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1,3-Dipolar cycloaddition reaction of [60]fullerene with thiocarbonyl ylide and synthetic application of the cycloadduct

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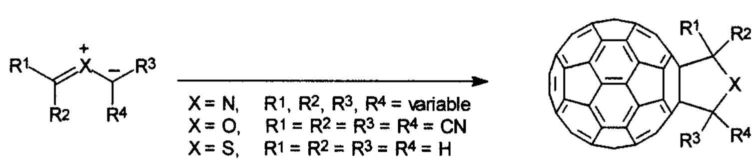
Abstract—C_{60} reacted with a thiocarbonyl ylide generated by thermal sila-Pummerer rearrangement of bis(trimethylsilylmethyl) sulfoxide to give a tetrahydrothiophene-fused derivative. The corresponding sulfoxide was obtained by oxidation with *m*-CPBA and further converted into α-acetoxyltetrahydrothiophene derivative by usual Pummerer rearrangement. The O,S-acetal-like moiety in this compound was utilized for electrophilic substitution which is favorable for fullerene chemistry, allowing introduction of various functional groups near the fullerene surface. © 2001 Elsevier Science Ltd. All rights reserved.

One of the fundamental applications of [60]fullerene is surface modification by organic synthesis, and a variety of methods for addition of functional groups to the spherical double bond have been developed in these years, ranging from nucleophilic, electrophilic and radical additions to concerted and stepwise cycloadditions.[1] Heterocyclic ring systems construct interesting combinations with this all sp^2-carbons ring system, and these have been successfully introduced on its surface mostly relying on the concerted manner. So far, three-, five-, and six-membered heterocycles are exemplified to fuse with [60]fullerene. Fusion with oxirane and aziridine was highlighted in the early stage,[2] and fusion with six-membered heterocycles was extended on the basis of the hetero-Diels–Alder reaction.[3] In association with these results, fusion with five-membered heterocyclic rings have been performed by using various 1,3-dipolar cycloaddition reactions.[1,4] This ring system with one hetero-atom is representative among them, and the pyrrolidine ring has been widely utilized to construct donor (a substituent on the pyrrolidine)–acceptor (fullerene core) hybrids.[5] On the other hand, the tetrahydrofuran ring has been demonstrated in only one case,[6] and the tetrahydrothiophene ring was not reported until we have undertaken synthesis of its prototype (Scheme 1). The first successful example was communicated for the reaction of [60]fullerene with a thiocarbonyl ylide generated by thermal sila-Pummerer rearrangement of bissilylated dimethylsulfoxide.[7]

Based on this synthesis, we have developed a new method for introduction of functionalities near the fullerene surface via the usual Pummerer rearrangement of the primary cycloadduct followed by acid-catalyzed electrophilic substitution. Furthermore, a mixture of bis-adducts was prepared from the pharmacological interest. In this paper, we wish to report the detailed results of these reactions.

1. Results and discussion

Thiocarbonyl ylides have been widely used for the construction of a tetrahydrothiophene ring preferably with electron-deficient olefins.[8] This trend is promising for 1,3-dipolar cycloaddition reaction with low-LUMO lying [60]fullerene. Recent development in the method of generation of this 1,3-dipole prompted us to use organosilicon chemistry (Achiwa's and Hosomi's methods). Although elimination reactions of bromo(trimethylsilyl)methyl trimethylsilylmethyl



Scheme 1.

Keywords: [60]fullerene; thiocarbonyl ylide; tetrahydrothiophene; Pummerer rearrangement; electrophilic substitution.
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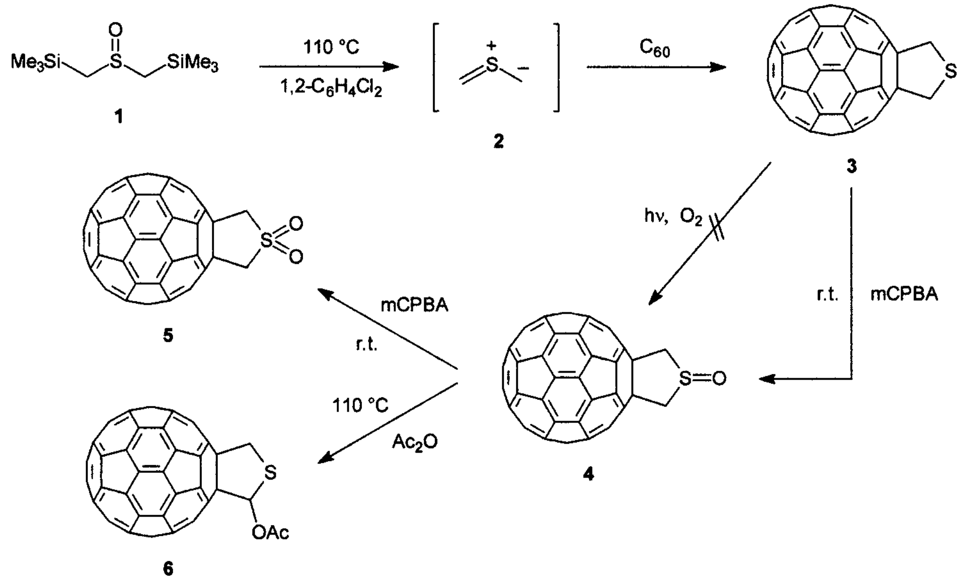


Scheme 2.

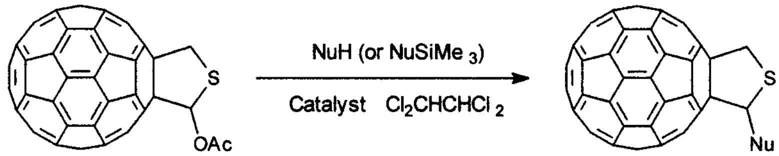
sulfide (thermolysis)[9] and chloromethyl trimethylsiylmethyl sulfide (CsF-catalysis)[10] could not be applied successfully to the cycloaddition with C_{60}, thermal sila-Pummerer rearrangement of bis(trimethylsilylmethyl) sulfoxide (**1**)[11] afforded the desired cycloadduct of C_{60} (Scheme 2). Thus, C_{60} reacted smoothly within a short period (10 min) with prototypical thiocarbonyl ylide (**2**) generated from **1** (1.2 equiv.) under heating conditions (110°C) in *o*-dichlorobenzene under an argon atmosphere. Although unreacted C_{60} could not be removed completely from the product by silica gel chromatography and even preparative HPLC, the structure of 1:1 cycloadduct was deduced as fullerotetrahydrothiophene (**3**) by informative spectral data without interference of pristine C_{60}; the expected molecular ion peak was shown at *m*/*z* 780 by FAB-MS, and the requisite C_{2v}-symmetricity was supported by ^{1}H and ^{13}C NMR with signals at δ 4.71 (s) due to tetrahydrothiophene ring methylene protons, and 16 lines (δ 136.37–154.88) due to core sp^2-carbons and 2 lines (δ 51.12 and 73.39) due to tetrahydrothiophene ring and junction sp^3-carbons, respectively.

Sulfides are known to be oxidized to sulfoxides with singlet oxygen.[12] This oxidant is produced effectively by photosensitization of a 1:1 cycloadduct of C_{60}.[13] Therefore, the sulfide functionality on the addend is intrinsically incompatible with fundamental nature of C_{60}. In fact, it was observed in our recent study that a methyl sulfide group was prone to self-sensitized photooxygenation at the remote position.[14] Nevertheless, the cyclic sulfide **3** remained intact under exposure to room light, indicating that it could be handled without regard for light. Since precedent fullerothiochroman was also insensitive,[3a] such stability seems to be attained by an electronic effect; this type of oxidation is initiated by nucleophilic attack of the sulfide group on the O=O bond,[12] yet nucleophilicity of this group near the fullerene core is decreased considerably by an interaction between the sulfur lone pair and the C_{60} cage.[15]

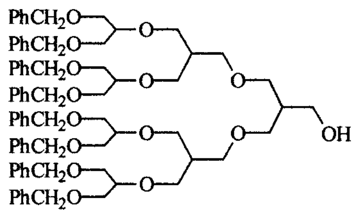
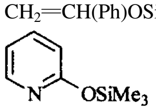
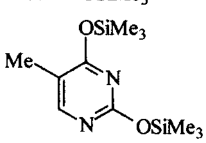
The oxidation of **3** to the corresponding sulfoxide **4** was realized by chemical conversion with *m*-chloroperbenzoic acid (*m*-CPBA). The product **3**, which was obtained without purification from the above cycloaddition reaction, was treated directly with *m*-CPBA (1 equiv.) at room temperature for 1 h to give **4** in 41% overall yield (61% yield based on consumed C_{60}). In this case, the polarized product and unreacted C_{60} were easily separable by flash chromatography on a silica gel column, and the structure of isolated **4** was determined unambiguously by the spectral data. FAB-MS peaks at *m*/*z* 796 (M) and 720 (C_{60}) and IR absorptions at 527 cm^{-1} (C_{60}) and 1067 cm^{-1} (S=O) indicated the 1:1-cycloadduct at 6,6-junction. ^{1}H and ^{13}C NMR evidenced the C_s-symmetric sulfoxide structure by a couple of doublet signals at δ 4.57 and 5.16 (J=13.5 Hz) due to tetrahydrothiophene ring methylene protons, and by 27 lines (δ 134.40–154.53) due to spherical sp^2-carbons and 2 lines (δ 65.36 and 71.26) due to tetrahydrothiophene ring and junction sp^3-carbons, respectively. The further oxidation of sulfoxide **4** to sulfone **5** was conducted under the same conditions as above, and the product was chromatographed on a silica gel column to give **5** in 73% yield (Scheme 2). Its structure returned again to C_{2v} symmetry, which was elucidated clearly by the spectral data analogous to **3**: FAB-MS *m*/*z* 812 (M), 748 (M−SO_2), 720 (C_{60}); IR 1329, 1137 (SO_2), 527 (C_{60}) cm^{-1}; ^{1}H NMR δ 4.91 (s); ^{13}C NMR δ 50.35, 63.66, 136.27–152.41 (16 lines).

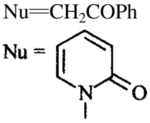
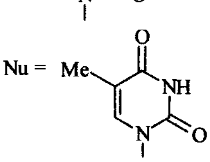
Usually, sulfoxides and sulfones are exploited in synthesis by the process of α-hydrogen abstraction with a strong base followed by nucleophilic substitution.[16] However, it is obvious that such nucleophilic conditions, if employed for functional conversion on the addend, are incompatible with the fullerene core (because of the low LUMO level). On the contrary, the Pummerer rearrangement of sulfoxides[17] affords α-acyloxy sulfides, which is regarded as an α-activated form and applicable to electrophilic substitution; this method is much suitable for derivatization of fullerene. Fortunately, the Pummerer rearrangement of sulfoxide **4** was successfully carried out by heating a solution of **4** in 1,1,2,2-tetrachloroethane including excess acetic anhydride

Table 1. Electrophilic substitution reaction of **6** with various nucleophiles



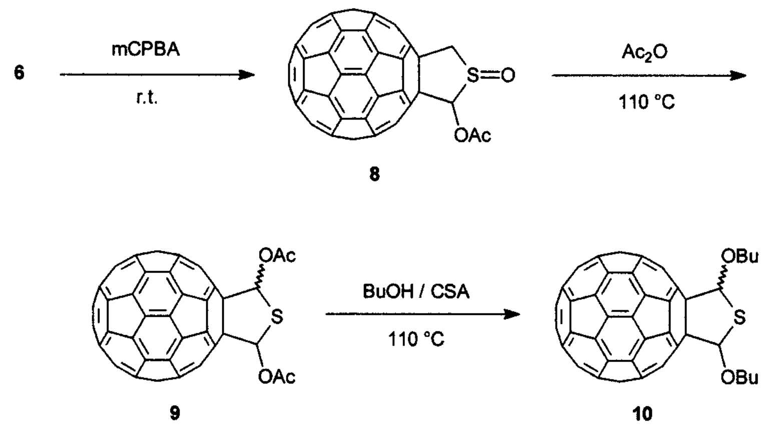
6 **7**

Entry	NuH	Catalyst	Temperature (°C)	Time (h)	Product	Yield (%)
1	$CH_2{=}CHCH_2OH$	TMSOTf	rt	3.5	**7a**	63
2	$CH_3CH_2CH_2OH$	CSA	110	16	**7b**	99
3	$(CH_3)_2CHCH_2CH_2OH$	CSA	120	13	**7c**	88
4	$HOCH_2(CH_2)_4CH_2OH$	CSA	100	15	**7d**	88
5	CF_3CH_2OH	CSA	100	15	**7e**	80
6	$PhCH_2OCONHCH_2CH_2CH_2OH$	CSA	110	22	**7f**	60[a]
7	$(CH_3)_2CHOH$	CSA	120	32	**7g**	95
8	$(CH_3CH_2)_2CHOH$	CSA	120	17	**7h**	79
9	$(BrCH_2)_2CHOH$	CSA	120	14	**7i**	78
10	$[(CH_3)_2CH]_2CHOH$	CSA	150	5	**7j**	90
11		CSA	100	40	**7k**	43[b]
12	MeO_2CCH_2SH	CSA	110	6	**7l**	93
13	$CH_2{=}CHCH_2SiMe_3$	TMSOTf	rt	17	**7m**	82
14	$CH_2{=}C(CH_3)CH_2SiMe_3$	TMSOTf	rt	28	**7n**	67
15	$CH_2{=}C(CH_2SiMe_3)CH_2CO_2Me$	TMSOTf	rt	25	**7o**	67
16	$CH_2{=}CH(Ph)OSiMe_3$	$TiCl_4$	rt	8	**7p**[c]	75
17		TMSOTf	rt	7	**7q**[d]	56
18		TMSOTf	rt	18	**7r**[e]	98

[a] 82% Yield based on consumed **6**.
[b] 87% Yield based on consumed **6**.
[c] Nu=CH_2COPh
[d] 
[e] 

at 110°C under an argon atmosphere for 4 h. Thereby, α-acetoxytetrahydrothiophene derivative **6** was obtained in 80% yield after chromatographic separation (Scheme 2). Determination of the structure of **6** was based on the spectral data; in this case, FAB-MS peaks [*m/z* 838 (M), 720 (C_{60})] and IR absorptions [1752 (OAc), 527 (C_{60}) cm^{-1}] were routinely assignable, but introduction of an α-substituent caused loss of symmetry, resulting in more complex NMR patterns. In the ^1H NMR spectra, signals due to ring protons were observed at δ 4.70 (dd, J=12.0, 1.5 Hz, 1H), 5.14 (d, J=12.0 Hz, 1H) and 7.68 (d, J=1.5 Hz, 1H); the last methine proton appeared at quite low field due to sum of deshielding effect of two hetero atoms and C_{60} core, while acetoxy methyl protons appeared at δ 2.32 (s). In the ^{13}C NMR spectra, two sp^3 junction carbons and sp^2 spherical carbons were observed at δ 73.19 and 79.35 and at δ 136.46–152.22 (52 lines), respectively, together with acetoxy and ring carbons at δ 22.25, 48.27, 90.71 and 170.52.

The α-acetoxylated tetrahydrothiophene **6** obtained as above has O,S-acetal-like reactivity, and acid-catalyzed electrophilic substitution should be operative to introduce some interesting functions near the fullerene surface. This reaction involves a mechanism participated with an carbocation intermediate adjacent to 1,2-dihydrofullerenyl group,



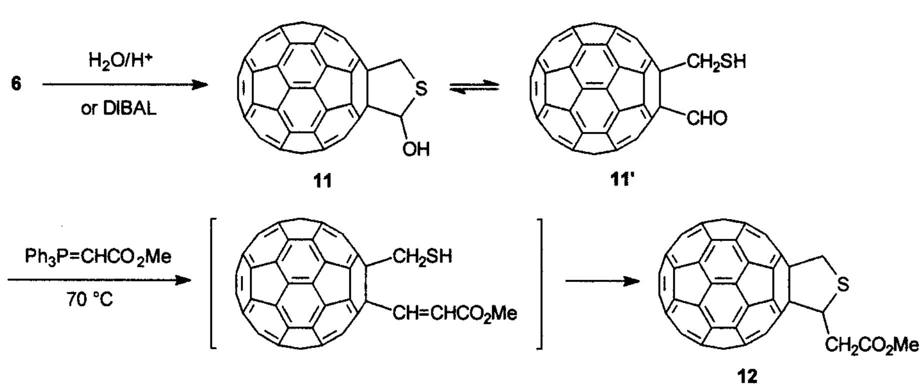
Scheme 3.

and this situation has been rarely encountered until now.[3b] Firstly, replacement with allyl alcohol was examined. Thus, **6** was allowed to react with large excess of allyl alcohol under catalytic conditions with equimolar amount of trimethylsilyl trifrate (TMSOTf) at 0°C and then at room temperature for 3.5 h. Usual work-up and chromatographic separation gave the expected substitution product **7a** in 63% yield (Table 1, entry 1). Under these conditions the related reaction with *n*-propyl alcohol was not effected to give **7b**, and forced conditions (60°C, 8 h) merely raised the yield up to 20% yield. Neither *p*-toluenesulfonic, trifluoroacetic, and trifluoromethanesulfonic acids nor $BF_3{\cdot}Et_2O$ catalyzed effectively (rt −70°C, 5–72 h: 0–10% yields). However, catalysis with camphorsulfonic acid (CSA) was hopeful (60°C, 72 h: 25% yield), and the yield reached 99% under heating conditions at 110°C for 16 h (entry 2). With these results in hand, the reactions with other primary and secondary alcohols were accomplished similarly to give the corresponding products **7c–j** in satisfactory yields. It is noted that a bulky alcohol such as 2,4-dimethyl-3-pentanol (entry 10), elongated from 2-propanol (entry 7) and 3-pentanol (entry 8), was reactive enough despite of steric hindrance due to the fullerene surface. Hence, in addition to halogen, hydroxyl and protected amino groups (entries 4, 5, 6 and 9), a dendritic groups leading to **7k** could be introduced by this method (entry 11). In analogy with these alcohols, a mercaptan was used to give **7l** (entry 12). Unsaturated organosilanes are other nucleophiles, and thereby, some allyl and phenacyl groups were appended as shown in entries 13–16 through the related electrophilic substitution reaction using the corresponding organosilicon reagents (catalyst: TMSOTf for **7m–o** and $TiCl_4$ for **7p**). Likewise heterocycles were attached (entries 17 and 18); after the model of a pyridone derivative **7q**, a thymine derivative **7r** was also obtained.[18] These results are summarized in Table 1.

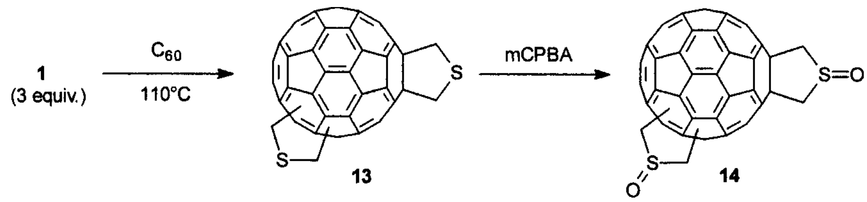
Interestingly, a series of reactions including *m*-CPBA oxidation, Pummerer rearrangement and acetal substitution at the α′-position of the tetrahydrothiophene ring could lead to the formation of a doubly substituted product[19] (**6** → **8** → **9** → **10**) as illustrated in Scheme 3.

As a result, steric and electronic effects of the fullerene core might influence the reactivity of an α-carbocation intermediate,[20] but if any, **6** underwent substitution reaction with various nucleophilic reagents, showing usefulness of **6** for introduction of functional groups near the fullerene surface.

In association with the above electrophilic substitution, thiolactol **11** was obtained from **6** by hydrolysis or reduction with diisobutylaluminum hydride (DIBAL). This heterocyclic ring is possible to tautomerize with an open-chain compound of mercapto aldehyde **11′**, which can afford an alternative functionalization route. Thus, a phosphorous ylide was allowed to react with **11** at 70°C, and an tetrahydrothiopheneacetate **12** was obtained as a substitution



Scheme 4.



Scheme 5.

type product in 36% yield as a result of condensation of **11′** with the ylide followed by intramolecular Michael addition as shown in Scheme 4.

The structure of all obtained α-substituted tetrahydrothiophenes **7–12** were interpreted by analogy with monosubstituted **6**; in the ^{1}H NMR spectra, characteristic coupling patterns were always observed in tetrahydrothiophene ring protons (vide supra), and complex coupling patterns were also observed due to diastereotopic methylene protons at the side chain. The other spectral data (^{13}C NMR, IR and MS) were obtained as expected.

Next attempted is multiaddition of the thiocarbonyl ylide. As was indicated in the foregoing reaction, the monoadduct **3** could be obtained with moderate selectivity if the ylide reagent **1** was used in slight excess. When the large excess of **1** (30 equiv.) was applied to C_{60}, a regioisomeric mixture of multiadducts, which was judged qualitatively by 13 peaks in HPLC analysis, was formed. The present addend is not so sizable that the observed behavior is not unexpected.[21] Nevertheless, bis-adduct of sulfoxide is attractive even as a mixture form from a pharmacological interest in relation to bis-pyrrolidinium salt, which was shown to inhibit *E. coli* growth.[22] Thus, a mixture product of bis-adducts **13** was prepared by the use of 3 equiv. of **1**, and further oxidized with *m*-CPBA to the corresponding mixture of bis-sulfoxides **14** to provide for a pharmacological test (Scheme 5).[23]

In conclusion, heterocyclization of [60]fullerene was performed by 1,3-dipolar cycloaddition reaction with thiocarbonyl ylides to give the corresponding tetrahydrothiophene-fused C_{60} derivatives. The prototypical 1:1 cycloadduct **3** was found to be insensitive to self-sensitized photooxygenation to the corresponding sulfoxide **4**. On the other hand, this sulfoxide was obtained by action of *m*-CPBA and further converted into the α-acetoxylated terahydrothiophene **6**, which was utilized for introduction of various functional groups near the fullerene surface under favorable electrophilic conditions. Although no appreciable selectivity was seen in an attempted multiaddition reaction with the unsubstituted thiocarbonyl ylide, a mixture of bis-sulfoxides was prepared for a pharmacological test.

2. Experimental

2.1. General

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 Hz, respectively, for sample in a designated solution with Me_4Si as internal standard. *J*-Values are given in Hz. FAB-mass spectra were obtained with JEOL JMS-AX 505HA mass spectrometer using *m*-nitrobenzyl alcohol as a matrix (negative ion mode). MALDI-TOF mass spectra were obtained with PE Biosystems Voyager System 6119. 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 solvent 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 4 Å molecular sieve, and toluene over Na.

2.1.1. 1,3-Dipolar cycloaddition reaction of C_{60} with bis(trimethylsilylmethyl) sulfoxide (1). According to Achiwa's method, a solution of C_{60} (108 mg, 0.15 mmol) and **1** (33 mg, 0.15 mmol) in *o*-dichlorobenzene (15 ml) was stirred under an argon atmosphere in a sealed tube and heated at 110°C for 10 min. After the solvent was removed under vacuum, the residue was chromatographed on a silica gel column eluted with hexane to give recovered C_{60} (18 mg, 17%) and crude fullerotetrahydrothiophene (**3**) (88 mg) including inseparable C_{60} (ca. 48% by HPLC analysis). Further purification with HPLC (toluene) failed. Since the contaminant was only C_{60}, this sample allowed some spectral assignments without difficulty: FAB MS *m*/*z* 780 (M), 720 (base peak); ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 4.71 (s, 4H, tetrahydrothiophene ring CH_2); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 51.12, 73.39, 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, 147.72, 154.88 (a peak was seen at δ 143.10 due to contaminant C_{60}). This cyclic sulfide **3** was irradiated with sun lamp under an oxygen atmosphere in an ice-cooling bath for 18 h, but no appreciable change was observed.

2.1.2. Oxidation of fullerotetrahydrothiophene (3) with *m*-CPBA. This reaction was carried out without purification of crude **3** obtained from the above cycloaddition. Thus, a solution of C_{60} (108 mg, 0.15 mmol) and **1** (33 mg, 0.15 mmol) in *o*-dichlorobenzene (15 ml) was heated in the same manner as above, and then the solvent was replaced with toluene (200 ml). To this solution was added *m*-CPBA (11 mg, 0.064 mmol) in CH_2Cl_2 (5 ml), and stirring was continued at room temperature for 1 h. The reaction mixture was neutralized with saturated $NaHCO_3$, washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column eluted with toluene/ether (3/1) to give recovered C_{60} (36 mg, 33%) and sulfoxide **4** (48 mg, 41% overall yield; 61% based on consumed C_{60}): FAB MS *m*/*z*

796 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1067, 527; UV ($CHCl_3$) λ (nm) 432; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 4.57 and 5.16 (d, J=13.5 Hz, each 2H, tetrahydrothiophene ring CH_2); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 65.36, 71.26, 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, 154.43.

2.1.3. Oxidation of fullerotetrahydrothiophene *S*-oxide (4) with *m*-CPBA. To a solution of sulfoxide **4** (39 mg, 0.049 mmol) in 1,1,2,2-tetrachloroethane (15 ml) was added a solution of *m*-CPBA (11 mg, 0.064 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized with saturated $NaHCO_3$, and diluted with water. The product was extracted several times with $CHCl_3$. The combined extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column eluted with toluene to give sulfone **5** (30 mg, 73%): FAB MS *m/z* 812 (M), 748 (M−SO_2), 720 (base peak); IR (KBr) ν (cm^{-1}) 1329, 1137, 527; UV ($CHCl_3$) λ (nm) 431; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 4.91 (s, 4H, tetrahydrothiophene ring CH_2); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 50.35, 63.66, 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.

2.1.4. Pummerer rearrangement of fullerotetrahydrothiophene *S*-oxide (4). A solution of sulfoxide **4** (80 mg, 0.1 mmol) in 1,1,2,2-tetrachloroethane (30 ml) including acetic anhydride (6 ml) was stirred under an argon atmosphere in a sealed tube and heated at 110°C for 4 h. After cooling, the solution was poured into saturated $NaHCO_3$ and the product was extracted several times with $CHCl_3$. The combined extracts were washed with water, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column eluted with toluene to give α-acetoxytetrahydrothiophene **6** (67 mg, 80%): FAB MS *m/z* 838 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1752, 1203, 526; UV ($CHCl_3$) λ (nm) 429; ^{1}H NMR ($Cl_2CDCDCl_2$) δ 2.32 (s, 3H, $COCH_3$), 4.70 and 5.14 (dd, J=12.0, 1.5 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 7.68 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 22.25, 48.27, 73.19, 79.35, 90.71, 136.46, 136.95, 137.79, 138.06, 140.32, 140.62, 140.94, 142.19, 142.22, 142.51, 142.54, 142.57, 142.63, 142.68, 142.82, 142.85, 142.93, 142.97, 143.28, 143.33, 143.34, 143.67, 143.72, 145.06, 145.08, 145.12, 145.20, 145.27, 145.76, 145.87, 145.93, 146.05, 146.14, 146.23, 146.29, 146.31, 146.42, 146.44, 146.71, 146.74, 146.77, 147.04, 147.07, 148.08, 148.14, 152.22, 152.52, 154.63, 155.22, 170.52.

2.2. Electrophilic substitution reaction of α-acetoxy-tetrahydrothiophene 6

2.2.1. General procedure. To a solution of **6** (15 mg, 0.018 mmol) in 1,1,2,2-tetrachloroethane (5 ml) including allyl alcohol (0.5 ml) was added 0.18 M solution of trimethylsilyl triflate in dry CH_2Cl_2 (0.1 ml, 0.018 mmol) at 0°C under an argon atmosphere, and the mixture was stirred at room temperature for 3.5 h. Then the reaction mixture was neutralized with saturated $NaHCO_3$ and diluted with water (20 ml). The product was extracted several times with $CHCl_3$, and the combined extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column eluted with hexane/toluene (1/1) to give α-allyloxytetrahydrothiophene **7a** (10 mg, 67%): FAB MS *m/z* 836 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1056, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($Cl_2CDCDCl_2$) δ 4.44 and 4.73 (ddt, J=13.5, 6.0, 1.5 Hz, and J=13.5, 4.5, 1.5 Hz, respectively, each 1H, OCH_2), 4.51 and 5.00 (dd, J=12.0, 1.5 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 5.30 and 5.50 (dq, J=11.0, 1.5 Hz, and J=17.5, 1.5 Hz, respectively, each 1H, CH_2=C), 6.07 (m, 1H, C=CH), 6.52 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($Cl_2CDCDCl_2$) δ 46.89, 70.76, 73.32, 79.97, 98.74, 118.78, 134.30, 136.60, 137.51, 137.65, 138.06, 140.32, 140.48, 140.52, 140.85, 142.13, 142.21, 142.38, 142.59, 142.63, 142.67, 142.84, 142.95, 142.98, 143.08, 143.12, 143.17, 143.21, 143.25, 143.33, 143.68, 143.70, 145.09, 145.10, 145.24, 145.27, 145.54, 145.87, 145.93, 145.98, 145.99, 146.04, 146.10, 146.16, 146.20, 146.33, 146.35, 146.53, 146.63, 146.68, 146.70, 146.98, 147.02, 148.07, 148.09, 153.69, 154.39, 155.01, 155.82.

Unless otherwise noted, the other substitution reactions with various alcohols were carried out in the same manner as above except for using camphorsulfonic acid as a catalyst under conditions (temperature and reaction time) indicated in Table 1. The yields were also listed in Table 1.

The reaction with *n*-propyl alcohol gave **7b** [elution with hexane/toluene (3/1)]: FAB MS *m/z* 838 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1083, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 4/1) δ 1.13 (t, J=7.3 Hz, 3H, CH_3), 1.85–1.93 (m, 2H, OCH_2CH_2), 3.80 and 4.23 (dt, J=9.5, 6.5 Hz, each 1H, OCH_2) 4.52 and 5.02 (dd, J=12.0, 1.5 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.47 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 4/1) δ 11.40, 23.21, 46.51, 71.70, 72.61, 79.45, 99.24, 136.26, 137.02, 137.29, 137.49, 139.79, 139.96, 140.01, 140.35, 141.60, 141.68, 141.84, 141.85, 142.06, 142.10, 142.12, 142.30, 142.39, 142.44, 142.53, 142.59, 142.69, 142.72, 142.81, 143.15, 143.17, 144.54, 144.56, 144.73, 144.93, 145.30, 145.34, 145.37, 145.42, 145.45, 145.53, 145.55, 145.65, 145.68, 145.76, 145.80, 145.91, 146.09, 146.12, 146.15, 146.43, 146.49, 147.49, 147.51, 153.09, 153.93, 154.44, 155.19.

The reaction with isoamyl alcohol gave **7c** [elution with hexane/toluene (3/1)]: FAB MS *m/z* 867 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1078, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 5/3) δ 1.02 and 1.05 (d, J=7.0 Hz, each 3H, CH_3), 1.73 and 1.80 (ddt, J=14.0, 7.0, 6.5 Hz, and dq, J=14.0, 6.8 Hz, respectively, each 1H, OCH_2CH_2), 1.91 (m, 1H, Me_2CH), 3.83 and 4.31 (dt, J=9.5, 6.5 Hz, each 1H, O–CH_2), 4.53 and 5.01 (dd, J=11.5, 1.5 Hz, and d, J=11.5 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.46 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 5/3) δ 22.78, 23.07, 25.78, 38.38, 46.58, 68.78, 72.60, 79.45, 99.46, 136.27, 137.01, 137.28, 137.47, 139.80, 139.97, 140.02, 140.36, 141.61, 141.69, 141.85, 141.86, 142.06, 142.11, 142.13, 142.31, 142.40, 142.46, 142.55, 142.58, 142.60, 142.70, 142.73, 142.82, 143.16, 143.18, 144.54, 144.57, 144.74, 144.93, 145.31, 145.35, 145.38, 145.43, 145.46, 145.54, 145.56, 145.66, 145.69, 145.76, 145.81, 145.91, 146.09, 146.13, 146.16, 146.44, 146.49, 147.51, 147.52, 153.11, 153.97, 154.44, 155.18.

The reaction with 1,6-hexanediol (47 mg, 0.4 mmol) gave **7d** [elution with $CHCl_3$/EtOH (20/1)]: FAB MS *m/z* 896 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 3422, 1083, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 3/5) δ 1.41 (br s, 1H, OH), 1.46–1.93 (m, 8H, $(CH_2)_4$), 3.62 (t, J=6.5 Hz, 2H, CH_2OH), 3.82 and 4.28 (dt, J=9.5, 6.5 Hz, each 1H, OCH_2), 4.52 and 5.00 (dd, J=12.0, 1.3 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.45 (d, J=1.3 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 5/3) δ 25.87, 26.62, 29.60, 33.11, 46.55, 63.00, 70.06, 72.56, 79.42, 99.33, 136.24, 136.94, 13728, 137.43, 139.75, 139.96, 140.00, 140.34, 141.57, 141.67, 141.83, 141.84, 142.04. 142.08, 142.10, 142.28, 142.37, 142.41, 142.49, 142.53, 142.58, 142.68, 142.71, 142.80, 143.14, 143.17, 144.52, 144.54, 144.70, 144.71, 144.89, 145.30, 145.32, 145.36, 145.40, 145.41, 145.53, 145.65, 145.67, 145.70, 145.78, 145.87, 146.05, 146.11, 146.14, 146.42, 146.47, 147.47, 147.50, 153.02, 153.89, 154.41, 155.12.

The reaction with 2,2,2-trifluoroethanol gave **7e** [elution with hexane/toluene (3/1)]: FAB MS *m/z* 878 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1106, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 1/1) δ 4.34 and 4.59 (dq, J=12.0, 8.4 Hz, each 1H, OCH_2), 4.58 and 5.03 (dd, J=12.0, 1.5 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.61 (d, J=1.5 Hz, 1H, terahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 46.42, 65.97 (q, J=34.5 Hz), 72.33, 79.14, 99.61, 123.65 (d, J=278 Hz), 136.07, 136.99, 137.42, 137.73, 139.90, 140.02, 140.07, 140.42, 141.70, 141.73, 141.89, 141.87, 141.90, 142.06, 142.10, 142.31, 142.34, 142.50, 142.52, 142.64, 142.73, 142.77, 142.85, 143.16, 143.18, 144.53, 144.66, 144.68, 144.71, 145.33, 145.41, 145.42, 145.50, 145.58, 145.60, 145.72, 145.75, 145.83, 145.92, 146.15, 146.16, 146.20, 146.50, 146.54, 147.54, 147.57, 152.01, 152.51, 153.74, 154.58.

The reaction with 3-(benzyloxycarbonylamino)propyl alcohol (74 mg, 0.38 mmol) gave **7f** [elution with toluene and then toluene/Et_2O (4/1)]: FAB MS *m/z* 987 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 3311, 1721, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 1/1) δ 1.81 and 2.28 (m, 2H, OCH_2CH_2), 3.43–3.54 (m, 2H, NCH_2), 3.86 and 4.44 (m, each 1H, OCH_2), 4.52 and 5.02 (dd, J=12.0, 1.0 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 5.01 (s, 2H, $COOCH_2$), 5.23 (br s, 1H, NH), 6.46 (d, J=1.0 Hz, 1H, tetrahydrothiophene ring CH), 7.23–7.32 (m, 5H, Ph); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 29.80, 39.90, 46.50, 66.64, 69.05, 72.47, 79.27, 99.61, 128.16, 128.38, 128.55, 136.18, 136.66, 137.29, 137.36, 139.91, 139.99, 140.35, 141.58, 141.67, 141.87, 142.05, 142.06, 142.31, 142.36, 142.42, 142.47, 142.62, 142.65, 142.70, 142.73, 142.78, 143.05, 143.15, 144.47, 144.53, 144.60, 144.71, 144.80, 145.31, 145.33, 145.40, 145.44, 145.54, 145.58, 145.67, 145.71, 145.75, 145.94, 146.08, 146.12, 146.15, 146.17, 146.39, 146.42, 146.45, 146.49, 147.49, 147.52, 152.67, 153.31, 154.10, 154.86, 156.15.

The reaction with 2-propanol gave **7g** [elution with hexane/toluene (2/1)]: FAB MS *m/z* 838 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1062, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 1/1) δ 1.41 and 1.53 (d, J=6.0 Hz, each 3H, respectively, CH_3), 4.46 (septuplet, J=6.0 Hz, 1H, OC*H*), 4.54 and 5.04 (dd, J=11.8, 1.5 Hz, and d, J=11.8 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.57 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 21.12, 23.59, 46.60, 71.67, 72.75, 79.39, 97.02, 136.25, 137.15, 137.19, 137.55, 139.85, 139.96, 140.01, 140.34, 141.62, 141.71, 141.85, 142.07, 142.10, 142.17, 142.30, 142.39, 142.44, 142.52, 142.60, 142.69, 142.72, 142.81, 143.14, 143.16, 143.18, 144.55, 144.56, 144.72, 144.73, 144.98, 145.32, 145.37, 145.41, 145.48, 145.54, 145.55, 145.66, 145.78, 145.83, 145.87, 146.06, 146.08, 146.11, 146.15, 146.42, 146.49, 147.50, 147.51, 153.21, 154.11, 154.49, 155.26.

The reaction with 3-pentanol gave **7h** [elution with hexane/toluene (2/1)]: FAB MS *m/z* 867 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1064, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 1/1) δ 0.98 and 1.22 (t, J=7.5 Hz, each 3H, respectively, CH_3), 1.78–1.88 (m, 4H, CH_3CH_2), 4.09 (m, 1H, OCH), 4.56 and 5.06 (dd, J=11.5, 1.0 Hz, and d, J=11.5 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.61 (d, J=1.0 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 9.26, 10.75, 25.25, 26.76, 46.71, 72.90, 79.58, 81.37, 97.43, 136.30, 137.15, 137.23, 137.46, 139.92, 140.05, 140.10, 140.42, 141.70, 141.79, 141.93, 142.15, 142.19, 142.27, 142.38, 142.50, 142.53, 142.65, 142.68, 142.77, 142.80, 142.89, 143.23, 143.24, 143.27, 144.63, 144.65, 144.81, 144.82, 145.09, 145.36, 145.40, 145.45, 145.50, 145.55, 145.61, 145.65, 145.73, 145.88, 145.90, 145.92, 146.16, 146.19, 146.21, 146.24, 146.50, 146.57, 147.60, 147.61, 153.40, 154.30, 154.65, 155.39.

The reaction with 1,3-dibromo-2-propanol gave **7i** [elution with hexane/toluene (2/1)]: FAB MS *m/z* 999, 997, 995 (1:2:1, M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1057, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 3/4) δ 3.77 and 3.82 (dd, J=12.0, 5.5 Hz, each 1H, CH_2Br), 3.89 (d, J=5.5 Hz, 2H, CH_2Br), 4.62 (quintet, J=5.5 Hz, 1H, OCH), 4.60 and 5.18 (dd, J=11.5, 1.5 Hz, and d, J=11.5 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.74 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 3/4) δ 32.09, 32.22, 46.81, 72.48, 79.33, 98.29, 136.13, 137.04, 137.34, 137.56, 139.84, 140.00, 140.08, 140.40, 141.69, 141.72, 141.86, 141.88, 141.97, 142.04, 142.10, 142.31, 142.33, 142.48, 142.49, 142.53, 142.62, 142.70, 142.74, 142.83, 143.14, 143.18, 144.51, 144.53, 144.70, 144.74, 145.31, 145.39, 145.42, 145.43, 145.45, 145.53, 145.57, 145.71, 145.74, 145.77, 145.84, 145.98, 146.12, 146.13, 146.16, 146.18, 146.45, 146.46, 146.50, 147.52, 147.54, 152.29, 153.16, 153.94, 154.75.

The reaction with 2,4-dimethyl-3-pentanol gave **7j** [elution with hexane/toluene (2/1)]: FAB MS *m/z* 894 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1058, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 3/4) δ 1.07, 1.11, 1.22 and 1.23 (d, *J*=7.0 Hz, each 3H, CH_3), 2.12 and 2.20 (d septuplet, *J*=4.5, 7.0 Hz, each 1H, Me_2CH), 3.76 (t, *J*=4.5 Hz, 1H, OCH), 4.55 and 5.03 (dd, *J*=12.0, 1.0 Hz, and d, *J*=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.71 (d, *J*=1.0 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 3/4) δ 18.81, 19.14, 20.58, 21.41, 30.17, 30.87, 46.86, 72.90, 79.48, 88.40, 99.04, 136.23, 136.98, 137.04, 137.16, 139.77, 140.06, 140.11, 140.39, 141.67, 141.75, 141.87, 141.89, 142.10, 142.16, 142.23, 142.32, 142.44, 142.49, 142.61, 142.63, 142.64, 142.73, 142.75, 142.84, 143.17, 143.22, 144.59, 144.74, 144.77, 145.06, 145.31, 145.34, 145.44, 145.51, 145.57, 145.59, 145.67, 145.80, 145.99, 146.06, 146.12, 146.15, 146.18, 146.19, 146.44, 146.51, 153.46, 154.32, 154.66, 155.26.

The reaction with a dendritic alcohol (60 mg, 0.046 mmol) which was prepared according to the reported procedure[24] gave **7k** [elution with hexane/toluene (1/1)]: MALDI MS *m/z* 2077 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 2858, 1101, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3$) δ 2.36 (m, 3H, CH_2CHCH_2), 3.48–3.68 (m, 38H, OCH_2 and OCH), 4.44 and 4.91 (dd, *J*=12.0, 1.0 Hz, and d, *J*=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 4.49 (s, 16H), 6.35 (d, *J*=1.0 Hz, 1H, tetrahydrothiophene ring CH), 7.28–7.30 (m, 40H); ^{13}C NMR ($CDCl_3$) δ 41.08, 46.45, 64.64, 68.83, 70.24, 70.31, 72.78, 73.55, 78.63, 79.82, 99.38, 127.77, 127.80, 128.56, 136.30, 136.90, 137.33, 137.41, 138.63, 139.91, 140.08, 140.12, 140.47, 141.66, 141.82, 142.02, 142.24, 142.25, 142.33, 142.47, 142.57, 142.61, 142.72, 142.73, 142.76, 142.88, 142.90, 142.96, 143.30, 143.34, 144.70, 144.73, 144.84, 144.93, 145.15, 145.43, 145.50, 145.58, 145.61, 145.66, 145.73, 145.75, 145.81, 145.97, 146.00, 146.26, 146.30, 146.32, 146.35, 146.59, 146.62, 146.64, 146.68, 147.71, 147.74, 153.26, 154.29, 154.84, 155.42.

The reaction with methyl mercaptoacetate gave **7l** [elution with hexane/toluene (1/1)]: FAB MS *m/z* 885 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1735, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 4/3) δ 3.68 and 4.06 (d, *J*=15.0 Hz, each 1H, SCH_2), 3.83 (s, 3H, CH_3), 4.61 and 5.17 (dd, *J*=12.0, 1.0 Hz, and d, *J*=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.40 (d, *J*=1.0 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 4/3) δ 35.55, 47.79, 52.69, 69.43, 73.41, 136.31, 136.42, 136.78, 137.73, 139.75, 140.14, 140.31, 140.34, 141.79, 141.81, 141.86, 141.99, 142.01, 142.06, 142.15, 142.28, 142.33, 142.38, 142.43, 142.52, 142.79, 142.83, 142.86, 143.18, 143.20, 144.61, 144.68, 144.73, 144.77, 145.20, 145.45, 145.51, 145.55, 145.60, 145.70, 145.71, 145.79,145.81, 146.21, 146.24, 146.29, 146.53, 146.55, 146.58, 147.57, 147.61, 151.60, 154.13, 154.28, 155.11, 169.96.

The substitution reactions with organosilicon reagents were carried out as follows. To a mixed solution of the reagent (0.36 mmol) in dry 1,1,2,2-tetrachloroethane (1 ml) and 0.18 M solution of trimethylsilyl triflate in dry CH_2Cl_2 (0.1 ml, 0.018 mmol) was added dropwise a solution of **6** (15 mg, 0.018 mmol) in dry 1,1,2,2-tetrachloroethane (8 ml) at −40°C under an argon atmosphere. After the reaction temperature was kept at this temperature for 1 h, the mixture was stirred at room temperature for the period indicated in Table 1. The same work-up and chromatography as employed for the above alcohols gave the product. In entries 16 and 18, the catalyst was added to the solution of the reagent and **6**. Reaction conditions (catalyst, temperature and time) and yields are indicated in Table 1.

The reaction with allyltrimethylsilane gave **7m** [elution with hexane/toluene (3/1)]: FAB MS *m/z* 820 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 990, 917, 527; ^{1}H NMR ($CDCl_3/CS_2$ 4/3) δ 3.04 and 3.64 (dddt, *J*=14.5, 11.5, 7.0, 1.5 Hz, and *J*=14.5, 6.1, 3.5, 1.5 Hz, respectively, each 1H, $C{=}CCH_2$), 4.68 and 4.71 (d, *J*=12.5 Hz, each 1H, tetrahydrothiophene ring CH_2), 4.85 (dd, *J*=11.5, 3.5 Hz, 1H, tetrahydrothiophene ring CH), 5.29 and 5.40 (dq, *J*=10.0, 1.5 Hz, and *J*=16.8, 1.5 Hz, respectively, each 1H, $CH_2{=}C$), 6.23 (m, 1H, C=CH); ^{13}C NMR ($CDCl_3/CS_2$ 4/3) δ 37.85, 49.06, 64.88, 74.83, 76.56, 118.10, 135.51, 135.71, 136.01, 136.81, 137.70, 139.60, 139.86, 140.25, 140.39, 141.65, 141.76, 141.96, 142.12, 142.16, 142.18, 142.19, 142.28, 142.35, 142.42, 142.44, 142.78, 142.80, 142.84, 143.12, 143.16, 143.28, 144.46, 144.50, 144.66, 144.81, 144.98, 145.38, 145.44, 145.45, 145.49, 145.58, 145.66, 145.84, 145.93, 146.12, 146.14, 146.19, 146.22, 146.41, 146.44, 146.52, 146.56, 147.44, 147.47, 152.19, 154.01, 155.09, 155.46.

The reaction with methallyltrimethylsilane gave **7n** [elution with hexane/toluene (3/1)]: FAB MS *m/z* 834 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 893, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 2.06 (t, *J*=0.5 Hz, 3H, CH_3), 2.99 and 3.58 (ddd, *J*=14.5, 12.0, 0.8 Hz, and dd, *J*=14.5, 3.0 Hz, respectively, each 1H, $C{=}CCH_2$), 4.67 and 4.71 (d, *J*=12.0 Hz, 1H, tetrahydrothiophene ring CH_2), 4.97 (dd, *J*=12.0, 3.0 Hz, 1H, tetrahydrothiophene ring CH), 5.05 and 5.16 (m, each 1H, $CH_2{=}C$); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 22.50, 41.74, 49.05, 63.32, 74.92, 76.61, 114.16, 135.45, 136.05, 136.82, 137.73, 139.55, 139.86, 140.28, 140.41, 141.64, 141.76, 141.98, 142.15, 142.18, 142.19, 142.21, 142.30, 142.37, 142.43, 142.44, 142.52, 142.79, 142.81, 142.86, 143.13, 143.17, 143.29, 144.45, 144.51, 144.68, 144.84, 144.96, 145.39, 145.44, 145.48, 145.49, 145.68, 145.87, 145.99, 146.12, 146.15, 146.21, 146.24, 146.26, 146.42, 146.45, 146.53, 146.58, 152.22, 153.95, 155.15, 155.53.

The reaction with methyl 3-(trimethylsilylmethyl)-3-butenoate gave **7o** [elution with toluene/Et_2O (40/1)]: FAB MS *m/z* 893 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1735, 902, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 3.06 and 3.78 (ddd, *J*=14.8, 12.0, 0.8 Hz, and dd, *J*=14.8, 3.3 Hz, respectively, each 1H, $C{=}CCH_2$), 3.37 and 3.43 (d, *J*=15.0 Hz, each 1H, CH_2COO), 3.70 (s, 3H, CH_3), 4.68 and 4.71 (d, *J*=12.5 Hz, each 1H, tetrahydrothiophene ring CH_2), 5.00 (dd, *J*=12.0, 3.3 Hz, 1H, tetrahydrothiophene ring CH), 5.24 and 5.42 (dd, *J*=0.8, 0.5 Hz, each 1H, $CH_2{=}C$); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 39.77, 41.51, 49.03, 52.00, 62.96, 74.84, 76.57, 117.77, 135.54, 136.05, 136.81, 137.79, 139.55, 139.63, 139.92, 140.30, 140.44, 141.70, 141.80, 142.01, 142.16, 142.17, 142.23, 142.24, 142.31, 142.39, 142.41, 142.44, 142.47, 142.82, 142.84, 142.89, 143.16, 143.31, 144.49, 144.54, 144.70, 144.85, 144.98, 145.42, 145.48, 145.47, 145.51, 145.52, 145.59, 145.62, 145.65, 145.70, 145.87, 145.96, 146.14, 146.16, 146.19, 146.24, 146.27, 146.46, 146.49, 146.57, 146.61, 147.49, 147.52, 151.99, 153.86, 155.06, 155.47, 171.18.

The reaction with trimethylsilyl enol ether of acetophenone gave **7p** (elution with hexane/toluene (1/1)); FAB MS *m/z* 898 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1692, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 4.05 and 4.39 (dd, 1H, *J*=17.0, 10.0 Hz and *J*=17.0, 4.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 4.75 and 4.81 (d, *J*=12.0 Hz, each 1H, CH_2CO), 5.48 (dd, *J*=10.0, 4.0 Hz, 1H, tetrahydrothiophene ring CH), 7.44–7.62 (m, 5H, Ph); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) δ 42.03, 49.59, 58.72, 74.43, 76.39, 128.43, 128.95, 133.71, 135.83, 136.18, 136.57, 136.67, 137.95, 139.74, 140.00, 140.28, 140.45, 141.80, 141.90, 141.92, 142.07, 142.08, 142.17, 142.24, 142.27, 142.36, 142.42, 142.50, 142.55, 142.79, 142.83, 142.86, 142.88, 143.20, 143.28, 144.52, 144.57, 144.60, 144.84, 145.00, 145.41, 145.42, 145.47, 145.52, 145.55, 145.63, 145.67, 145.69, 145.73, 145.77, 146.18, 146.21, 146.23, 146.48, 146.50, 146.52, 146.62, 147.48, 147.54, 151.91, 153.86, 154.99, 155.53, 196.07.

The reaction with 2-(trimethylsiloxy)pyridine gave **7q** [elution with toluene/Et_2O (10/1)]; FAB MS *m/z* 873 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1655, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 1/2) δ 4.81 and 4.99 (d, *J*=12.0 Hz, each 1H, tetrahydrothiophene ring CH_2), 6.26, 6.59, 7.31 and 8.05 (td, *J*=6.8, 1.0 Hz, ddd, *J*=9.0, 1.0, 0.5 Hz, ddd, *J*=9.0, 6.8, 1.0 Hz, and, ddd, *J*=6.8, 1.0, 0.5 Hz, respectively, each 1H, pyridone ring CH), 8.16 (s, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 1/2) δ 46.85, 71.73, 72.84, 75.93, 106.70, 121.63, 135.31, 135.54, 136.31, 136.59, 137.99, 139.79, 139.80, 140.13, 140.22, 140.56, 141.56, 141.82, 141.98, 142.12, 142.13, 142.16, 142.43, 142.50, 142.56, 142.60, 142.76, 142.82, 142.87, 142.90, 143.17, 143.18, 144.43, 144.46, 144.53, 144.61, 144.65, 145.34, 145.35, 145.36, 145.51, 145.58, 145.61, 145.62, 145.63, 145.68, 145.74, 145.86, 146.21, 146.29, 146.44, 146.53, 146.56, 146.64, 147.51, 147.57, 149.03, 153.05, 153.56, 155.18, 162.02.

The reaction with 5-methyl-2,4-bis(trimethylsiloxy)pyrimidine gave **7r** [elution with $CHCl_3$/EtOH (20/1)]; FAB MS *m/z* 904 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1686, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($Cl_2CDCDCl_2$) δ 1.91 (d, *J*=1.5 Hz, 3H, CH_3), 4.80 and 4.92 (d, *J*=12.5 Hz, each 1H, tetrahydrothiophene ring CH_2), 7.69 (s, 1H, tetrahydrothiophene ring CH), 7.81 (d, *J*=1.5 Hz, 1H, thymine ring CH), 8.79 (br s, 1H, thymine ring NH); ^{13}C NMR ($Cl_2CDCDCl_2$) δ 13.32, 47.20, 72.38, 72.92, 76.23, 112.62, 136.01, 136.37, 136.90, 138.29, 138.59, 140.65, 140.77, 140.88, 141.15, 142.10, 142.47, 142.57, 142.62, 142.67, 142.70, 142.85, 142.92, 142.93, 142.95, 143.29, 143.36, 143.43, 143.69, 143.76, 144.92, 144.99, 145.23, 145.44, 145.68, 145.70, 145.88, 145.92, 145.93, 146.03, 146.12, 146.19, 146.20, 146.23, 146.47, 146.74, 146.81, 147.01, 147.04, 147.07, 147.21, 148.09, 148.10, 148.62, 151.31, 152.99, 154.05, 155.27, 164.04.

2.2.2. Electrophilic double substitution reaction of α,α'-diacetoxytetrahydrothiophene 9. A series of reactions were carried out according to the same procedures as employed for the monosubstitution case (**3**$\rightarrow$**4**$\rightarrow$**6**) except for prolonged reaction time (6 h) in the oxidation of **6** with *m*-CPBA. Thus, **8** was obtained as a 9:1 sereoisomeric mixture in 82% yield from **6**, and **9** was obtained as a 3:1 sereoisomeric mixture in 67% yield from **8**. The reaction of **9** with butanol under the same conditions as shown in entry 2 of Table 1 except heating for 27 h gave **10** in 77% yield as a 2:1 sereoisomeric mixture.

8. FAB MS 854 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1764, 1091, 527; UV ($CHCl_3$) λ (nm) 431; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 2.33 and 2.38 (s, 3H×9/10 and 3H×1/10, respectively, CH_3), 4.67 and 4.69 (dd, *J*=14.0, 1.0 Hz, and d, *J*=14.0 Hz, 1H×9/10 and 1H×1/10, respectively, one of tetrahydrothiophene ring CH_2), 5.13 and 5.14 (d, *J*=14.0 Hz and d, *J*=14.0 Hz, 1H×9/10 and 1H×1/10, respectively, the other one of tetrahydrothiophene ring CH_2), 7.33 and 7.40 (d, *J*=1.0 Hz and s, 1H×9/10 and 1H×1/10, respectively, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 3/5) δ 20.65, 59.85, 74.43, 79.48, 93.03, 134.70, 135.23, 136.91, 137.68, 137.71, 139.99, 140.29, 140.41, 140.51, 141.68, 141.76, 141.81, 141.88, 141.91, 142.11, 142.22, 142.24, 142.27, 142.35, 142.78, 142.80, 142.82, 142.83, 143.26, 143.35, 144.43, 144.52, 144.71, 144.75, 144.83, 145.34, 145.45, 145.47, 145.50, 145.53, 145.68, 145.84, 145.88, 145.91, 146.15, 146.19, 146.30, 146.31, 146.42, 146.48, 146.50, 147.56, 149.65, 152.01, 153.14, 153.66, 169.04 (cf. Only the peaks of the major isomer were recorded).

9. FAB MS 896 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1751, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 1/1) δ 2.33 and 2.34 (s, 3H×1/4 and 3H×3/4, respectively, CH_3), 7.82 and 7.91 (s, 1H×3/4 and 3H×1/4, respectively, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 1/1) major isomer: δ 21.51, 78.01, 90.53, 135.90, 137.95, 139.99, 140.38, 141.70, 141.97, 142.18, 142.25, 142.29, 142.52, 142.81, 142.94, 144.66, 144.70, 144.85, 145.58, 145.64, 145.75, 145.84, 145.93, 145.96, 146.32, 146.36, 146.67, 146.70, 151.28, 151.63, 169.32. Minor isomer: δ 23.22, 86.73, 136.96, 137.85, 139.91, 140.31, 141.90, 141.99, 142.19, 142.37, 142.43, 142.87, 143.22, 143.24, 143.31, 144.59, 144.63, 145.33, 145.50, 145.54, 145.60, 145.77, 145.81, 145.91, 146.30, 146.64, 150.79, 151.71, 169.22 (cf. One signal due to junction sp^3 carbon was superimposed with solvent signals).

10. FAB MS 924 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1079, 527; UV ($CHCl_3$) λ (nm) 430; ^{1}H NMR ($CDCl_3/CS_2$ 4/5) δ 0.97 and 1.00 (t, *J*=7.0 Hz, 6H×1/3 and 6H×2/3, respectively, CH_3), 1.48–1.57 and 1.50–1.54 (m, 4H×1/3 and 4H×2/3, respectively, $CH_2CH_2CH_3$), 1.77–1.84 (m, 4H, $CH_2CH_2CH_3$), 3.73 and 3.91 (dt, *J*=9.0, 6.5 Hz, 2H×1/3 and 2H×2/3, respectively, one of OCH_2), 4.20 and 4.23 (dt, *J*=9.0, 6.5 Hz, 2H×1/3 and 2H×2/3, respectively, the other one of OCH_2), 6.61 and 6.65 (s, 1H×1/3 and 2H×2/3, respectively, tetrahydrothiophene ring H); ^{13}C NMR ($CDCl_3/CS_2$ 4/5) major isomer: δ 14.21, 19.93, 31.79, 71.96, 79.20, 97.11, 136.80, 137.19, 139.79, 139.99, 141.77, 141.80, 142.27, 142.30, 142.39, 142.69, 142.81, 142.83, 143.12, 143.21, 144.57, 144.73, 145.34, 145.39, 145.49, 145.50, 145.67, 145.70, 146.14, 146.16, 146.50, 146.59, 147.53, 147.65, 153.13, 153.29. Minor isomer: δ 14.35, 20.06, 31.61, 70.20, 80.72, 100.26, 137.72, 138.19, 139.71, 140.11, 141.61, 141.80, 142.12, 142.25, 142.45, 142.47, 142.60, 142.80, 144.79, 145.31, 145.61, 145.64, 145.80, 146.18, 146.19, 146.40, 146.47, 146.53, 146.55, 147.69, 148.06, 153.56, 153.69.

2.2.3. Formation of thiolactol 11. *Hydrolysis method.* A solution of **6** (84 mg, 0.1 mmol) and *p*-toluenesulfonic acid (2 mg, 0.01 mmol) in 1,1,2,2-tetrachloroethane (13 ml) was mixed with water (10 ml) and this suspension was stirred in a sealed tube at 70°C for 5 h under an argon atmosphere. The same work-up and chromatography as employed for the preparation of **7a** gave thiolactol **11** (49 mg, 62%).

Reduction method. To a solution of **6** (84 mg, 0.1 mmol) in dry CH_2Cl_2 (30 ml) was added dropwise a 0.95 M solution of diisobutylaluminum hydride in toluene (0.13 ml, 0.12 mmol) at −78°C, and the mixture was stirred for 2 h at this temperature under an argon atmosphere. Then, the reaction mixture was quenched with saturated NaCl (10 ml). The organic layer was separated, washed with brine, dried over $MgSO_4$, and evaporated to dryness. The followed chromatography gave **11** (44 mg, 55%).

11. FAB MS *m/z* 796 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1034, 526; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($Cl_2CDCDCl_2$) δ 4.65 and 5.23 (dd, J=12.0, 1.5 Hz, and d, J=12.0 Hz, respectively, each 1H, tetrahydrothiophene ring CH_2), 6.90 (d, J=1.5 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($Cl_2CDCDCl_2$) δ 47.48, 73.31, 80.57, 91.95, 136.49, 137.26, 137.62, 138.36, 140.37, 140.58, 140.86, 142.19, 142.25, 142.43, 142.46, 142.60, 142.62, 142.65, 142.85, 142.94, 142.97, 143.01, 143.08, 143.19, 143.25, 143.28, 143.32, 143.70, 145.09, 145.10, 145.17, 145.25, 145.37, 145.91, 145.95, 146.00, 146.02, 146.03, 146.05, 146.06, 146.19, 146.21, 146.22, 146.30, 146.56, 146.59, 146.68, 146.71, 146.73, 147.02, 148.07, 148.09, 153.13, 153.46, 155.14, 155.61.

2.2.4. Reaction of thiolactol 11 with a phosphorous ylide. A solution of **11** (21 mg, 0.026 mmol) and methyl (triphenylphosphoranylidene)acetate (88 mg, 0.26 mmol) in 1,1,2,2-tetrachloroethane (15 ml) was heated at 70°C for 2.5 h in a sealed tube under an argon atmosphere. Then the reaction mixture was poured into water, and followed work-up as employed for the preparation of **7a** and chromatography [hexane/toluene (3/1)] gave **12** (8 mg, 36%): FAB MS *m/z* 852 (M), 720 (base peak); IR (KBr) ν (cm^{-1}) 1738, 527; UV ($CHCl_3$) λ (nm) 430; ^1H NMR ($CDCl_3/CS_2$ 3/5) δ 3.31 and 3.81 (dd, J=16.0, 10.5 Hz and J=16.0, 4.3 Hz, each 1H, CH_2COO), 3.80 (s, 3H, CH_3), 4.74 (s, 2H, tetrahydrothiophene ring CH_2), 5.24 (dd, J=10.5, 4.3 Hz, 1H, tetrahydrothiophene ring CH); ^{13}C NMR ($CDCl_3/CS_2$ 3/5) δ 38.35, 49.20, 52.16, 59.52, 74.35, 76.05, 136.72, 136.11, 136.51, 137.82, 139.92, 140.21, 140.36, 141.71, 141.81, 141.86, 141.96, 141.98, 142.13, 142.16, 142.21, 142.27, 142.29, 142.33, 142.42, 142.73, 142.75, 142.77, 142.80, 143.12, 143.18, 144.44, 144.51, 144.71, 144.93, 145.26, 145.34, 145.35, 145.41, 145.44, 145.45, 145.49, 145.55, 145.60, 145.63, 145.65, 146.10, 146.12, 146.15, 146.16, 146.40, 146.42, 146.46, 146.54, 147.40, 147.45, 151.35, 153.63, 154.81, 155.14, 170.66.

2.2.5. Attempted multiaddition reaction with thiocarbnoyl ylide 1. This reaction was carried out by the use of large excess of **1** (30 equiv.) under conditions similar to the monoadduct formation except for heating for 30 min. The used C_{60} disappeared completely, but HPLC analysis of the reaction mixture showed at least 13 peaks due to the regioisomers of multiadducts formed; no effort was made to separate them.

On the other hand, a mixture of bis-adducts was prepared by the use of 3 equiv. of **1** under the same conditions as described for the formation of monoadduct **4** (vide supra). Starting from 60 mg of C_{60}, the mixture product was collected by chromatography on a silica gel column eluted with hexane/toluene 3/1 (30 mg, 43% crude yield: no monoadduct was included, but small amount of tris-adduct might be included in the mixture: FAB-MS *m/z* 840 (M), 780 (M−60), 720 (base peak); IR (KBr) ν (cm^{-1}) 527; ^1H and ^{13}C NMR were not recorded because of no usefulness. This mixture (30 mg. 0.036 mmol) was oxidized to the corresponding bis-sulfoxide with *m*-CPBA (12 mg, 0.07 mmol) in the same manner as employed for the preparation of **4**, and the crude product was supplied as obtained for a pharmacological test.

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19. A stereoisomeric mixture was obtained in a 3:1 ratio for **8** and 2:1 for **9** (^{1}H NMR measurement), and the major isomer is estimated to be *trans* from mechanistic considerations; the second nucleophile is believed to attack the less hindered *trans*-side, and the *trans*-isomer of α,α'-diacetoxytetrahydrothiophene is calculated to be 1.3 kcal/mol more stable than the *cis*-isomer (PM 3).
20. Sterically, attack of a nucleophile on the concerned thiocarbocation intermediate may be interfered at both sides of sp^2 carbocation center by the symmetrical fullerene surface to some extent, and electronically, 1,2-dihydrofullerenyl group has intrinsically an electron-accepting nature; these effects seem to work more or less disadvantageously.
21. At the stage of bis-adducts formation, eight regioisomers are possible in theory, and their distribution was demonstrated in [2+1], [3+2] and [4+2]cycloaddition reactions: (a) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437. (b) Lu, Q.; Schuster, D. I.; Wilson, S. R. *J. Org. Chem.* **1996**, *61*, 4764. (c) Nakamura, Y.; O-kawa, K.; Matsumoto, M.; Nishimura, J. *Tetrahedron* **2000**, *56*, 5429.
22. Usui, N.; Okuda, K.; Hirota, T.; Hirobe, M.; Mochizuki, M.; Mashino, T. The 18th Fullerene General Symposium (Japan), Abstract Paper, 72pp.
23. The product was found to be a mixture, which was indicated by 5 peaks in HPLC analysis. The test of the mixture of bis-sulfoxides will be collaborated with Professor T. Mashino.
24. Jayaraman, M.; Fréchet, J. M. F. *J. Am. Chem. Soc.* **1998**, *120*, 12996.