

SYNTHESIS OF A THIOPHENE DERIVATIVE OF C₆₀ FROM [4+2]CYCLOADDITION REACTION WITH 2,3-DIMETHYLENE-2,3-DIHYDROTHIOPHENE

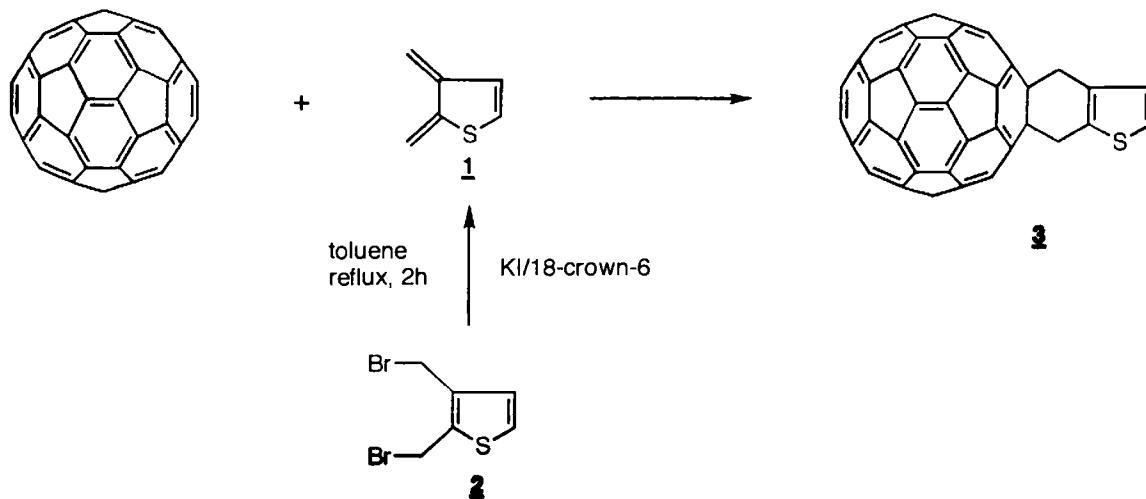
Masatomi Ohno, Naoya Koide, and Shoji Eguchi*

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Abstract: A thiophene ring was introduced to C₆₀ by heterocyclic quinodimethane type Diels-Alder cyclization using 2,3-dimethylene-2,3-dihydrothiophene.

Since the discovery of the macroscopic-scale fullerenes synthesis by Krätschmer et al. (1), methods for the isolation and purification of the most abundant buckminsterfullerene C₆₀ have been continuously improved (2-12). Thus, shortly after C₆₀ become available in large quantities, synthetic chemists developed interest in its derivatization. The cycloaddition reaction is one of the fascinating methods for this aim (13), because C₆₀ possesses low-lying LUMO orbitals (14). While some [4+2]cycloaddition reactions of C₆₀ as a dienophile were studied with selected dienes (for example, cyclopentadiene and anthracene) (15-19), it was demonstrated that they are fruitful in a case that a cycloadduct can avoid cycloreversion by stabilization of the resulted double bond with intrinsic aromaticity. In fact irreversible cycloadditions were performed in the reaction with quinodimethane (20-25) and the product obtained therefrom was used for the first X-ray analysis of the C₆₀-cycloadduct structure (21). We are interested in a heterocyclic derivative of C₆₀ with its physical and biological potentiality. Recently, a variety of heterocyclic analogs of quinodimethane have been developed (26) and these dienes seem to be promising to construct the desired ring system. First of all, we decided to undertake introduction of a thiophene ring to the C₆₀ surface using 2,3-dimethylene-2,3-dihydrothiophene 1 (27).

The required diene **1** is *in situ* prepared from 1,4-elimination of dibromide **2** with KI according to the reported procedure (27). In this case a crown ether was used to facilitate the reaction carried out in toluene. Thus, C_{60} (36 mg, 0.05 mmol) in toluene (20 ml) was heated to reflux for 2 h with **2** (20.3 mg, 0.15 mmol), KI (25.1 mg, 0.075 mmol), and 18-crown-6 (158 mg, 0.3 mmol). The products were separated by silica gel chromatography eluted with hexane and then hexane/toluene (9/1) to give 1:1 cycloadduct **3** as the second fraction (8.9 mg, 36 % yield based on consumed C_{60}) after recovery of C_{60} (14.5 mg) as the first fraction. The use of equimolar **2** raised the yield (63%) but starting C_{60} was largely recovered. On the other hand, the increased ratio of C_{60} to **2** (e.g. 1/4) expended most of C_{60} but resulted in the major formation of multiaddition products (*i.e.* 1:2 and 1:3 cycloadducts).



The structure of the cycloadduct **3** was elucidated by the spectral inspections. The FAB-MS indicated the molecular ion peak at m/z 830, corresponding to the expected 1:1 addition product. The IR and UV spectra showed absorptions at 527 cm^{-1} and at 433 nm ($\log \epsilon=2.94$), respectively, each diagnostic for the 1:1 cycloadduct of C_{60} (28). In the $^1\text{H-NMR}$ spectrum, together with AB quartet ($J=5.5\text{ Hz}$) at δ 7.40 and 7.47 due to a thiophene ring, two singlet signals were observed at δ 4.63 and 4.75. They are assigned to six-membered ring methylene protons and indicated that the ring flipping occurred freely at ambient temperature. The equivalency of the methylene proton supported the fusion across 6,6-ring junction. Furthermore, the $^{13}\text{C-NMR}$ confirmed the C_S symmetry expected from this fusion, which was indicated by the presence of 32 lines at δ 135.76, 135.93, 136.13, 138.83, 140.38, 140.39, 141.84, 141.86, 142.33, 142.49, 142.56, 142.84, 143.31, 143.36, 144.93, 144.95,

145.49, 145.55, 145.62, 145.69, 145.71, 145.73, 145.77, 146.01, 146.48, 146.52, 146.74, 147.76, 147.93, 147.94, 156.77, and 157.19 (sp^2 carbons), and 2 lines at δ 66.90 and 67.25 (sp^3 carbons), all attributed to C₆₀ framework except 2 lines belonging to thiophene sp^2 carbons; also observed were signals at δ 123.69 and 127.22 (thiophene ring carbons) and at δ 41.16 and 41.89 (methylene carbons).

Thus obtained thiophene-containing C₆₀ derivative may be useful for further conversions through Friedel-Crafts type functionalizations and various ring transformations. The [4+2]cycloaddition reactions utilizing other heterocyclic quinodimethanes are in progress in our laboratory.

Acknowledgements

Our research was supported by the Grants of Ministry of Education, Science and Culture of Japan (Grant-in-Aid for General Scientific Research No. 04403017 and for Scientific Research on Priority Area No. 05233105).

References and Notes

- (1) W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990)
- (2) P. -M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Am. Chem. Soc.* **113**, 1050 (1991)
- (3) K. C. Khemani, M. Prato, and F. Wudl, *J. Org. Chem.* **57**, 3254 (1992)
- (4) A. Mittelbach, W. Hoenle, H. G. v. Schnerring, J. Carlsen, R. Janiak, and H. Quast, *Angew. Chem. Int. Ed. Engl.* **31**, 1640 (1992)
- (5) K. Jinno, K. Yamamoto, T. Ueda, H. Nagashima, K. Itoh, J. C. Fetzer, and W. R. Biggs, *J. Chromatogr* **594**, 105 (1992)
- (6) M. S. Meier and J. P. Selegue, *J. Org. Chem.* **57**, 1924 (1992)
- (7) W. A. Scrivens, P. V. Bedworth, and J. M. Tour, *J. Am. Chem. Soc.* **114**, 7917 (1992)
- (8) A. Govindraj and C. N. R. Rao, *Fullerene Science and Technology* **1**, 557 (1993)
- (9) A. D. Darwish, H. W. Kroto, R. Taylor, and D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **15** (1994)
- (10) W. A. Scrivens, A. M. Cassell, B. L. North, and J. M. Tour, *J. Am. Chem. Soc.* **116**, 6939 (1994)
- (11) J. L. Atwood, G. A. Koutsantonis, and C. L. Raston, *Nature (London)* **368**, 229 (1994).
- (12) 'Soot on Column' method (combination of extraction and separation of C₆₀ on Nont I-Celite column under reflux of toluene) was developed by us
- (13) For a recent review, see
 - a) R. Taylor and D. R. M. Walton, *Nature (London)* **363**, 685 (1993)
 - b) G. A. Olah, I. Bucsi, R. Aniszfeld, and G. K. S. Prakash, *Carbon* **30**, 1203 (1992)
 - c) S. Eguchi and M. Ohno, *Kikan Furaren* **1**(3), 99 (1993)
- (14) H. W. Kroto, A. W. Allaf, and S. P. Balm, *Chem. Rev.* **91**, 1213 (1991)

(15) V. M. Rotello, J. B. Howard, T. Yadav, M. M. Conn, E. Viani, L. M. Giovane, and A. L. Lafleur, *Tetrahedron Lett.* **34**, 1561 (1993)

(16) M. Tsuda, T. Ishida, T. Nogami, S. Kurono, and M. Ohashi, *J. Chem. Soc. Chem. Commun.* 1296 (1993)

(17) K. I. Gühr, M. D. Greaves, and V. M. Rotello, *J. Am. Chem. Soc.* **116**, 5997 (1994)

(18) J. A. Schlueter, J. M. Seaman, S. Taha, H. Cohen, K. R. Lykke, H. H. Wang, and J. M. Williams, *J. Chem. Soc. Chem. Commun.* 972 (1993)

(19) K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, and T. S. M. Wan, *Tetrahedron Lett.* **34**, 8473 (1993)

(20) M. Prato, V. Lucchini, M. Maggini, E. Stimpfl, G. Scorrano, M. Eiermann, T. Suzuki, and F. Wudl, *J. Am. Chem. Soc.* **115**, 8479 (1993)

(21) Y. Rubin, S. Khan, D. I. Freedberg, and C. Yeretzian, *J. Am. Chem. Soc.* **115**, 344 (1993)

(22) P. Belik, A. Gügel, J. Spickermann, and K. Müllen, *Angew. Chem. Int. Ed. Engl.* **32**, 78 (1993)

(23) F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf, and C. Thilgen, *Helv. Chim. Acta* **76**, 2445 (1993)

(24) A. Gügel, A. Kraus, J. Spickermann, P. Belik, and K. Mullen, *Angew. Chem. Int. Ed. Engl.* **33**, 559 (1994)

(25) W. Bidell, R. E. Douthwaite, M. L. H. Green, A. H. H. Stephens, and J. F. C. Turner, *J. Chem. Soc. Chem. Commun.* 1641 (1994)

(26) T. Chou and R. -C. Chang, *Tetrahedron Lett.* **33**, 8121 (1987) and references cited therein

(27) D. K. Chadwick and A. Plant, *Tetrahedron Lett.* **28**, 6085 (1987)

(28) L. Isaacs, A. Wehrsig, and F. Diederich, *Helv. Chim. Acta* **76**, 1231 (1993)

Received November 10, 1994