Pergamon

Tetrahedron Letters 40 (1999) 1543–1546

TETRAHEDRON
LETTERS

The First 1,3-Dipolar Cycloaddition Reaction of [60]Fullerene with Thiocarbonyl Ylide

Hiroshi Ishida and Masatomi Ohno*

Department of Molecular Design and Engineering, Graduate School of Engineering,
Nagoya University, Chikusa, Nagoya 464-8603, Japan

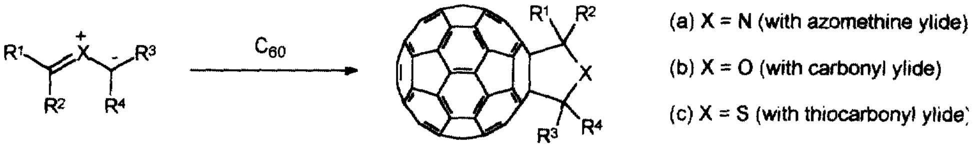
Received 9 November 1998; revised 14 December 1998; accepted 18 December 1998

Abstract: A thiocarbonyl ylide generated by *sila*-Pummerer rearrangement of bis(trimethylsilylmethyl) sulfoxide reacted with C_{60} to give a tetrahydrothiophene-fused C_{60} derivative. The cycloadduct was readily oxidized with mCPBA to give the corresponding sulfoxide and sulfone derivatives, which are useful for further functionalization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: [60]fullerene; thiocarbonyl ylide; cycloaddition; oxidation

Organic functionalization of fullerenes continues to attract attention in material and pharmaceutical applications[1] because of its unique spherical structure and feasibility in bulk production, especially for [60]fullerene.[2] We have been interested in heterocycle-fused C_{60}, since heterocycles are intriguing and important functional groups to obtain novel characteristics by covalent linking with C_{60} and to perform functional conversions inside and outside the heterocyclic ring after attaching to C_{60}. Apparently, a heterocycloaddition reaction is one of the most reliable strategies to this end. In this context we have previously demonstrated hetero Diels-Alder reactions of C_{60} with various heterodienes[3-7] to fuse with six-membered heterocycles. On the other hand, 1,3-dipolar cycloaddition reactions are suitable to fuse with five-membered heterocycles and were reported for nitrones[8] by us and for diazoalkanes,[9] azides,[10] nitrile oxides[11] by other authors, all of which afford five-membered fulleroheterocycles with more than two hetero atoms. Likewise, fulleroheterocycles with one hetero atom were obtained with azomethine ylides[12] and carbonyl ylides[13] [Scheme 1, (a) and (b)].[14]

Scheme 1

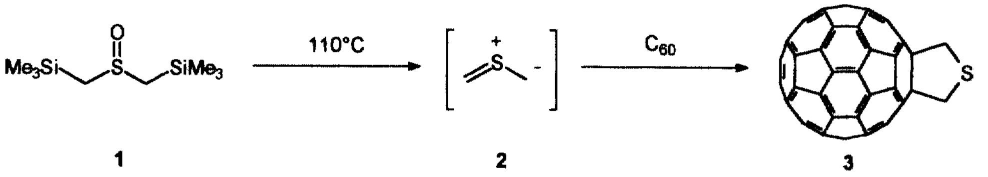


PII: S0040-4039(98)02706-3

However, the sulfur version in this series [Scheme 1, (c)] has not yet been covered, although a cyclic thioether is expected to be a useful functionality. We now wish to report the first 1,3-dipolar cycloaddition reaction of C_{60} with a prototypical thiocarbonyl ylide to give a tetrahydrothiophene-fused C_{60} derivative.

Thiocarbonyl ylides have so far been utilized as effective 1,3-dipolar reagents in organic synthesis.[15] Recently, elegant methods for generation of this 1,3-dipole have been newly developed by Hosomi and Achiwa, who used organosilicon chemistry, and accordingly, we decided to apply these protocols. Among them, CsF-induced elimination reaction of chloromethyl trimethylsilylmethyl sulfide (Hosomi's method[16]) and thermal elimination reaction of bromo(trimethylsilyl)methyl trimethylsilylmethyl sulfide (Achiwa's method[17a]) were not successful. However, another of Achiwa's methods[17b] involving *sila*-Pummerer rearrangement of bis(trimethylsilylmethyl) sulfoxide (**1**) as shown in Scheme 2 (**1** → **2**) gave a fruitful result. Thus, C_{60} was allowed to react with **1** (1.2 equiv.) in *o*-dichlorobenzene at 110 °C for 10 min under an argon atmosphere, during which the solution color changed from purple to dark brown, and the formation of cycloadducts with *in situ* generated thiocarbonyl ylide **2** was indicated by TLC analysis. Unfortunately, unreacted C_{60} could not be removed completely from the product on silica gel chromatography and even preparative HPLC. Nevertheless, the structure of 1:1 cycloadduct **3** could be analyzed as a crude form without interference of the pristine C_{60}. The FAB-MS showed the expected molecular ion peak at m/z 780 and the NMR data unambiguously explained the C_{2v} symmetricity; methylene protons were observed as a singlet signal at δ 4.71 in ^{1}H NMR (500 MHz), and 16 lines[18] at δ 136.37-154.88 due to sp^2 spherical carbons which were contaminated by 1 line at δ 143.10 due to C_{60} itself were observed together with 2 lines at δ 51.12 and 73.39 assignable to sp^3 methylene and fusion carbons, respectively, in ^{13}C-NMR (125 MHz).

Scheme 2

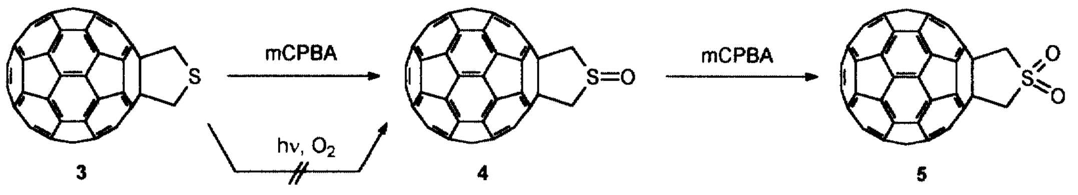


Sulfides are known to be oxidized to sulfoxides with singlet oxygen[19] and this oxidant can be generated by photosensitization of the 1:1 cycloadduct of C_{60}.[20] We have previously shown that self-sensitized photooxygenation products arose from responsive furan- and oxazole-linked C_{60} derivatives by sunlamp irradiation under an oxygen atmosphere.[21] In the present case, cyclic sulfide **3** remained intact under exposure to room light; also, an attempt for the intended photooxidation of **3** to the corresponding sulfoxide **4** under the above conditions effected no substantial change. This is the same result as observed in the case of the thiochroman-fused C_{60} derivative.[5]

In contrast, oxidation of **3** to **4** using a sample obtained without purification from the above 1,3-dipolar cycloaddition could be performed by treating with 1 equiv. of *m*-chloroperbenzoic acid (mCPBA) at room temperature for 1 h (Scheme 3). In this case, the product could be separated easily by flash chromatography on a silica gel column (toluene/ether 3/1) in 41% overall yield (61% yield based on consumed C_{60}), and the structure of **4** was characterized clearly by spectroscopic means: FAB-MS m/z 796 (M^+), 720 (C_{60}); IR (KBr) 1067 (S=O), 527 cm^{-1}; UV($CHCl_3$) 431 nm; ^1H-NMR δ 4.57 (d, J = 13.5 Hz, 1 H), 5.16 (d, J = 13.5 Hz, 1 H); ^{13}C-NMR δ 65.36, 71.26, 134.40-154.53 (27 lines[22]).

The further oxidation of **4** under the same conditions as above gave sulfone **5** in 73% yield, after chromatographic separation on a silica gel column (toluene). The structure was again elucidated by FAB-MS peaks at m/z 812 (M^+), 748 (M^+-SO_2) and 720 (C_{60}), IR absorptions at 1329, 1137 (SO_2) and 527cm^{-1}, ^1H-NMR signals at δ 4.91 (s, 4 H), and ^{13}C-NMR signals at δ 50.35, 63.66 and 136.37-152.41 (16 lines[23]).

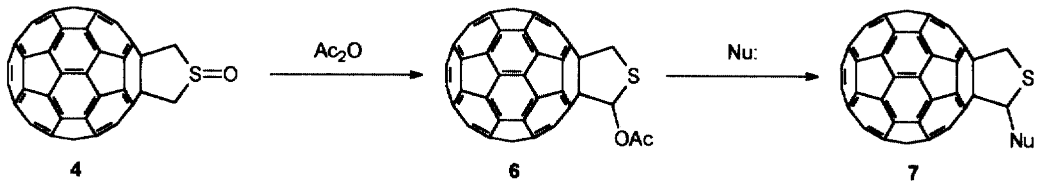
Scheme 3



Finally, we note the result of a reaction with large excess (30 equiv.) of **1**. As might be expected, HPLC and TLC analyses indicated that many cycloadducts were produced (at least 13 peaks were observed on HPLC), suggesting no selective formation of a multi-adduct, for example, originated from the highly symmetric octahedral pattern.

In summary, the 1,3-dipolar cycloaddition of C_{60} with a thiocarbonyl ylide was demonstrated to occur for the first time to give a tetrahydrothiophene-fused C_{60} derivative. This product was not photooxidizable and thus could be handled without regard for light. On the other hand, peracid oxidation was effective to give the corresponding sulfoxide and sulfone derivatives successively. In our preliminary experiment, the sulfoxide **4** was shown to undergo smooth Pummerer rearrangement to lead to the formation of an α-acetoxylated derivative **6**, which is useful for introduction of some interesting functions by replacement with nucleophilic reagents (Nu:) as shown in Scheme 4; for example, an allylic group was appended by the acid-catalyzed reaction with allyl alcohol (*i.e.*, **7**: Nu = $OCH_2CH=CH_2$).[24]

Scheme 4



Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Area (A) (No. 10146101) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1. Hirsch, A. *Synthesis* **1995**, 895.
2. Kraetschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffmann, D. R. *Nature*, **1990**, *347*, 354
3. Ohno, M.; Azuma, T.; Eguchi, S. *Chem. Lett.* **1993**, 1833.
4. Ohno, M.; Kojima, S.; Eguchi, S. *J. Chem. Soc., Chem. Commun.* **1995**, 565.
5. Ohno, M.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Tetrahedron Lett.* **1995**, *36*, 6899.
6. Ohno, M.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Tetrahedron Lett.* **1996**, *37*, 9211.
7. Ohno, M.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Heterocycles*, **1997**, *46*, 49.
8. Ohno, M.; Yashiro, A.; Eguchi, S. *Synlett.* **1996**, 815.
9. a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301. b) Smith III, A. B.; 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.
10. Grosser, T.; Prato, M.; Lucchini, V.; Hirsch, A.; Wudl, A. *Angew. Chem. Int. Ed. Engl.* **1994**, *34*, 1343.
11. a) Meier, M. S.; Poplawska, M. *Tetrahedron* **1996**, *52*, 5043. b) Ros, T. D.; Prato, M.; Novello, F.; Maggini, M.; Amici, M. D.; Micheki, C. D. *J. Chem. Soc., Chem. Commun.* **1997**, 59.
12. a) Imahori, H.; Yamada, K.; Hasagawa, K.; Taniguchi, S.; Okada, T.; Sakata, Y. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2626. b) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519.
13. Jagerovic, N.; Elguero, J.; Aubagnac, J.-L. *J. Chem. Soc., Perkin Trans. 1.* **1996**, 499.
14. The peculiar reaction with β-diketone and β-ketoester was reported by us to give dihydrofuran-fused C_{60} derivatives in an oxidative [3+2] cycloaddition manner: see, Ohno, M.; Yashiro, A.; Eguchi, S. *J. Chem. Soc., Chem. Commun.* **1996**, 291.
15. Padwa, A. Intermolecular 1,3-Dipolar Cycloadditions In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I. Eds.; Pergamon Press: Oxford, 1991; Vol. 4, chap. 9, pp. 1093-1095.
16. Hosomi, A.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1073.
17. a) Terao, Y.; Aono, M.; Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 1734. b) Aono, M.; Hyodo, C.; Terao, Y.; Achiwa, K. *Tetrahedron* **1986**, *27*, 4039.
18. δ ($CDCl_3/CS_2$ 1/1) 136.37, 140.15, 141.86, 142.16, 142.35, 142.71, 143.10, 144.56, 145.29, 145.39, 145.55, 145.58, 146.12, 146.42, 147.42, 154.88.
19. a) Akasaka, T.; Ando, W. Peroxides from Photosensitized Oxidation of Heteroatom Compounds in *Organic Peroxides*; Ando, W. Ed.; John Wiley and Sons: New York, 1992; pp. 599-657. b) Pasto, D. J.; Cottard, F.; Jumelle, L. *J. Am. Chem. Soc.* **1994**, *116*, 8978.
20. Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *59*, 1135.
21. Ohno, M.; Koide, N.; Sato, H.; Eguchi, S. *Tetrahedron.* **1997**, *53*, 9075.
22. δ ($CDCl_3/CS_2$ 1/1) 134.40, 137.08, 140.13, 140.15, 141.51, 141.91, 141.98, 142.10, 142.13, 142.20, 142.66,* 143.28, 144.34, 144.54, 144.71, 145.11, 145.34,* 145.40, 145.80, 145.95, 146.00, 146.20, 146.32, 146.36,* 147.43, 153.97, 154.53 (cf. Because of accidental overlapping, 27 lines of the required 30 lines were observed. Asterisks show doubly intensed lines).
23. δ ($1,2\text{-}Cl_2C_6D_4$) 136.37, 140.38, 141.91, 141.96, 142.27, 142.88, 143.38, 144.78, 144.82, 145.72, 145.89, 145.92, 146.56, 146.71, 148.02, 152.41.
24. The Pummerer rearrangement was performed by heating a solution of **4** (50 mg) in 1,1,2,2-tetrachloroethane (20 mL) including acetic acid (3 mL) at 110 °C for 4 h, and after evaporation of the solvent and the acid, the product was purified by chromatography on a silica gel column (toluene) to give **6** in 75% yield. The following replacement with allyl alcohol was carried out as follows; a solution of **6** (15 mg) in 1,1,2,2-tetrachloroethane (5 mL) including this alcohol (0.5 mL) was treated with a 0.18 M solution of trimethylsilyl triflate in dichloromethane (0.1 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 3.5 h. The product was isolated in the same manner as above except for washing with aqueous $NaHCO_3$ to remove an acid portion to give **7** (Nu = $OCH_2CH{=}CH_2$) in 63% yield.