

Regioselective [2 + 2] Cycloaddition of a Fullerene Dimer with an Alkyne Triggered by Thermolysis of an Interfullerene C—C Bond

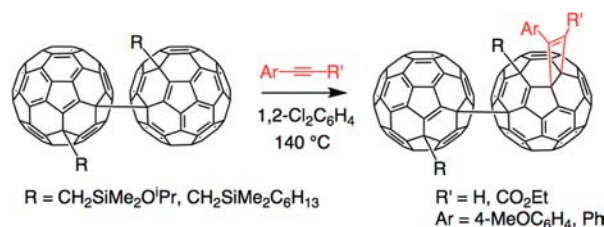
Zuo Xiao, Yutaka Matsuo,* Masashi Maruyama, and Eiichi Nakamura*

Department of Chemistry, School of Science, The University of Tokyo, Hongo,
Bunkyo-ku, Tokyo 113-0033, Japan

matsuo@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

Received March 18, 2013

ABSTRACT



Heating of a singly bonded fullerene dimer in the presence of an alkyne forms a cyclobutene structure on only one of the two fullerene moieties, through a stereo- and regioselective [2 + 2] cycloaddition. Experimental and theoretical data suggest that the reaction is triggered by cleavage of the interfullerene C—C bond and formation of a monomeric fullerene radical.

Fullerenes continue to serve as a rich source of inspiration for our laboratory¹ and others,² because of the intrinsic reactivity these compounds and their applicability to solar cells.³ In this Letter, we report an intriguing thermal reaction of a fullerene dimer ($[\text{C}_{60}(\text{CH}_2\text{SiMe}_2\text{O}^i\text{Pr})_2$ (**1**) and $[\text{C}_{60}(\text{CH}_2\text{SiMe}_2\text{C}_6\text{H}_{13})_2$ (**2**) used as a diastereomeric mixture), in which a cyclobutene is formed on only one of the two fullerene moieties in a stereo- and regioselective manner (Figure 1). On the basis of the known thermal lability of the interfullerene C—C bond and mechanistic analysis, we posit that thermolysis of the dimer first generates a monomeric fullerene radical. This radical undergoes a [2 + 2] cycloaddition with an acetylene, exclusively at the C24—C25 bond (numbering in Figure 2) to give regioselectively a [2 + 2] cyclobutene product, which then recombine with the remaining radical partner

to regenerate a dimeric structure as a diastereomeric mixture.

The chemistry of singly bonded fullerene dimers started with Morton's discovery in 1992 that an equilibrium exists between fullerene dimer $[\text{C}_{60}\text{R}]_2$ and monomer radical RC_{60}^\bullet .⁴ Several reports followed^{5,6} and established the dimeric structure by single-crystal X-ray analysis.⁷ The two expected isomers, namely, the *meso* and *racemic* diastereomers, were separated and found to exist in thermal equilibrium with each other.⁸ Other types of singly bonded dimers, such as $(\text{C}_{60}^-)_2$ and $(\text{C}_{70}^-)_2$, are known to form as crystalline ionic complexes. Dimers with multiple addends, such as $(\text{C}_{60}\text{Cl}_5)_2$ and $[\text{C}_{60}(\text{biPh})_5]_2$, have also been reported.⁹

(1) (a) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807.
(b) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016.

(2) (a) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049.
(b) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083.
(c) Guldi, D. M.; Illescas, B. M.; Atienza, C. M.; Wielopolski, M.; Martin, N. *Chem. Soc. Rev.* **2009**, *38*, 1587.

(3) (a) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58. (b) Matsuo, Y. *Chem. Lett.* **2012**, *41*, 754.

(4) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454.

(5) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023.

(6) Yoshida, M.; Sultana, F.; Uchiyama, N.; Yamada, T.; Iyoda, M. *Tetrahedron Lett.* **1999**, *40*, 735.

(7) Cheng, F.; Murata, Y.; Komatsu, K. *Org. Lett.* **2002**, *4*, 2541.

(8) Wang, G.-W.; Wang, C.-Z.; Zhua, S.-E.; Murata, Y. *Chem. Commun.* **2011**, *47*, 6111.

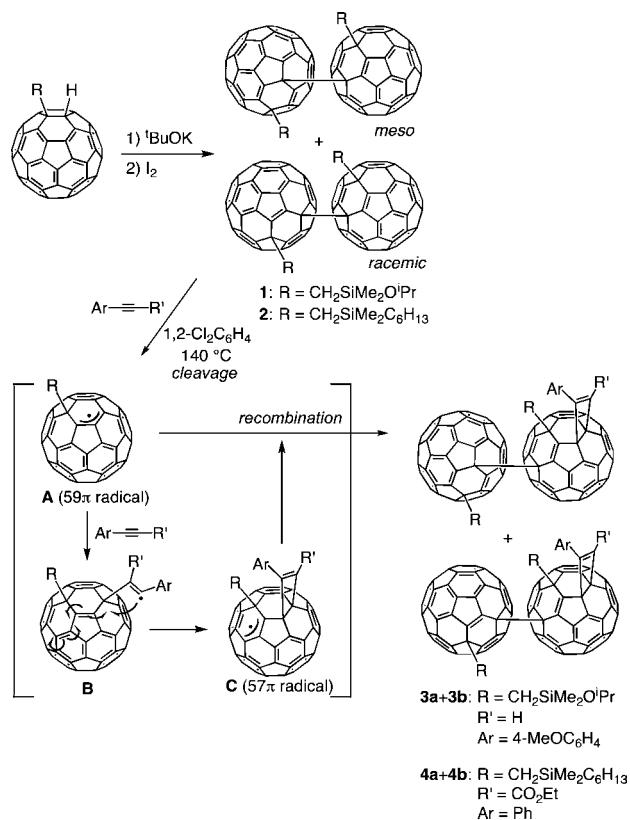


Figure 1. [2 + 2] Cycloaddition of fullerene dimer and alkyne triggered by C–C bond cleavage.

The fullerene dimers $[C_{60}(\text{CH}_2\text{SiMe}_2\text{O}^i\text{Pr})_2]$ (**1**) and $[C_{60}(\text{CH}_2\text{SiMe}_2\text{C}_6\text{H}_{13})_2]$ (**2**) were synthesized through a deprotonation–oxidation process that we reported previously.¹⁰ Thus deprotonation of monoadducts $C_{60}\text{RH}$ ($R = \text{CH}_2\text{SiMe}_2\text{O}^i\text{Pr}$, $\text{CH}_2\text{SiMe}_2\text{C}_6\text{H}_{13}$) with $t\text{BuOK}$ followed by addition of a single-electron oxidant (I_2) afforded dimers **1** and **2** with a *meso*/*racemic* ratio of 2.2:1 (for both **1** and **2**) in 89% and 86% yield, respectively. The *meso* and *racemic* isomers easily interconvert with each other upon heating or light irradiation.⁶

Heating dimer **1** (80 mg) with 4-ethynylanisole (10 equiv.) in *o*-dichlorobenzene (ODCB, 8 mL) at 140 °C for 2.5 h gave a 1:1 diastereomeric mixture of the [2 + 2] products **3a** and **3b** in yields of 23% (15 mg) and 22% (14 mg), respectively, after separation on silica gel. Similarly, heating dimer **2** and the internal alkyne ethyl 3-phenylpropionate (10 equiv) in ODCB at 140 °C for 8 h afforded two inseparable diastereomers, **4a** and **4b**, in 31% combined yield (Figure 1). Products **3** and **4** were the only products detected by HPLC, and the remainder was the starting

dimer. We cannot yet assign the diastereomeric structure of the **a** and **b** series, since so far we know the crystal structure of only **4** for an approximately 1:1 mixture of the two diastereomers (see below).

The isomerically pure forms of **3a** and **3b** allowed us to thoroughly characterize them by NMR. Taking **3a** for example, the ^1H NMR spectrum shows a singlet signal at 7.26 ppm, which is due to the proton on the newly formed cyclobutene ring. The protons with the chemical shifts at 6.81, 7.71, and 3.11 ppm are due to the anisole group. Signals at 2.39, 2.21, 2.10, and 1.80 ppm can be assigned to the two sets of methylene protons, while the signals at 0.25, 0.22, 0.17, and 0.15 ppm can be assigned to the four characteristic silyl methyl protons. The anisole protons and the silyl methyl protons have the same intensity indicating that only one alkyne molecule reacted with the dimer. The ^1H NMR spectrum indicates that **3a** has C_1 symmetry.

The ^{13}C NMR spectrum of **3a** contains 103 peaks between 170 and 110 ppm corresponding to 122 sp^2 carbons, including 8 sp^2 carbons of the cyclobutene moiety.¹¹ The six sp^3 carbons due to fullerene appear at 75.22, 66.89, 65.88, 63.59, 57.68, and 55.96 ppm. With the aid of HMBC spectra, we assigned these sp^3 signals to the characteristic carbons. The 75.22 and 66.89 ppm peaks are due to the two fullerene carbons in the cyclobutene ring; they correlate with the cyclobutene proton at 7.26 ppm. The 57.68 and 55.96 ppm peaks are due to the two fullerene carbons connected to the two silyl methyl groups; they correlate with the methylene protons at 2.39, 2.21, 2.10, and 1.80 ppm. The 65.88 and 63.59 ppm peaks are due to the two pivot carbons, which correlate with no protons (see Supporting Information).

The above spectral data on **3a** offer a wealth of structure information, but do not tell us exactly which double bond of the fullerene reacted with the alkyne. This information was obtained from the single-crystal structure of a 1:1 mixture of diastereomers **4a** and **4b**. Single crystals were obtained by slow diffusion of EtOH into their CS_2 solution. The crystal structure was solved by assuming equal occupancy of **4a** and **4b**. Only one diastereomer is shown in Figure 2 for clarity. We thus ascertained that the reaction took place exclusively at the C24–C25 double bond of the dimer, with exclusive bond formation between C24 and the acetylenic carbon next to the ester group. The length of the cyclobutene double bond is 1.330 Å. The length for the interfullerene C–C bond is 1.599 Å, which is similar to that of other reported dimers.^{5,6}

A “cleavage–recombination” mechanistic rationale is proposed for this highly regioselective [2 + 2] cycloaddition reaction (Figure 1). As demonstrated by literature, the pivot C–C bond of the fullerene dimer can be easily cleaved by heat at elevated temperatures. The resulting 59π -electron fullerene radical **A** undergoes a 1,4-radical addition to the triple bond of alkyne to form a vinyl radical intermediate **B**. Due to the stabilization effect of the vicinal Ar group for the vinyl radical, this radical addition

(9) (a) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Saito, G. *J. Am. Chem. Soc.* **2002**, *124*, 8520. (b) Konarev, D. V.; Khasanov, S. S.; Saito, G.; Otsuka, A.; Yoshida, Y.; Lyubovskaya, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 10074. (c) Troyanov, S. I.; Kemnitz, E. *Chem. Commun.* **2007**, 2707. (d) Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 8457.

(10) (a) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086. (b) Li, C.-Z.; Matsuo, Y.; Nakamura, E. *Tetrahedron* **2011**, *67*, 9944.

(11) Some peaks are overlapped.

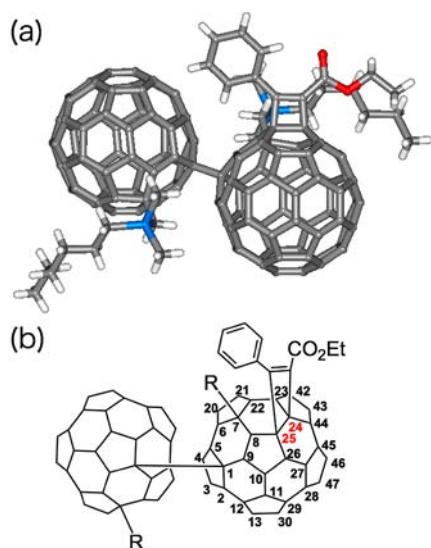


Figure 2. (a) X-ray crystal structure of one of the diastereomers, **4a** or **4b**. (b) Numbering for fullerene carbons according to IUPAC nomenclature.¹²

selectively took place at the sp carbon next to the carboxylic ester group of the alkyne. Intermediate **B** further undergoes an intramolecular radical cyclization to afford a 57π -electron fullerene radical **C**. Finally, the recombination of 59π and 57π radicals gives two diastereomers of the product. We consider that the coupling of two 57π radicals is unfavorable because of their steric bulkiness.

With only the relevant carbon atoms focused upon, this seemingly complex reaction can be simplified into the reaction shown in Figure 3a: a new type of cycloaddition triggered by thermal cleavage of a C–C bond. Here, the C–C bond next to a 1,3-diene system is thermally cleaved, and the resulting pentadienyl radical **A** reacts at its terminal position with the acetylene. The apparently unstable vinyl radical **B** immediately and irreversibly forms cyclobutene **C**, accompanied by formation of the C–C bond. The regioselective C–C bond formation at the terminal carbon of the pentadienyl radical is unusual, and this puzzle was resolved by turning to theory.

Figure 3b shows the spin density of the 59π -electron fullerene radical generated by cleaving the pivotal C–C bond. The largest value of spin density of 0.52 is expected at C2, and a smaller value of 0.26, at C4 (UB3LYP/6-31G

level). We here note that the C2 position is next to the silylmethyl group and hence much more sterically hindered than the C4 position. This provides a rationale that the acetylene reacts with **A** first at C4 followed by intramolecular C–C bond formation at C3. Similarly, in Figure 3c, we note that $[2 + 2]$ cycloadduct **C** has the highest spin density (0.62) at a greatly hindered carbon. Therefore, a dimeric structure is regenerated at the carbon atom that has a spin density of 0.40.

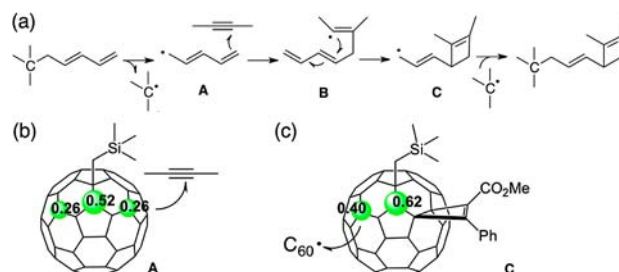


Figure 3. $[2 + 2]$ Cycloaddition triggered by thermal C–C bond cleavage. (a) Simplified path. (b) Spin density after C–C cleavage (UB3LYP/6-31G level). The sp^3 carbon atom connected to the silylmethyl group is C1; the next carbon atom is C2. (c) Spin density after $[2 + 2]$ cycloaddition.

In summary, we found a new type of $[2 + 2]$ cycloaddition of a singly bonded fullerene dimer with an alkyne. We have so far been able to study in depth only two examples, owing to the insolubility of fullerene dimers, the difficulty of purifying products for characterization, and a seeming lack of reactivity with other dienophiles. However, the experimental and theoretical data indicate that the reaction occurs with high stereo- and regioselectivity that can be satisfactorily explained by electronic and steric effects.

Acknowledgment. This work was generously supported by the Funding Program for Next-Generation World-Leading Researchers (Y.M.) and Strategic Promotion of Innovative Research and Development from Japan Science and Technology Agency (E.N.).

Supporting Information Available. Spectral data of all new compounds and crystallographic data of the mixture of **4a** and **4b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

(12) Powell, W. H.; Cozzi, F.; Moss, G. P.; Thilgen, C.; Hwu, R. J.-R.; Yerin, A. *Pure Appl. Chem.* **2002**, *74*, 629.