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Synthesis of Heterocycle-Linked [60]Fullerene Derivatives by Heterocyclic *o*-Quinodimethane Diels-Alder Reaction and Self-Sensitized Photooxygenation of the Cycloadducts

Masatomi Ohno, Naoya Koide, Haruhiko Sato, and Shoji Eguchi*

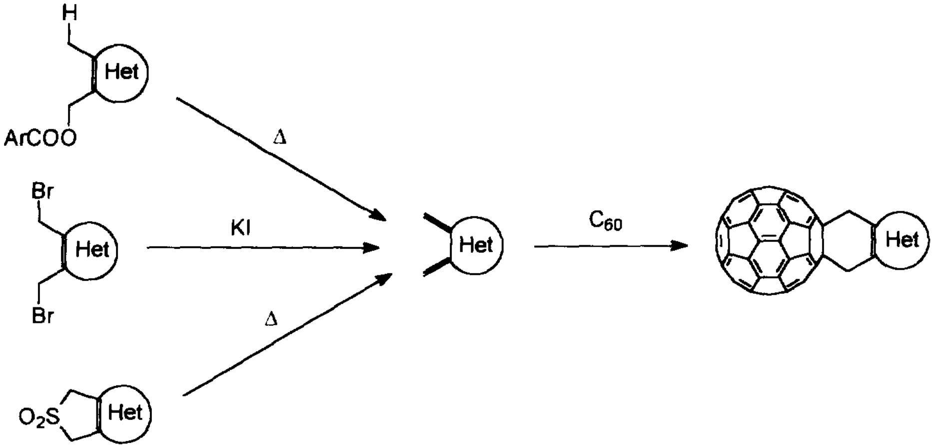
Department of Molecular Design and Engineering, Graduate School of Engineering,
Nagoya University, Chikusa, Nagoya 464-01, Japan

Abstract [60]Fullerene underwent [4+2]cycloaddition reaction smoothly with heteroaromatic analogs of *o*-quinodimethanes including furan, thiophene, oxazole, thiazole, indole and quinoxaline to give the corresponding heterocycle-linked [60]fullerenes. Among them, the furan and oxazole derivatives were prepared with all equipments covered with an aluminum foil, because of lability to oxygen under exposure to room and sun lights. Intended self-sensitized photooxygenation afforded epoxy-γ-lactone from the former and diester from the latter after methanolysis and hydrolysis. © 1997 Elsevier Science Ltd.

Organic functionalization of fullerene is fascinating and promising for new material chemistry and pharmacological application because of its unique spherical structure and feasibility in bulk production, especially for C_{60}.[1] The double bond involved in C_{60} surface, intrinsically, is more pyramidalized than the usual one[2] and has extremely low LUMO energy level,[3] which could effect a variety of addition reactions despite of the aromatic character.[4] Among them is the cycloaddition reaction, which has two major advantages from a synthetic point of view; the monoaddition product is obtainable relatively with ease and the addition site is limited at the 6,6-ring junction with few exceptions.[5] In this respect, the Diels-Alder reaction of C_{60} has been developed extensively and revealed to be useful to obtain a stable cycloadduct if it is not reversible.[6] The early examples and followings of this reaction, in fact, relied on the *o*-quinodimethane-type of compound as an effective diene.[7] We have been interested in fullerene derivatives functionalized with heterocycles,[8] because (a) even a simple combination of fullerenes with structurally diverse heterocycles provides a multitude of derivatives, (b) heterocycles are themselves intriguing and important functional groups, and (c) functional conversions can be carried out by heterocyclic modification and heterocyclic ring-opening. Recently, heterocyclic *o*-quinodimethanes have been exploited for a convenient route to polyheterocycles[9] and are considered to be fruitful reaction partners with the C_{60} dienophile. Thus, we decided to undertake the Diels-Alder reaction using heterocyclic analogs of *o*-quinodimethane. In our previous communication,[10] we reported the thiophene case as the first example of this type. Later, the similar result was obtained by Spanish chemists.[11] Further extension was carried out for the heterocycles such as furan, oxazole, thiazole, indole and quinoxaline. Among them, the first two were found to be oxygen-labile. However, it is not unexpected because C_{60} is known to be a good photosensitizer for producing singlet oxygen.[12] We now report the detailed results in this context.

RESULTS AND DISCUSSION

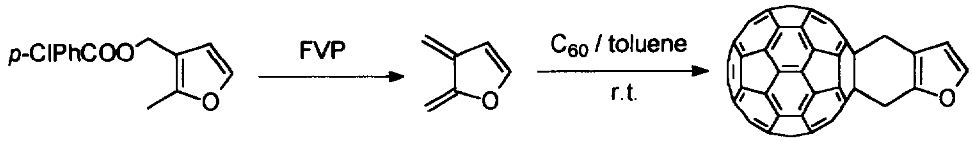
Applied methods in our experiment for generation of reactive heterocyclic *o*-quinodimethanes are categorized in three types of elimination reactions: 1,4-elimination of a benzoate derivative on flash vacuum pyrolysis, 1,4-elimination of dibromide derivatives on action of KI, and cheletropic elimination of 3-sulfolene derivatives on thermolysis (Scheme 1).



Scheme 1

The furan-linked C_{60} derivative **3** was obtained by treating C_{60} with the isolated furan analog **2** of *o*-quinodimethane (Scheme 2). According to the Trahanovsky's method,[13] *p*-chlorobenzoate ester of 2-methyl-3-furylmethyl alcohol (**1**) (1.5 equiv.) was decomposed by FVP (620 °C, 0.2 mmHg) to give 2,3-dimethylene-2,3-dihydrofuran (**2**) trapped with liquid nitrogen, to which a chlorobenzene solution of C_{60} was added and the mixture was allowed at room temperature. While stirring was continued overnight under N_2 atmosphere, the reaction flask was covered with aluminum foil to avoid photooxidation. This care must be made for all the following operations. The product was chromatographed with a silica gel column to give the expected monocycloadduct **3** in 35% yield (based on consumed C_{60}) after recovery of C_{60}. The structure was determined by spectroscopy. The FAB-MS proved the 1:1 addition product by the molecular ion peak at m/z 814. The IR and UV spectra had absorptions at 527 cm^{-1} and 432 nm, respectively, characteristic of a 1:1 cycloadduct of C_{60}. The ^{1}H-NMR and ^{13}C-NMR supported C_s-symmetry by two singlet signals at δ 4.50 and 4.67 due to cyclohexane ring CH_2, indicative of free flipping of this ring, and by 2 lines at δ 66.62 and 66.76 and 32 lines at δ 135.47-157.25 (including 2 furan-ring carbons) due to sp^3 and sp^2 C_{60} framework carbons, compatible with the fusion across 6,6 junction. The other signals due to a furan ring were observed at δ 6.77 and 7.62 (each 1 H, d, *J*=2.0 Hz) in the ^{1}H-NMR and at δ 110.65 and 118.71 in the ^{13}C-NMR.

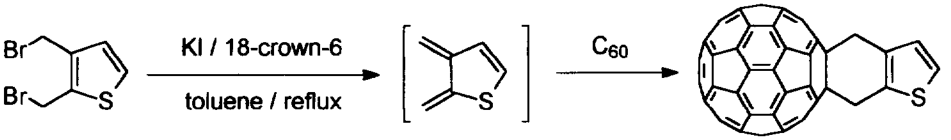
The thiophene-linked C_{60} derivative **6**[10] was obtained from the reaction with the thiophene analog **5** of *o*-quinodimethane *in situ* formed from dibromide **4**[14] according to the established procedure by Müllen[7c] (Scheme 3). Thus, a solution of C_{60} and **4** (1.5 equiv.) in toluene was heated to reflux in the presence of KI and 18-crown-6, and the product was separated by silica gel chromatography. After recovery of unreacted C_{60}, the expected 1:1 cycloadduct **6** was obtained in 36% yield (based on consumed C_{60}). It is noted that the



1 **2** **3**

Scheme 2

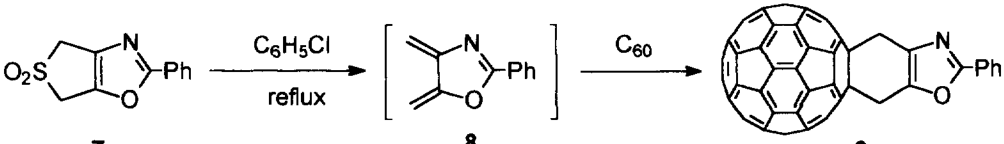
amount of the reagent used is critical for selective formation of the monoadduct; the HPLC analysis of the product mixture showed that increased ratio of **4**/C_{60} (*e.g.*, 4/1) resulted in the major formation of multiaddition products (more than 6 peaks were detected), although no effort was made for their separation (cf. FAB-MS of the mixture products eluted after the monoadduct had the peak at m/z 940 assignable to a 1:2 cycloaddition product). When an equimolar amount of the reagent was used, the multiaddition was suppressed but C_{60} was largely recovered (74% recovery). The C_s-symmetric structure of the obtained monoadduct was characterized by FAB-MS (m/z 830) , IR (527 cm^{-1}), UV (433 nm), ^{1}H-NMR [δ 4.63 and 4.75 (each s, 2 H)] and ^{13}C-NMR (δ 41.16, 41.89, 66.90 and 67.25 for sp^3 carbons and 34 lines δ 123.69-157.19 for sp^2 carbons).



4 **5** **6**

Scheme 3

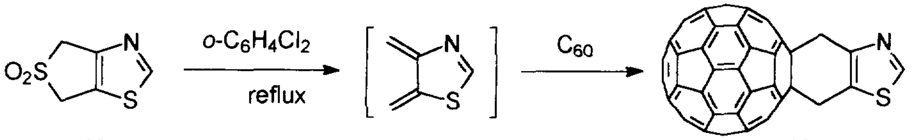
The oxazole-linked C_{60} derivative **9** was obtained from the reaction with the 2-phenyl-substituted oxazole analog **8** of *o*-quinodimethane generated by cheletropic elimination (Scheme 4). Again, all the operations in this case also required the same care as for the aforementioned reaction with furan. Thermolysis of the oxazole-fused 3-sulfolene **7**[15] (2 equiv.) was conducted by refluxing a chlorobenzene solution which included C_{60}, and chromatographic separation afforded the 1:1 cycloadduct **9** in 39% yield (based on consumed C_{60}). The structure was elucidated by spectral inspections. In addition to adequate FAB-MS peaks and IR/UV absorptions as above, definitive two singlet signals were observed at δ 4.69 and 4.84 together with multiplet signals due to a phenyl ring at δ 7.49-8.19 in the ^{1}H-NMR. Also, two pair of sp^3-carbon signals (at δ 38.59 and 40.22 due to a cyclohexane ring and 66.20 and 66.26 due to C_{60} fusion carbons) and sp^2-carbon signals (30+3+4 lines at δ 126.40-156.70 due to C_{60}, oxazole and phenyl rings) were observed in the ^{13}C-NMR.



7 **8** **9**

Scheme 4

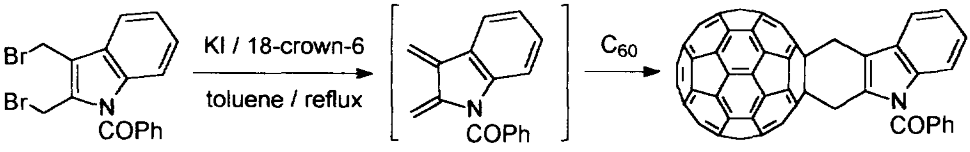
The thiazole-linked C_{60} derivative **12** was obtained from the reaction with the corresponding analog **11** in the same manner as employed for the above oxazole case (Scheme 5). The precursor synthesis was reported to start from the formation of bromohydrin of 3-sulfolene.[16] The procedure for this step involved epoxidation followed by ring-opening with HBr (total yield 39%), but was replaced in our experiment by simply treating with NBS/H_2O (yield 69%). Thermolysis of the thiazole-fused 3-sulfolene **10** with C_{60} in *o*-dichlorobenzene at reflux temperature and chromatographic separation afforded the 1:1 cycloadduct **12** in 51% yield (based on consumed C_{60}). The structural determination was based on the analogy of the above oxazole case (see the experimental section for the NMR assignment).



10 **11** **12**

Scheme 5

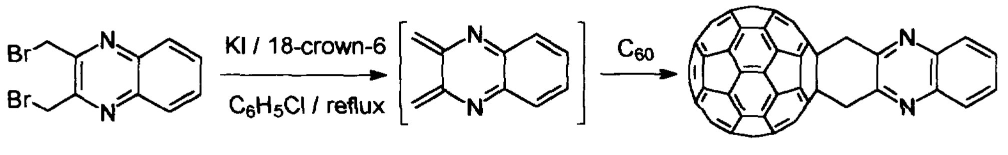
The indole-linked C_{60} derivative **15** was obtained successfully from the reaction with the indole analog **14** of *o*-quinodimethane by following the procedure employed for the thiophene derivative **6** (Scheme 6). Thus, *N*-benzoyl-2,3-bis(bromomethyl)indole **13**[17] (2 equiv.) was allowed to react with C_{60} under the same conditions as for **4** to give the 1:1 cycloadduct **15** in 48% yield (based on consumed C_{60}). The structure was compatible with the spectral data, which were ascribable to the expected C_{60} derivative with an indole ring (see the experimental section for the NMR assignment).



13 **14** **15**

Scheme 6

Finally, the reaction with the quinoxaline analog **17** of *o*-quinodimethane was attempted as an example of six-membered heteroaromatic compound (Scheme 7). The required dibromide **16** was prepared by the reported procedure[18] and applied to the Diels-Alder reaction with C_{60} under the conditions as above. In the previous case,[19] methyl vinyl ketone and *N*-phenylmaleimide (which is demonstrated to have the Diels-Alder reactivity similar to C_{60}[20]) were reported not to undergo [4+2]cycloaddition with **17**, probably because they do not possess lower energy in LUMO than this heteroaromatic *o*-quinodimethane, which, in such a situation, resulted in dimerization or abnormal addition. However, this is not the case for C_{60}. Fig. 1 shows HOMO and LUMO energy levels of these reactants calculated by PM3; the LUMO of C_{60} is lower than that of **17** and this relation is opposite between *N*-phenylmaleimide and **17**. Thus, it is suggested that **17** can cycloadd to C_{60} without the dimerization. While the amount of KI/18-crown-6 as was used in the thiophene case was not sufficient for this cycloaddition, the use of large excess amount (22.5 equiv.) effected the formation of the desired 1:1 cycloadduct **18** (27% yield based on consumed C_{60}). Because of symmetry of the reagent, the product was explained by C_{2v}-symmetric structure; the ^{13}C-NMR indicated two lines at δ 47.69 and 64.73 each attributed to a cyclohexane ring carbon and C_{60} fusion sp^3 carbon and 19 lines at δ 128.33-155.39 (for the required 16+4 lines of C_{60} and quinoxaline sp^2 carbons). In the ^{1}H-NMR spectrum, methylene signals appeared at δ 4.95 and 5.18 as a nearly broad singlet (or collapsed broad doublet) because a cyclohexane ring was just before free flipping.[7t]



16 **17** **18**

Scheme 7

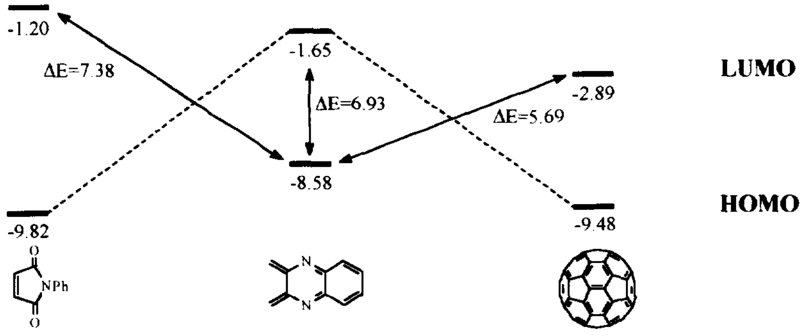
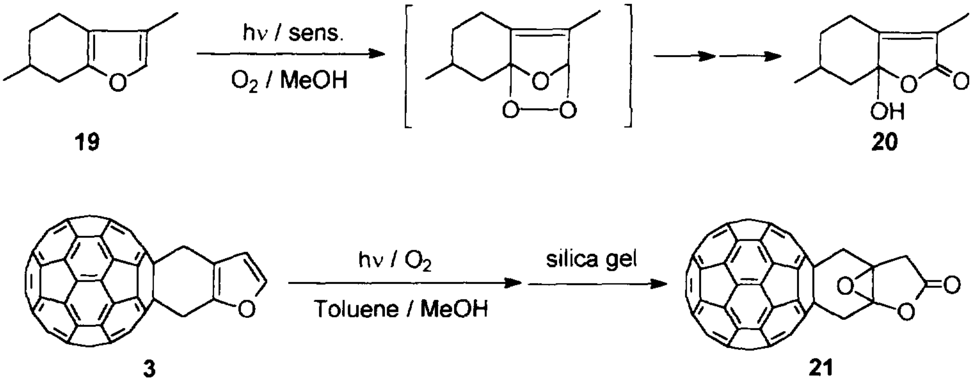


Fig. 1 Orbital interaction between 2,3-dimethylene-2,3-dihydroquinoxazline and C_{60} or *N*-phenylmaleimide.

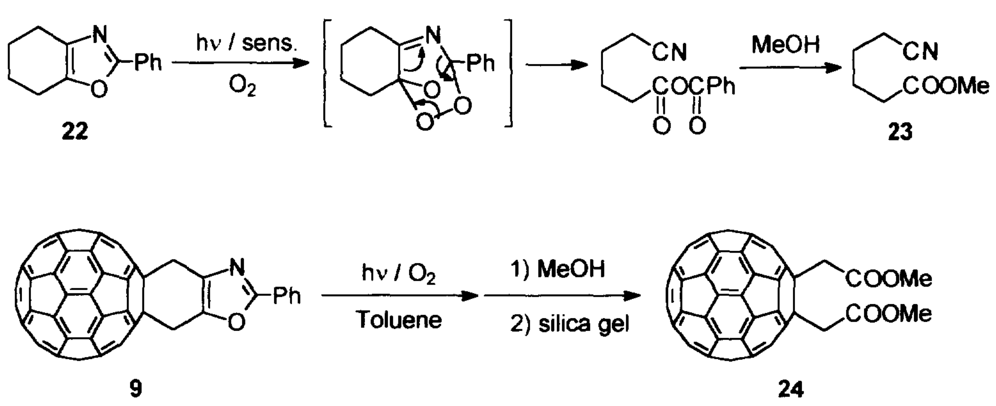
Among these cycloadducts obtained, the furan and oxazole derivatives were found to be photosensitive if not shielded from room and sun lights.[21] Nevertheless, this property is conceivable since C_{60} is known as a good sensitizer for producing singlet oxygen,[12] and in fact, furan is devoted to examine a sensitizing ability of C_{60} itself and its derivatives.[22] If C_{60} is connected with a $^1O_2$-labile functional group, photolysis of this system results in self-sensitized photooxygenation.[23] Foote et al. reported the first example of this type by using an ynamine-C_{60} cycloadduct.[24] We scrutinized the intended photooxygenation of these derivatives. Firstly, a toluene solution of the furan-containing C_{60} derivative **3** including methanol was irradiated with 500 W sun lamp under an atmosphere of oxygen. The reaction was found to occur within 10 min. After evaporation of the solvent, the reaction mixture which consisted of two major products (HPLC analysis) were subjected to silica gel chromatography by which only one product was isolated; it was assumed that one product changed to the other product during this operation. Further purification with preparative HPLC gave a desired photooxygenated product, and the structure was assigned to be epoxy γ-lactone **21** on the analogy of the reported menthofuran case (*i.e.*, **19** → **20**)[25] as shown in Scheme 8.

FAB-MS peaks were observed at m/z 846 (M), 802 (M-CO_2), 720 (base), suggesting that O_2 was added to the molecule. The ^{1}H-NMR indicated no enone olefinic signal but AB quartet signals at δ 3.28 and 3.42 (each 1 H, d, J=18.5 Hz) together with cyclohexane ring methylene at δ 4.12, 4.24, 4.32 and 4.49 (each 1 H, d, J=15.0 Hz). It is reasonable to estimate that the primary product formed is a 4-hydroxybutenolide such as **20** according to the result of the reaction of menthofuran which proceeds through collapsing of an endo-peroxide cycloadduct. In this case, however, the rigid framework of C_{60} seems to force the hydroxyl group on the butenolide ring to be eclipsed with p-orbital of C_2-C_3 double bond (model study). Therefore, the epoxide may instead arise (contact with silica gel might assist the conversion of 4-hydroxybutenolide to 3,4-epoxybutanolide) and explain the above spectrum . The ^{13}C-NMR were consistent with this partial structure as was shown by the signals at δ 36.12, 37.39, 39.70, 58.87 and 86.49 together with a carbonyl signal at δ 171.46. The signals due to C_{60} were observed at δ 60.97 and 61.27 for sp^3-carbons and at δ 125.43-156.74 (53 lines) for sp^2-carbons.



Scheme 8

Similarly, the oxazole derivative **9** was irradiated in toluene for 30 min and then treated with methanol for 3 days. The closely related reaction of an oxazole **22** was previously reported by Wasserman as shown in Scheme 9;[26] the major product was formed *via* [4+2]cycloaddition of singlet oxygen, rearrangement to 5-cyanopentanoic benzoic anhydride, and methanolysis to the cyano ester **23**. In the case of the oxazole-linked [60]fullerene **9**, however, the treatment with methanol for a long time to ensure methanolysis might result in further conversion of the once formed cyano ester (such as **23**) into an imidate ester with catalytic action of benzoic acid which should be formed as a byproduct on methanolysis. Although this intermediacy was not checked, the final product diester **24** could be produced probably by hydrolysis during silica gel chromatography. The structure was firstly supported by FAB-MS molecular ion peak at m/z 866 and definitively confirmed by only two singlet signals due to a CH_2COOCH_3 moiety in the ^{1}H-NMR and 17 lines due to a C_{60} framework, characteristic of C_{2v}-symmetry, in the ^{13}C-NMR. The IR spectrum had an absorption band at 1736 cm^{-1}due to the ester group but no sign of a cyano group.



Scheme 9

In conclusion, a variety of heterocycle-linked C_{60} derivatives were supplied by Diels-Alder methodology using heteroaromatic analogs of *o*-quinodimethanes, and the results indicate the usefulness of this reaction to introduce heterocycles on the fullerene surface.[27] Among the cycloadducts obtained, the furan and oxazole derivatives were shown to be prone to self-sensitized photooxygenation.

EXPERIMENTAL

IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained with Varian XL500 spectrometer at 500 and 125 MHz, respectively, for sample in $CDCl_3$ or $CDCl_3/CS_2$ solution with $SiMe_4$ as internal standard. *J*-Values are given in Hz. FAB-mass spectra were obtained with JEOL JMS-AX 505HA mass spectrometer using *m*-nitrobenzylalcohol as a matrix (negative ion mode). UV/vis spectra were recorded on SHIMAZU UV-2200. Flash chromatography for separation of products was performed on a silica gel column (Fuji-Davison BW-300) eluted with the mixed solvents noted. HPLC was performed with JASCO 880-PU, 875-UV (at 340 nm) using a column of Buckyprep Waters (4.6 × 250 mm) for analysis, and JASCO PU-986, UV-976 (at 340 nm) using a column of Buckyprep Waters (10 × 250 mm) for separation. Halobenzene was dried over 4Å molecular sieve, and toluene over Na.

Diels-Alder Reaction of C_{60} with 2,3-Dimethylene-2,3-dihydrofuran (2).

According to the Trahanovsky's method,[13] 2-methyl-3-furylmethyl 4-chlorobenzoate (**1**) (23.6 mg, 0.09 mmol) was vaporized at 100 °C/0.2 mmHg and pyrolyzed by passing through a quartz tube heated to 620 °C with an electric furnace. The pyrolysate including **2** was collected with liquid nitrogen-cooled trap and mixed with a solution of C_{60} (43.2 mg, 0.06 mmol) in chlorobenzene (12 ml) in an ice-salt bath. The solution was gradually warmed to room temperature and stirred overnight, while the mixture was covered with an aluminum foil to shield from light (Similarly, the product should be protected from light throughout the following operations). After removal of the solvent in a vacuum, the residue was chromatographed on a silica gel column eluted with hexane to remove unreacted C_{60} (3.3 mg) and then with hexane/toluene 85/15 to give a 1:1 cycloadduct **3** (15.7 mg, 35% yield based on consumed C_{60}): FAB-MS m/z 814 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 527; UV/vis (hexane) λ (nm) 432; ^{1}H-NMR ($CDCl_3$) δ 4.50 (s, 2 H), 4.67 (s, 2 H), 6.77 (d, *J*=2.0 Hz, 1

H), 7.62 (d, J=2.0 Hz, 1 H); ^{13}C-NMR ($CDCl_3$) δ 39.39, 39.91, 66.62, 66.76, 110.65, 118.71, 135.47, 135.60, 140.28, 140.35, 141.74, 141.76, 141.90, 142.13, 142.23, 142.26, 142.32, 142.45, 142.75, 143.20, 143.27, 144.69, 144.81, 145.01, 145.14, 145.33, 145.55, 145.60, 145.63, 145.64, 145.91, 146.37, 146.65, 146.67, 147.81, 151.36, 156.83, 157.25. FAB HRMS obsd 814.0410, calcd for $C_{66}H_6O$ 814.0419.

Diels-Alder Reaction of C_{60} with 2,3-Dimethylene-2,3-dihydrothiophene (5).

The mixture of 2,3-bis(bromomethyl)thiophene (**4**)[14] (20 mg, 0.075 mmol), C_{60} (36 mg, 0.05 mmol), potassium iodide (25 mg, 0.15 mmol) and 18-crown-6 ether (158 mg, 0.6 mmol) in toluene was heated to reflux under N_2 in a sealed tube for 2 h. After evaporation of the solvent, separation by silica gel chromatography (hexane, hexane/toluene 9/1, and then hexane/toluene 4/1) gave a 1:1 adduct **6** (8.9 mg, 36%) and a mixture of 1:2 adducts (4.3 mg, 15%) with 14.5 mg (40%) of recovered C_{60}.

Spectral data of the 1:1 adduct: FAB-MS m/z 830 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 527; UV/vis (hexane) λ (nm) 433; ^{1}H-NMR ($CDCl_3$) δ 4.63 (s, 2 H), 4.75 (s, 2 H), 7.40 (d, J=5.0 Hz, 1 H), 7.47 (d, J=5.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 41.16, 41.89, 66.90, 67.25, 123.69, 127.22, 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, 146.76, 147.93, 147.94, 156.77, 157.19. FAB HRMS obsd 830.0176, calcd for $C_{66}H_6S$ 830.0190.

Diels-Alder Reaction of C_{60} with 4,5-Dimethylene-4,5-dihydro-2-phenyloxazole (8).

In the following operations, the same care as for the aforementioned furan case was required. The mixture of 2-phenyl-4,6-dihydrothieno[3,4-*d*]oxazole-5,5-dioxide (**7**)[15] (18 mg, 0.077 mmol) and C_{60} (31.4 mg, 0.044 mmol) in chlorobenzene (13 ml) was heated to reflux under N_2 in a sealed tube for 2 h. After removal of the solvent, the residue was chromatographed on a silica gel column with hexane/toluene (1/1) to remove unreacted C_{60} (3.8 mg) and with toluene to give a 1:1 cycloadduct **9** (13.3 mg, 39%): FAB-MS m/z 891 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 527; UV/vis (hexane) λ (nm) 432; ^{1}H-NMR ($CDCl_3/CS_2$ 1/1) δ 4.69 (s, 2 H), 4.84 (s, 2 H), 7.49-8.19 (m, 5 H); ^{13}C-NMR ($CDCl_3/CS_2$ 1/1) δ 38.59, 40.22, 66.20, 66.26, 126.40, 127.80, 128.64, 128.97, 129.72, 130.35, 135.15, 135.52, 136.83, 140.25, 140.39, 141.69, 141.73, 142.16, 142.23, 142.28, 142.70, 142.72, 142.82, 143.20, 144.66, 144.72, 144.77, 145.01, 145.54, 145.57, 145.59, 145.63, 145.82, 146.31, 146.33, 146.59, 146.65, 146.75, 146.73, 156.12, 156.70. FAB HRMS obsd 891.0687, calcd for $C_{71}H_9NO$ 891.0684.

Diels-Alder Reaction of C_{60} with 4,5-Dimethylene-4,5-dihydrothiazole (11).

In the preparation of 4,6-dihydrothieno[3,4-*d*]thiazole-5,5-dioxide (**10**), the reported two-step conversion from 3-sulfolene to 3-bromo-4-hydroxysulfolane[16] was carried out by our own one-step procedure; to a solution of 3-sulfolene (3.54 g, 30 mmol) in water (100 ml) was added *N*-bromosuccinimide (10.68 g, 60 mmol) in small portions at room temperature. The mixture was warmed to 70 °C and stirred for 3 h. The white precipitates formed on cooling at 0 °C were separated by filtration. The collected precipitates were further suspended in fresh water (40 ml) and stirred for 1 h at room temperature to remove the remaining succinimide. Filtration gave 3-bromo-4-hydroxysulfolane (4.44 g, 69%); mp 194-195 °C (lit.[16] mp 192-193 °C).

A solution of **10** (7.9 mg, 0.045 mmol), C_{60} (21.6 mg, 0.03 mmol) in *o*-dichlorobenzene (3 ml) was heated at 180 °C in a sealed tube under N_2 for 1 h. After removal of the solvent, the residue was chromatographed on a silica gel column eluted with hexane/toluene 1/1 to remove unreacted C_{60} (3.6 mg) and with toluene to give a 1:1 cycloadduct **12** (10.6 mg, 51%): FAB-MS m/z 831 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 527; UV/vis (1,4-dioxane) λ (nm) 432; ^1H-NMR ($CDCl_3/CS_2$ 1/1) δ 4.82 (s, 2 H, cyclohexane ring CH_2), 4.83 (s, 2 H, cyclohexane ring CH_2), 8.93 (s, 1 H, thiazole ring CH); ^{13}C-NMR ($CDCl_3/CS_2$ 1/1) δ 39.78 (cyclohexane ring carbon), 42.24 (cyclohexane ring carbon), 66.58 (C_{60} fusion sp^3 carbon), 66.63 (C_{60} fusion sp^3 carbon), 128.84, 135.43, 135.85, 140.27, 140.37, 141.73, 141.78, 142.13, 142.21, 142.24, 142.27, 142.70, 142.73, 143.21, 144.66, 144.81, 145.02, 145.16, 145.56, 145.59, 145.62, 145.64, 145.78, 146.33, 146.36, 146.60, 146.65, 147.73, 147.80, 151.04, 154.47, 155.81, 156.43. FAB HRMS obsd 831.0149, calcd for $C_{65}H_5NS$ 831.0143.

Diels-Alder Reaction of C_{60} with *N*-Benzoyl-2,3-dimethylene-2,3-dihydroindole (14).

The mixture of *N*-benzoyl-2,3-bis(bromomethyl)indole (**13**)[17] (36.6 mg, 0.09 mmol), C_{60} (43.2 mg, 0.06 mmol), potassium iodide (30 mg, 0.18 mmol) and 18-crown-6 ether (48 mg, 0.18 mmol) in toluene (25 ml) was heated to reflux under N_2 in a sealed tube for 2 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluted with hexane/toluene 85/15 to remove unreacted C_{60} (4.3 mg, 10%) and with toluene to give a 1:1 cycloadduct **15** (25.2 mg, 48%): FAB-MS m/z 967(M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1686, 527; UV/vis (hexane) λ (nm) 432; ^1H-NMR ($CDCl_3/CS_2$ 1/1) δ 4.69 (s, 2 H, cyclohexane ring CH_2), 4.72 (s, 2 H, cyclohexane ring CH_2), 7.09-7.85 (m, 9 H, phenyl ring H); ^{13}C-NMR ($CDCl_3/CS_2$ 1/1) δ 38.01 (cyclohexane ring carbon), 40.28 (cyclohexane ring carbon), 66.44 (C_{60} fusion sp^3 carbon), 66.80 (C_{60} fusion sp^3 carbon), 115.70, 118.27, 119.78, 123.68, 124.34, 125.42, 128.32, 128.60, 129.08, 129.74, 132.92, 135.45, 135.53, 135.56, 136.89, 137.45, 137.64, 140.20, 140.34, 141.69, 141.73, 142.18, 142.26, 142.38, 142.71, 143.18, 144.72, 144.75, 145.14, 145.26, 145.55, 145.57, 145.60, 145.81, 146.33, 146.59, 146.62, 147.74, 156.31, 156.76, 168.36 (C=O). FAB HRMS obsd 967.1023, calcd for $C_{77}H_{13}NO$ 967.0997.

Diels-Alder Reaction of C_{60} with 2,3-Dimethylene-2,3-dihydroquinoxaline (17).

The mixture of 2,3-bis(bromomethyl)quinoxaline (**16**)[18] (23.7 mg, 0.075 mmol), C_{60} (36 mg, 0.05 mmol), potassium iodide (187 mg, 1.13 mmol) and 18-crown-6 ether (297 mg, 1.13 mmol) in chlorobenzene (18 ml) was heated to reflux under N_2 in a sealed tube for 2 h. After the solvent was removed under reduced pressure, the residue was washed with acetone and chromatographed on silica gel column eluted with hexane/toluene 4/1 to remove unreacted C_{60} (2.5 mg, 7%) and with toluene to give a 1:1 cycloadduct **18** (11.0 mg, 27.0%): FAB-MS m/z 876(M), 720 (base peak); IR (KBr) ν (cm^{-1}) 527; UV/vis (1,4-dioxane) λ (nm) 433; ^1H-NMR ($CDCl_3/CS_2$ 1/1) δ 4.95 and 5.18 (br s, each 1 H), 7.86 (dd, *J*=3.5 and 6.5 Hz, 2 H), 8.26 (dd, *J*=3.5 and 6.5 Hz, 2 H); ^{13}C-NMR ($CDCl_3/CS_2$ 1/1) δ 47.69, 64.73, 128.33, 129.09, 129.61, 130.00, 135.34, 140.33, 141.69, 141.97, 142.18, 142.70, 142.91, 144.72, 145.56, 145.84, 146.36, 146.58, 147.78, 153.40, 155.39. FAB HRMS obsd 876.0677, calcd for $C_{70}H_8N_2$ 876.0687.

Self-Sensitized Photooxygenation of The Furan Derivative 3.

A solution of **3** (9.8 mg, 0.012 mmol) in toluene (4 ml) including 10 drops of methanol was irradiated with 500 W tungsten lamp for 10 min, under an atmosphere of oxygen. After evaporation of the solvent, the product was separated roughly with a silica gel column (toluene) and then completely with HPLC (toluene) to give a γ-lactone **21** (4.8 mg, 47%): FAB-MS m/z 846 (M), 802, 720 (base peak); IR (KBr) ν (cm^{-1}) 1813, 527;

UV/vis (1,4-dioxane) λ (nm) 433; ^{1}H-NMR ($CDCl_3/CS_2$ 1/1) δ 3.28 (d, *J*=18.5 Hz, 1 H), 3.42 (d, *J*=18.5 Hz, 1 H), 4.12 (d, *J*= 15.0 Hz, 1 H), 4.24 (d, *J*=15.0 Hz, 1 H), 4.32 (d, *J*=15.0 Hz, 1 H), 4.49 (d, *J*=15.0 Hz, 1 H); ^{13}C-NMR ($CDCl_3/CS_2$ 1/1) δ 36.12, 37.39, 39.70, 58.87, 60.97, 61.27, 86.49, 125.43, 128.33, 129.10, 133.87, 133.90, 136.75, 136.81, 140.29, 140.36, 140.38, 140.41, 141.42, 141.51, 141.74, 141.77, 141.87, 141.91, 142.02, 142.18, 142.20, 142.27, 142.73, 142.76, 142.79, 143.36, 143.40, 144.50, 144.65, 144.74, 144.87, 144.92, 145.02, 145.49, 145.53, 145.58, 145.61, 145.63, 145.70, 145.80, 145.87, 146.05, 146.30, 146.45, 146.49, 146.58, 146.62, 146.64, 147.89, 147.92, 154.92, 155.04, 156.45, 156.74, 171.46. FAB HRMS obsd 846.0311, calcd for $C_{66}H_6O_3$ 846.0317.

Self-Sensitized Photooxygenation of The Oxazole Derivative 9.

A solution of **9** (23.1 mg, 0.026 mmol) in toluene (50 ml) was irradiated with 500 W tungsten lamp for 30 min under an atmosphere of oxygen. Then, dry methanol (10 ml) was added and the solution was further stirred at room temperature for 3 days. After evaporation of the solvent, the product was chromatographed on a silica gel column eluted with toluene to give an unidentified product (1.8 mg; this compound may be a same type of byproduct obtained in the related experiment by Wasserman[26]) and a diester **24** (5.7 mg, 25%): FAB-MS m/z 866 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1736, 527; UV/vis (hexane) λ (nm) 430; ^{1}H-NMR ($CDCl_3/CS_2$ 1/1) δ 3.97 (s, 3 H), 4.70 (s, 2 H); ^{13}C-NMR ($CDCl_3/CS_2$ 1/1) δ 46.00, 52.55, 62.60, 128.85, 130.82, 136.36, 139.89, 141.53, 141.85, 142.29, 142.69, 143.17, 144.80, 144.90, 145.55, 145.59, 146.32, 146.64, 156.09, 172.62. FAB HRMS obsd 866.0580, calcd for $C_{66}H_{10}O_4$ 866.0579.

Calculations

FMO's of 2,3-dimethylene-2,3-dihydroquinoxaline (**17**), *N*-phenylmaleimide and C_{60} were calculated using MNDO PM3 by HyperChem® 4.0 (HyperCube Inc.) on IBM-PC compatible computer.

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