as bond cleavage and formation, is the most general and efficient means for preparation of the endohedral fullerene derivative. For the first step of this approach, selective C=C bond cleavage on the surface of fullerene is an important operation. Although several techniques for this purpose have been reported, none of them have succeeded in creating a suitable molecule with sufficient hole.[3–5] Described herein is a novel oxidative bond cleavage of a tetrasubstituted bis(fulleroid) which affords a 12-membered ring diketone on the surface of fullerene.

Since bis(fulleroid) derivative **1** (**1a**: $R^1=R^2=$ $COOCH_3$; **1b**: $COOCH_2CF_3$; **1c**: $COOC(CH_3)_3$)[6] has the same 60 π electron structure as C_{60}, **1** is a good agent for generation of $^1O_2$ like C_{60}.[7–9] Indeed, irradiation of chloroform or toluene solutions of **1a** and **1b** with white visible light in the presence of atmospheric oxygen at 30°C afforded **2a** and **b** in 95 and 87% yields,



1 3 2

Figure 1. **1a** and **2a**: $R^1=R^2=COOCH_3$; **1b** and **2b**: $R^1=R^2=COOCH_2CF_3$; **1c** and **2c**: $R^1=R^2=COOC(CH_3)_3$; **1a** and **2d**: $R^1=R^2=COOCH_3$; $2R^2=CH_2OCH_2$; **1e** and **2e**: $R^1=COO(CH_3)_3$; $2R^2=CH_2OCH_2$; **1f** and **2f**: $R^1=COOCH_3$; $2R^2=$ $CH_2N(Boc)CH_2$.

---

* Corresponding author. Fax: +81-(0)52-789-4765; e-mail: murata@info.human.nagoya-u.ac.jp

0040-4039/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(00)02126-2

respectively. Conversion of **1c** into **2c** proceeded slowly under the similar conditions. The oxidation of **1c** was carried out under the forcing conditions (80°C; irradiated by stronger lamp; air bubbling) to give **2c** in 97% yield based on conversion (58%). The bis(fulleroid) derivatives with oxygen and nitrogen heterocycles (**1d**–**f**) were oxidized quantitatively to diketone **2d**–**f**, respectively (Fig. 1).[10]

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra of **2a** showed four kinds of ester groups (CH_3O: $\delta=3.88$, 3.89, 4.03, 4.22; COO: $\delta=164.83$, 166.50, 169.41, 170.82) together with 58 aromatic sp^2 carbons. Four kinds of ester groups of **2b** and **2c** were observed similarly by NMR spectra. These NMR signal patterns are consistent with those of fullerene derivatives with C_1 symmetry. In addition, two signals typical for ketone carbonyl groups were recommended in ^{13}C NMR spectra of **2** (**2a**: $\delta=189.56$ and 192.06; **2b**: 190.53 and 190.99; **2c**: 189.53 and 192.99). Molecular ions (M^+ or M^-) of **2a**, **2b**, and **2c** ($m/z=1036$, 1308, and 1204, respectively) were consistent with the diketone formulas (**1**+32). When **1a**, whose ^{13}C contents are 20% in the fullerene part and natural in ester groups was converted to **2a**, ^{13}C NMR signal intensities of ketones increased in the comparison with those of esters.[11] Therefore, it is evident that the ring cleavage took place on the ^{13}C-enriched fullerene skeleton.

In spite of the same 60 π electronic structure as C_{60}, whose photooxygenation affords $C_{60}O$ (epoxide),[5,9,12,13] [2+2] cycloaddition of **1** with $^1O_2$ followed by symmetrical ring opening of dioxetane **3** predominantly occurred to give **2**.[4d,5a,13] On the contrary, oxidation and Diels–Alder reaction of the mother compound (**1**: $R^1=R^2=H$)[3] were reported to occur not on the fullerene skeleton but on the outside part.[9,14] Since AM1 calculations on **1a** shows that the C=C bond on which the oxidative ring cleavage occurred has the largest HOMO density, the bond is the most reactive toward electrophilic attack of $^1O_2$. The C=C bond is sterically affected by the ester groups, and the bulky *t*-butyl group of **1c** prevents the attack of $^1O_2$. The oxidation of less hindered **1d**–**f** proceeded rapidly. Therefore, the diketone-forming photooxidation of **1** is a characteristic process of tetrasubstituted bis(fulleroid). The related oxidation of an azafulleroid derivative has been reported by Rubin,[4d] although the product is not sufficient for the tailor-made procedure because of steric hindrance caused by neighboring aromatic substituents. Since both the *t*-butyl ester of **2c** and **2e** and the *N*-Boc group of **2f** can be removed by usual acidic reactions suitable for conversion of fullerene derivatives, **2** might be used as versatile precursors not only for the tailor-made approach but also for various new materials.

The following procedure is representative: In the presence of atmospheric oxygen, a solution of **1a** (20 mg, 0.02 mmol) in chloroform (50 ml) was irradiated by a 300 W tungsten halogen lamp (Pyrex®) at 30°C (with water cooler) for 10 h. The solvent was removed, and the residue was subjected to SiO_2 column chromatography eluting with 10% ethyl acetate in toluene. Pure **2a** (19 mg, 95%) was obtained as a dark brown powder (mp 345–348°C dec.). ^{1}H and ^{13}C NMR spectra of **2a** and **2c** are summarized in Ref. 15.

Acknowledgements

We thank Mr. Y. Andoh and Y. Hayashi (Nagoya University), Mr. T. Omaru (Institute for Molecular Sciences), and Ms. R. Imajo and S. Furusho (JASCO International Co.) for technical support.

References

1. (a) Shinohara, H. *Adv. Metal Semicond. Clust.* **1998**, *4*, 205–226; (b) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123–128; (c) Nagase, S.; Kobayashi, K.; Akasaka, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2131–2142.
2. (a) Saunders, M.; J.-Vázquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993**, *259*, 1428–1430; (b) Shimshi, R.; Khong, A.; J.-Vázquez, H. A.; Cross, R. J.; Saunders, M. *Tetrahedron* **1996**, *52*, 5143–5148; (c) Giblin, D. E.; Gross, M. L.; Saunders, M.; J.-Vázquez, H.; Cross, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 9883–9890.
3. (a) Dong, G.-X.; Li, J.-S.; Chan, T.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 1725–1726; (b) Birkett, P. R.; Avent, A. G.; Derwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1869–1870; (c) Grösser, T.; Prato, M.; Lucchini, V.; Hirsch, A.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1343–1345; (d) Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grösser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257–2259; (e) Nuber, B.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1996**, 1421–1422; (f) Schick, G.; Hirsch, A.; Mauser, H.; Clark, T. *Chem. Eur. J.* **1996**, *2*, 935–943; (g) Shen, C. K.-F.; Chien, K.-M.; Juo, C.-G.; Her, G.-R.; Luh, T.-Y. *J. Org. Chem.* **1996**, *61*, 9242–9244.
4. (a) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775–3776; (b) Rubin, Y. *Chem. Eur. J.* **1997**, *3*, 1009–1016; (c) Rubin, Y. *Chimia* **1998**, *52*, 118–126; (d) Schick, G.; Jarrosson, T.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2360–2363.
5. (a) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003–7004; (b) Keshavarz-B., M.; González, R.; Hicks, R. G.; Srdanov, G.; Srdanov, V. I.; Collins, T. G.; Hummelen, J. C.; B.-Lund, C.; Pavlovich, J.; Wudl, F.; Holczer, K. *Nature* **1996**, *383*, 147–150; (c) Hummelen, J. C.; Keshavarz-K, M.; van Dongen, J. L. J.; Janssen, R. A. J.; Meijer, E. W.; Wudl, F. *J. Chem. Soc., Chem. Commun.* **1998**, 281–282; (d) Nuber, B.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1998**, 405–406.
6. Inoue, H.; Yamaguchi, H.; Suzuki, T.; Akasaka, T.; Murata, S. *Synlett* **2000**, 1178–1180.
7. Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11–12.

8. (a) Orfanopoulos, M.; Kambourakis, S. *Tetrahedron Lett.* **1994**, *35*, 1945–1948; (b) Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *59*, 1135–1138; (c) Orfanopoulos, M.; Kambourakis, S. *Tetrahedron Lett.* **1995**, *36*, 435–438.
9. (a) An, Y.-Z.; Ellis, G. A.; Viado, A. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 6353–6361; (b) An, Y.-Z.; Viado, A. L.; Arce, M.-J.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 8330–8331; (c) Rubin, Y. *NATO ASI Ser, Ser. E* **1996**, *316*, 295–328.
10. Compounds **1d**–**f** were synthesized using palladacyclopentadiene derivatives prepared from diacetylenic ether and diacetylenic amine, such as di(3-methoxycarbonyl-2-propynyl)ether: see Ref. 6 and Yamamoto, Y.; Nagata, A.; Itoh, K. *Tetrahedron Lett.* **1999**, *40*, 5035–5038.
11. ^{13}C-Enriched **1a** was prepared by the reaction of ^{13}C-enriched (20%) C_{60} with non-enriched tetracarbomethoxy-palladacyclopentadiene: see Ref. 6.
12. Hirsch, A. *The Chemistry of Fullerenes*; Georg Thieme Verlag: Stuttgart, 1994, Chapter 8, pp. 163–165.
13. Taliani, C.; Ruani, G.; Zamboni, R.; Danieli, R.; Rossini, S.; Denisov, V. N.; Burlakov, V. M.; Nagri, F.; Orlandi, G.; Zerbetto, F. *J. Chem. Soc., Chem. Commun.* **1993**, 220–222.
14. Hsiao, T.-Y.; Santhosh, K. C.; Liou, K.-F.; Cheng, C.-H. *J. Am. Chem. Soc.* **1998**, *120*, 12232–12236.
15. Compound **2a**: ^{13}C NMR ($CDCl_3$): 52.94, 53.36, 53.87, 54.24, 58.13, 62.53, 127.95, 128.22, 128.27, 128.46, 128.81, 129.46, 129.77, 130.06, 130.70, 130.86, 131.56, 131.84, 132.39, 133.50, 134.18, 134.46, 136.97, 137.22, 136.77, 138.22, 138.55, 139.21, 139.64, 140.10, 140.32, 140.49, 141.16, 141.44, 141.82, 142.26, 142.31, 142.59, 142.82, 142.83, 143.12, 143.68, 143.89, 144.11, 144.45, 144.80, 145.00, 145.20, 145.38, 145.51, 145.70, 145.72, 145.96, 146.26, 146.46, 146.59, 146.77, 147.49, 147.74, 147.77, 147.93, 148.83, 149.42, 150.05, 150.30, 152.71, 164.83, 166.50, 169.41, 170.82, 189.59, 192.06. Compound **2c**: ^{1}H NMR ($CDCl_3$): 1.44, 1.46, 1.64, 1.90; ^{13}C NMR ($CDCl_3$): 27.85, 27.99, 28.14, 28.23, 63.54, 68.1, 83.3, 83.9, 84.2, 84.71, 125.29, 128.21, 128.86, 128.99, 129.02, 130.24, 131.83, 132.08, 132.76, 133.37, 134.89, 135.87, 136.84, 137.49, 138.06, 138.37, 138.61, 138.95, 139.01, 139.10, 139.39, 139.48, 139.96, 140.07, 140.17, 140.25, 141.23, 141.87, 142.02, 142.13, 142.23, 142.54, 142.72, 142.97, 143.53, 143.89, 144.22, 144.27, 144.61, 144.69, 145.15, 145.20, 145.49, 145.53, 145.65, 145.72, 145.85, 146.07, 146.16, 146.30, 146.77, 147.31, 147.58, 147.63, 147.82, 147.86, 148.72, 150.21, 163.34, 164.51, 167.33, 169.1, 189.53, 192.99.