Molecular Design by Cycloaddition Reactions. 38.[1] Cycloaddition Reactions of Dimethyl 7-[Bis(methylthio)methylene]bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate

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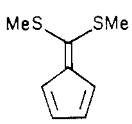
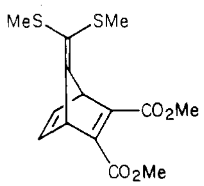
The cycloaddition reactions of the title compound **2** with cyclic polyolefins have been investigated. The reaction with tetracyclone **4** gave exo,exo [4 + 2] adduct **5** along with 6,6-dithiafulvene **6**. The stereochemistry of **5** was assigned on the basis of spectral data and supported by the chemical conversion to cyclic ether **7**. Fulvene **6** was obtained in quantitative yield by the reaction of **2** with tetrazine **9**. Tropone and tropolone reacted with **2** to give exo,endo [4 + 2] adducts **13a** and **13b**, respectively. While isobenzofuran **14** gave only exo,exo adduct **15**, hexachlorocyclopentadiene (**16**) afforded exo,endo adduct **17**. In contrast, *o*-chloranil (**20**) reacted with **2** exclusively at the electron-deficient double bond to give adducts **21** and **22**. The reactivity of **2** was compared with that of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**23**) in order to evaluate the effect of the 7-bis(methylthio)methylene group in **2**. The cycloaddition reaction of fulvene **6** was also investigated.

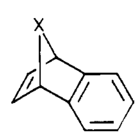
Various 6-heterosubstituted fulvenes have been synthesized to date.[2] Although interesting physical properties[2d] and biological activities[3] are expected, dithiafulvene derivatives have been less investigated. Recently, Yates and Lokensgard reported that 6,6-bis(methylthio)fulvene (**1**) undergoes the Diels–Alder reaction with dimethyl acetylenedicarboxylate to give 1:1 adduct **2**, whereas other 6-heterosubstituted fulvenes are inactive in these reactions.[4]



1



2



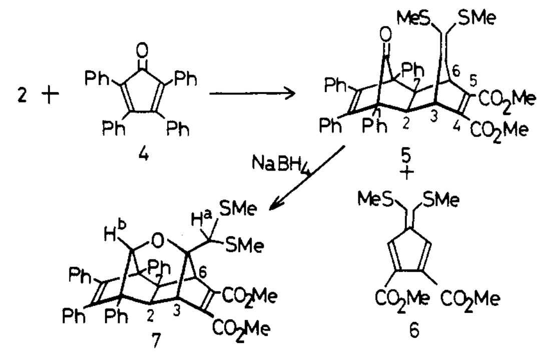
3a, X = O
b, X = NR
c, X = =<

We have reported that 7-substituted benzonorbornadienes **3a–c** are effective dienophiles and dipolarophiles.[5] The high reactivities of **3** are due to both ring strain and orbital participation of 7-substituents. As a continuation of our systematic studies on the chemistry of 7-substituted norbornadiene systems, we have investigated the cycloaddition reactions of the title compound **2**[4] with various cyclic polyenes and compared its reactivity with that of 7-unsubstituted compound. We also describe the facile generation of 3,4-bis(methoxycarbonyl)-6,6-bis(methylthio)fulvene (**6**) by cycloaddition and cycloreversion reactions of **2**.

Results and Discussion

Cycloaddition Reaction of 2 with Cyclic Polyenes. Reaction of **2** with tetraphenylcyclopentadienone (**4**) in toluene at 100 °C gave two products **5** and **6** in 67% and 3.5% yields, respectively (Scheme I). The nature of the major product **5** (mp 220–223 °C) as a 1:1 adduct was apparent from the elemental analysis and the structure was determined on the basis of the spectroscopic data and chemical conversion. The IR spectrum of **5** showed a characteristic band of a five-membered-ring carbonyl at 1770 cm^{-1}. The ^1H NMR spectrum (see Experimental Section) suggested the symmetrical structure of **5**. The signals of H-2 and H-3 appeared as singlets at δ 3.32 and 4.29, respectively. The absence of vicinal coupling between H-2 and H-3 indicated the bridgehead protons (H-2 and H-7) to be endo to the 7-methylenenorbornene system. The exo configuration regarding the norbornen-7-one system was deduced from its chemical properties. Treatment of **5** with $NaBH_4$ in methanol gave a 43% yield of cyclic ether **7**: mp 233–235 °C; IR 1710, 1170 cm^{-1}. This transannular ether formation[6] indicated that the carbonyl bridge in **5** is located on the same side of the norbornene skeleton as the bis(methylthio)methylene bridge. Thus, the adduct **5** was assigned to be the exo,exo [4 + 2] cycloadduct.[7]

Scheme I



It is worthwhile to note that the similar reaction of phencyclone with 7-substituted norbornadienes afforded only exo,endo [4 + 2] cycloadducts **8**.[8]

The structural assignment for the minor product **6**, mp 59–62 °C, was based on the elemental analysis and spectral data: IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (s, 6 H), 3.79 (s, 6 H), 7.12 (s, 2 H). Compound **6** is considered to be formed by successive loss of carbon monoxide and tetraphenylbenzene from adduct **5** under the reaction

(1) Part 37 of this series: see ref 5e.

(2) (a) Hafner, K.; Schulz, G.; Wagner, K. *Chem. Ber.* **1964**, *678*, 39. (b) Hartke, K.; Schmidt, E., Castillo, M.; Bartulin, J. *Ibid.* **1966**, *99*, 3268. (c) Bergmann, E. D. *Chem. Rev.* **1968**, *41*, 68. (d) Gompper, R.; Kutter, E. *Chem. Ber.* **1965**, *98*, 2825.

(3) Seitz, G.; Lehmann, H. G. *Arch. Pharm.* **1974**, *307*, 853.

(4) Yates, P.; Lokensgard, J. P. *Synth. Commun.* **1975**, *5*, 37.

(5) (a) Sasaki, T.; Kanematsu, K.; Hayakawa, K.; Uchide, M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2750. (b) Sasaki, T.; Kanematsu, K.; Hayakawa, K.; Kondo, A. *J. Org. Chem.* **1973**, *38*, 4100. (c) Sasaki, T.; Manabe, T.; Nishida, S. *Ibid.* **1980**, *45*, 476, 479. (d) Sasaki, T.; Manabe, T.; Wakabayashi, E. *Tetrahedron* **1980**, *36*, 2119. (e) Sasaki, T.; Hayakawa, K.; Manabe, T.; Nishida, S. *J. Am. Chem. Soc*, in press.

(6) (a) Schmid, H.; Naab, P.; Hayakawa, K. *Helv. Chim. Acta* **1978**, *61*, 1427. (b) Frater, Gy. *Ibid.* **1974**, *57*, 172. (c) Gammil, R. B.; Gold, P. M.; Mizsak, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 3095.

(7) The former prefix always refers to the configuration with respect to the 7-[bis(methylthio)methylene]norbornadiene.

(8) Sasaki, T.; Kanematsu, K.; Iizuka, K. *J. Org. Chem.* **1976**, *41*, 1105.

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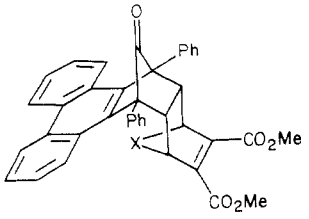
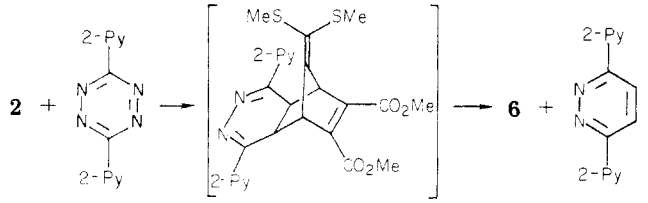


8, X = O; =

conditions. This result led us to undertake the reaction of **2** with 3,6-di(2-pyridyl)-*s*-tetrazine (**9**) which is more suitable for a mild fragmentation reaction.[9] Thus, treatment of **2** with **9** in chloroform at room temperature afforded a quantitative yield of **6** along with pyridazine **11**. The reaction probably proceeded by a multistep re-

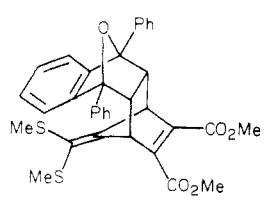


9 **10** **11**

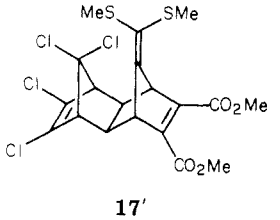
action via adduct **10**, though no such intermediates could be detected by NMR analysis of the reaction mixture. Fulvene **6** is moderately stable at room temperature and undergoes Diels–Adler reaction with an appropriate dienophile (vide infra).

Reaction of **2** with tropone (**12a**) and tropolone (**12b**) in toluene at 110–130 °C afforded 1:1 adducts **13a** (40%) and **13b** (41%), respectively (Scheme II). The presence of the bicyclo[3.2.2]nona-3,6-dien-2-one skeleton in these adducts was apparent from the spectral comparison with numerous tropone adducts.[5b,d] In the ^{1}H NMR spectrum of **13a** (mp 164–168 °C), the absence of appreciable couplings between H-1 and H-2 (H-7 and -8), and H-2 and H-3 (H-6 and -7) clearly indicated the exo,endo configuration as depicted in **13a**. Adduct **13b** (mp 122–125 °C) was similarily concluded to be the exo,endo [4 + 2] cycloadduct on the basis of its spectral data (see Experimental Section).

1,3-Diphenylisobenzofuran (**14**) and hexachlorocyclopentadiene (**16**) reacted with **2** (toluene, 110–130 °C) to give [4 + 2] cycloadducts **15** (76%) and **17** (16%), respectively. In the ^{1}H NMR spectrum of **15** (mp 210–212 °C), the absence of the coupling between H-2 and H-3 indicated the exo configuration with respect to the 7-methylenenorbornene system. Of two possible structures, the *exo,endo*-**15′** was ruled out by the "normal" chemical shift of methylthio groups (δ 1.98), because the strong high-field shift of these signals would be expected for **15′** due to the anisotropic effect of the proximate aromatic ring.[8] Thus, **15** was assigned to the exo,exo configuration like **5**.



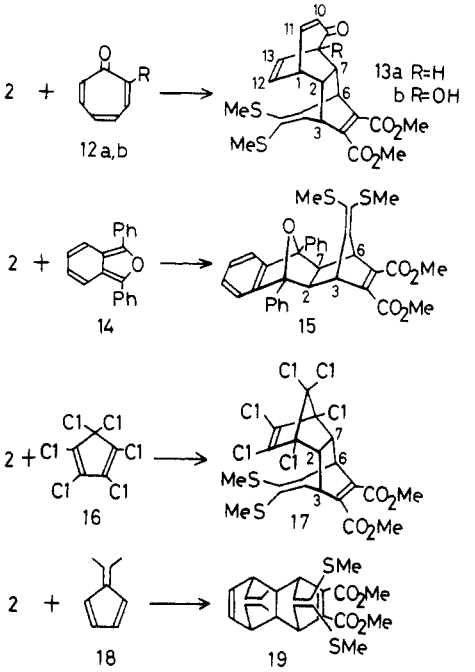
15′



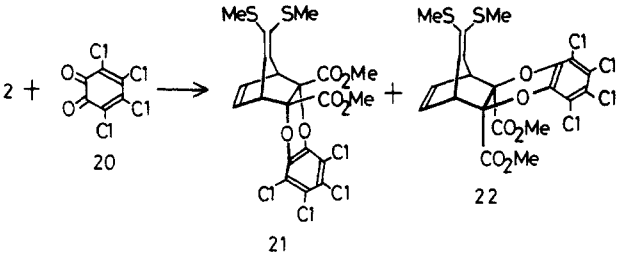
17′

(9) Priestley, G. M.; Warrener, R. N. *Tetrahedron Lett.* **1972**, 4295 and references cited therein.

Scheme II



Scheme III



The ^{1}H NMR spectrum of **17** (mp 125–128 °C) also suggested the exo configuration regarding the 7-methylenenorbornene skeleton. In this case, however, exo,exo adduct **17′** would experience the severe steric hindrance because of the bulkiness of dichlorinated carbon bridge. In fact this type of adduct of **16** has not been reported so far.[10] Therefore, **17** was concluded to be exo,endo adduct.

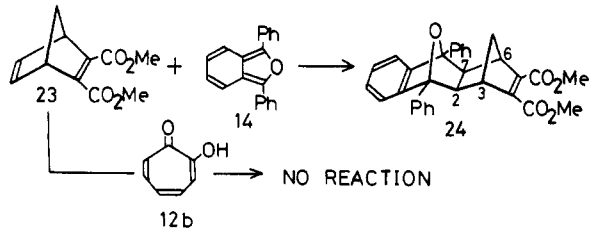
Similar reaction of **2** with 6,6-dimethylfulvene (**18**) gave [4 + 2] adduct **19** (33%) as an unstable oil which could not be thoroughly purified. While the symmetrical structure of **19** was apparent from its ^{1}H NMR spectrum (Experimental Section), the stereochemistry remained unclear.

All reactions examined so far took place only at the unsubstituted double bond of **2**. In sharp contrast, *o*-chloranil (**20**) reacted with **2** exclusively at the substituted (electron deficient) double bond. Thus, heating a mixture of **2** and **20** in benzene at 65–85 °C for 20 h resulted in the formation of two 1:1 adducts, **21** (63%, mp 149–151 °C) and **22** (31%, mp 160–162 °C), as shown in Scheme III.

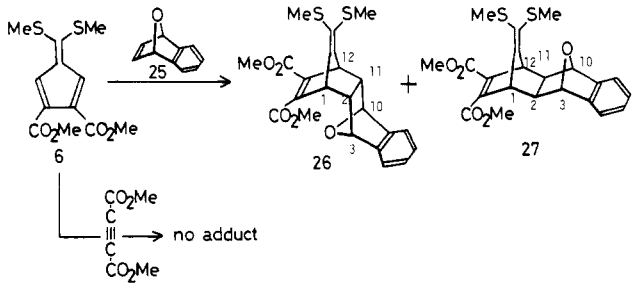
The dioxene structure of the adducts was suggested by their IR spectra which showed no 1,2-diketone absorption. The ^{1}H NMR spectra revealed characteristic signals for olefinic protons [**21**, δ 6.72 (2 H, dd); **22**, δ 6.95 (2 H, dd)], indicating that *o*-chloranil addition occurred at the double bond bearing the carbomethoxy groups of **2**. The upfield shift ($\Delta\delta$ = 0.23 ppm) of the vinyl proton signal of **21**

(10) (a) Pfaendler, H. R.; Tanida, H.; Haselbach, E. *Helv. Chim. Acta* **1974**, *57*, 383. (b) Haywood-Farmer, J.; Malkus, H.; Battiste, M. A. *J. Am. Chem. Soc.* **1972**, *94*, 2209.

Scheme IV



Scheme V



compared with that of **22** can be attributed to the anisotropic effect of the endo aromatic ring of **21**. Thus, **21** as concluded to be an endo adduct and **22** to be an exo adduct. Both adducts were inert toward diimide reduction and catalytic hydrogenation (Pd/C).

It should be noted that **20** reacted as a heterodiene with **2**, while **20** is known to react mainly as a 1,3-diene with norbornadiene.[11] Although norbornadiene derivatives are known to be good dipolarophiles,[12] the attempted reactions of **2** with various 1,3-dipolar compounds were unsuccessful and only intractable mixtures were obtained.

In order to evaluate the effect of the 7-bis(methylthio)methylene group in **2**, we have investigated the cycloaddition reaction of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**23**).[13] While **23** reacted with isobenzofuran **14** to give 1:1 adduct **24** (mp 203–204 °C) in comparable yield (72%), **23** was completely recovered from the reaction with tropolone (**12b**) under the same conditions applied for the reaction of **2** (Scheme IV).

These results show the remarkable effect of orbital participation of the 7-substituent of **2** which increases the dienophilicity of the endocyclic double bond toward electron-deficient dienes.

Reactivity of 6,6-Dithiafulvene 6. Although the Diels–Alder reactions of fulvenes have been extensively explored,[14] such reactions of 6-heterosubstituted fulvenes as dienes have been less investigated because of their low reactivity.[4]

We have examined the cycloaddition reaction of 6,6-dithiafulvene **6** obtained readily as above. Compound **6** was allowed to react with 7-oxabenzonorbornadiene (**25**),[5a] an electron-rich olefin, in toluene at 120–140 °C for 60 h. Two 1:1 adducts, **26** (21%) and **27** (9%), were obtained after chromatographic separation (Scheme V).

The structures of adducts were proved by NMR analysis. The presence of the coupling between H-1 and H-2 (H-11 and -12), and the absence of appreciable coupling between H-2 and H-3 (H-10 and -11) indicated the major product **26** (mp 171–173 °C) to be the endo,exo adduct. The absence of vicinal couplings ($J_{2,1} = J_{11,12} = J_{2,3} = J_{11,10} = 0$) indicated the minor product **27** (mp 141–143 °C) to be the exo,exo adduct. On the other hand, the reaction of **6** with dimethyl acetylenedicarboxylate, an electron-poor olefin, did not occur even under drastic conditions. This is a sharp contrast to the fact that fulvene **1** reacts with electron-poor olefins in good yields[4] but does not react with an electron-rich olefin such as **25**.

(11) Warrener, R. N.; Numm, E. E.; Wilson, W. S. *Tetrahedron Lett.* **1972**, 175.
(12) (a) Huisgen, R.; Grashey, R.; Sauer, J. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964, and references cited therein. (b) Taniguchi, H.; Ikeda, T.; Yoshida, Y.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2694.
(13) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 236.
(14) Yates, P. *Adv. Alicycl. Chem.* **1968**, *2*, 59.

Experimental Section

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyser. NMR spectra were taken with JEOL FX 60 FT NMR and JEOL C-60-HL spectrometers, with tetramethylsilane as an internal standard. IR spectra were obtained with a Hitachi IRA-1 spectrometer.

Reactions of Dimethyl 7-[Bis(methylthio)methylene]bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate with Cyclic Polyenes. (a) With Tetraphenylcyclopentadienone (4). A solution of **2** (252 mg, 0.81 mmol) and tetraphenylcyclopentadienone (**4**; 310 mg, 0.81 mmol) in toluene (2 mL) was heated at 100 °C in a sealed tube for 47 h. Chromatography of the reaction mixture on a silica gel column (ether–*n*-hexane) gave **5** (378 mg, 67%) and **6** (8.1 mg, 3.5%) in that order of elution.

Adduct **5**: mp 220–223 °C; IR (KBr) 1770, 1700, 1435, 1248, 1182, 759, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.94 (6 H, s, 2 SMe), 3.32 (2 H, s, H-2 and H-7), 3.86 (6 H, s, 2 OMe), 4.29 (2 H, s, H-3 and H-6), 6.5–7.1 (10 H, m, Ar H), 7.1–7.4 (6 H, m, Ar H), 7.4–7.8 (4 H, m, Ar H).

Anal. Calcd for $C_{43}H_{36}S_2O_5$: C, 74.11; H, 5.21. Found: C, 73.84; H, 5.26.

Compound **6**: mp 59–62 °C; IR (KBr) 1700, 1480, 1300, 1210 cm^{-1}; NMR ($CDCl_3$) δ 2.46 (6 H, s, 2 SMe), 3.79 (6 H, s, 2 OMe), 7.12 (2 H, s).

Anal. Calcd for $C_{12}H_{14}O_4S_2$: C, 50.33; H, 4.93. Found: C, 50.62; H, 5.05.

Reduction of Adduct 5 with $NaBH_4$. The ketone **5** (70 mg, 0.10 mmol) was added to a stirred solution of $NaBH_4$ (5 mg, 0.13 mmol) in methanol (2 mL) at 0 °C. The reaction was continued for 6 h, whereupon dilute hydrochloric acid was added to bring the solution to pH 4. Methanol was removed under reduced pressure and the aqueous residue was extracted with ether. The organic layer was dried over Na_2SO_4 and evaporated. Chromatography on a silica gel column with ether–*n*-hexane followed by recrystallization from ether–*n*-hexane gave **7** (30 mg, 43%) as colorless crystals: mp 233–235 °C; IR (KBr) 1710, 1432, 1170, 1000 cm^{-1}; NMR ($CDCl_3$) δ 1.91 (3 H, s, SMe), 1.98 (3 H, s, S Me), 2.91 (2 H, s, H-2 and H-7), 3.28 (2 H, m, H-3 and H-6), 3.63 (3 H, s, OMe), 3.69 (1 H, s, H-a or H-b), 3.78 (1 H, s, H-a or H-b), 3.87 (3 H, s, OMe), 6.5–7.1 (10 H, m, Ar H), 7.1–7.4 (6 H, m, Ar H), 7.4–7.8 (4 H, m, Ar H).

Anal. Calcd for $C_{43}H_{38}S_2O_5$: C, 73.90; H, 5.48. Found: C, 73.85; H, 5.53.

(b) With 3,6-Di(2-pyridyl)-*s*-tetrazine (9). A solution of **2** (304 mg, 1.0 mmol) and 3,6-di(2-pyridyl)-*s*-tetrzine (**9**; 236 mg, 1.0 mmol) in chloroform (3 mL) was stirred for 8 h at room temperature. After evaporation of solvent, the resulting residue was well agitated in 30 mL of ether. Insoluble pyridazine **11** (160 mg, 69%) was removed by filtration. The ethereal solution was concentrated in vacuo to give almost pure **6** as solid. Chromatography on a short silica gel column (ether–*n*-hexane) gave pure **6** (272 mg, 95%).

(c) With Tropone (12a). A solution of **2** (939 mg, 3.0 mmol) and tropone (**12a**; 379 mg, 3.57 mmol) in toluene (5 mL) was heated at 110–130 °C in a sealed tube for 2 weeks. The solvent was removed under reduced pressure and chromatography on a silica gel column with benzene followed by recrystallization from dichloromethane–*n*-hexane gave adduct **13a** (396 mg, 40%) as colorless crystals: mp 164–168 °C; IR (KBr) 1717, 1708, 1656, 1210, 1180 cm^{-1}; NMR ($CDCl_3$) δ 2.17 (6 H, s, 2 SMe), 2.47 (1 H, d, J = 9.0 Hz, H-7), 2.68 (1 H, d, J = 9.0 Hz, H-2), 3.33 (1 H, t, J = 8.2 Hz, H-1), 3.54 (1 H, dd, J = 8.0, 2.0 Hz, H-8), 3.79 (6 H, s, 2OMe), 3.80 (2 H, s, H-3 and H-6), 5.66 (1 H, dd, J = 11.0, 2.0 Hz, H-10), 5.87 (1 H, t, J = 8.2 Hz, H-13), 6.24 (1 H, t, J = 8.2

Hz, H-12), 7.11 (1 H, dd, J = 11.0, 8.2 Hz, H-11).

Anal. Calcd for $C_{21}H_{22}O_5S_2$: C, 60.27; H, 5.30. Found: C, 59.98; H, 5.37.

(d) With Tropolone (12b). A solution of **2** (957 mg, 3.07 mmol) and tropolone (**12b**; 374 mg, 3.07 mmol) in toluene (4 mL) was heated at 110–130 °C in a sealed tube for 2 weeks. The same workup afforded adduct **13b** (234 mg, 41%) as colorless crystals: mp 122–125 °C; IR (KBr) 3440, 1712, 1700, 1648, 1200 cm^{-1}; NMR ($CDCl_3$) δ 2.18 (1 H, s, exchangeable OH), 2.22 (6 H, s, 2 SMe), 2.24 (1 H, d, J = 8.1 Hz, H-2), 2.57 (1 H, d, J = 8.1 Hz, H-7), 3.41 (1 H, t, J = 8.5 Hz, H-1), 3.78 (6 H, s, 2 OMe), 4.38 (1 H, s, H-3), 4.59 (1 H, s, H-6), 5.72 (1 H, d, J = 10.5 Hz, H-10), 5.88 (1 H, d, J = 7.5 Hz, H-12), 7.27 (1 H, dd, J = 10.5, 8.5 Hz, H-11).

Anal. Calcd for $C_{21}H_{22}O_6S_2$: C, 58.05; H, 5.10. Found: C, 57.99; H, 5.16.

(e) With 1,3-Diphenylisobenzofuran (14). A solution of **2** (200 mg, 0.64 mmol) and 1,3-diphenylisobenzofuran (**14**) in toluene (1 mL) was heated at 100 °C in a sealed tube for 5.5 h. After evaporation to dryness at reduced pressure, the mixture was chromatographed on a silica gel column (ether–n-hexane) to give adduct **15** (220 mg, 76%) as colorless crystals: mp 210–212 °C; IR (KBr) 1717, 1435, 1250, 1180 cm^{-1}; NMR ($CDCl_3$) δ 1.98 (6 H, s, 2 SMe), 2.93 (2 H, s, H-2 and H-7), 3.75 (6 H, s, 2 OMe), 3.88 (2 H, s, H-3 and H-6), 7.02 (4 H, m, Ar H), 7.3–7.9 (10 H, m, Ar H).

Anal. Calcd for $C_{34}H_{30}S_2O_5$: C, 70.08; H, 5.19. Found: C, 70.11; H, 5.22.

(f) With Hexachlorocyclopentadiene (16). A solution of **2** (959 mg, 3.07 mmol) and hexachlorocyclopentadiene (**16**; 839 mg, 3.07 mmol) in toluene (4 mL) was heated at 110–130 °C in a sealed tube for 2 weeks. After removal of solvent, the residue was subjected to chromatography on a silica gel column with dichloromethane–n-hexane and recrystallization from dichloromethane–n-hexane to give adduct **17** (259 mg, 16%) as colorless crystals: mp 125–128 °C; IR (KBr) 1717, 1700, 1243, 1170 cm^{-1}; NMR ($CDCl_3$) δ 2.19 (6 H, s, 2 SMe), 3.10 (2 H, s, H-2 and H-7), 3.83 (6 H, s, 2 OMe), 4.15 (2 H, s, H-3 and H-6).

Anal. Calcd for $C_{19}H_{16}O_4S_2Cl_6$: C, 39.00; H, 2.76. Found: C, 39.15; H, 2.89.

(g) With 6,6-Dimethylfulvene (18). A solution of **2** (312 mg, 1.14 mmol) and 6,6-dimethylfulvene (**18**; 115 mg, 1.08 mmol) in toluene (1 mL) was heated at 100 °C in a sealed tube for 2 weeks. Chromatography of the reaction mixture on a silica gel column (ether–n-hexane) gave adduct **19** (136 mg, 32.5%) as an oily product: IR (neat) 1717, 1438, 1257, 1086 cm^{-1}; NMR ($CDCl_3$) δ 1.51 (6 H, s, 2 Me), 2.19 (6 H, s, 2 SMe), 2.50 (2 H, m, H-2 and H-7), 3.35 (2 H, m, H-1 and H-8), 3.80 (8 H, s, 2 OMe, H-3, and H-6), 5.99 (2 H, t, H-9 and H-10). A pure sample for elemental analysis and mass spectroscopy could not obtained due to the instability of **19**.

(h) With o-Chloranil (20). A solution of **2** (638 mg, 2.1 mmol) and o-chloranil (**20**; 516 mg, 2.10 mmol) in benzene (3 mL) was heated at 65–85 °C in a sealed tube for 20 h. The reaction mixture was subjected to silica gel chromatography and fractional crystallization from dichloromethane–n-hexane to give adduct **21** (727 mg, 63%) as less soluble crystals and adduct **22** (358 mg, 31%) as more soluble crystals.

Adduct **21**: mp 149–151 °C; IR (KBr) 1710, 1430, 1260, 1180 cm^{-1}; NMR ($CDCl_3$) δ 2.28 (6 H, s, 2 SMe), 3.79 (6 H, s, 2 OMe), 4.11 (2 H, dd, J = 3.0, 1.95 Hz, bridgehead H), 6.72 (2 H, dd, J = 3.0, 1.95 Hz, olefin H).

Anal. Calcd for $C_{20}H_{16}O_6S_2Cl_4$: C, 43.03; H, 2.89. Found: C, 42.83; H, 3.19.

Adduct **22**: mp 160.5–162.5 °C; IR (KBr) 1718, 1420, 1400, 1180, 1000 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (6 H, s, 2 SMe), 3.82 (6 H, s, 2 OMe), 4.10 (2 H, dd, J = 3.0, 1.95 Hz, bridgehead H), 6.95 (2 H, dd, J = 3.0, 1.95 Hz, olefin H).

Anal. Calcd for $C_{20}H_{16}O_6S_2Cl_4$: C, 43.03; H, 2.89. Found: C, 43.01; H, 2.90.

Reaction of 23 with 1,3-Diphenylisobenzofuran (14). A solution of **23** (133 mg, 0.64 mmol) and 1,3-diphenylisobenzofuran (**14**; 135 mg, 0.5 mmol) in toluene (1 mL) was heated at 100 °C in a sealed tube for 5.5 h. After evaporation to dryness at reduced pressure, the mixture was chromatographed on a silica gel column (ether–n-hexane) to give adduct **24** (239 mg, 72%) as colorless crystals: mp 203–204 °C; IR (KBr) 1708, 1280, 1095, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (2 H, br d, J = 9.0 Hz, methylene H), 2.80 (2 H, s, H-2 and H-7), 3.01 (2 H, br s, H-3 and H-6), 7.01 (4 H, m, Ar H), 7.3–7.9 (10 H, m, Ar H).

Anal. Calcd for $C_{31}H_{26}O_5$: C, 77.80; H, 5.48. Found: C, 77.42; H, 5.86.

Reaction of 6 with 7-Oxabenzonorbornadiene (25). A solution of **6** (572 mg, 2.0 mmol) and 7-oxabenzonorbornadiene (**25**; 288 mg, 2.0 mmol) in toluene (10 mL) was heated at 120–140 °C in a sealed tube for 60 h. Chromatography of the reaction mixture on a silica gel column (ether–n-hexane) gave adduct **27** (66 mg, 9%) and adduct **26** (181 mg, 21%) in that order of elution.

Adduct **27**: mp 141–143 °C; IR (KBr) 1700, 1620, 1440, 1290 cm^{-1}; NMR ($CDCl_3$) δ 2.22 (6 H, s, 2 SMe), 2.24 (2 H, s, H-2 and H-11), 3.77 (6 H, s, 2 OMe), 4.12 (2 H, s, H-1 and H-12), 5.13 (2 H, s, H-3 and H-10), 7.0–7.4 (4 H, m, Ar H).

Anal. Calcd for $C_{22}H_{22}O_5S_2$: C, 61.38; H, 5.15. Found: C, 61.08; H, 5.15.

Adduct **26**: mp 171–173 °C; IR (KBr) 1700, 1620, 1440, 980 cm^{-1}; NMR ($CDCl_3$) δ 2.15 (6 H, s, 2 SMe), 2.46 (2 H, m, H-2 and H-11), 3.85 (6 H, s, 2 OMe), 4.20 (2 H, m, H-1 and H-12), 5.26 (2 H, s, H-3 and H-10), 7.0–7.4 (4 H, m, Ar H).

Anal. Calcd for $C_{22}H_{22}O_5S_2$: C, 61.38; H, 5.15. Found: C, 61.37; H, 5.16.

Registry No. 2, 55359-69-8; **4**, 479-33-4; **5**, 76773-60-9; **6**, 76773-61-0; **7**, 76773-62-1; **9**, 1671-87-0; 11, 36901-11-8; **12a**, 539-80-0; **12b**, 533-75-5; **13a**, 76773-63-2; **13b**, 76773-64-3; **14**, 5471-63-6; **15**, 76773-65-4; **16**, 77-47-4; **17**, 76773-66-5; **18**, 2175-91-9; **19**, 76773-67-6; **20**, 2435-53-2; **21**, 76773-68-7; **22**, 76821-83-5; **23**, 947-57-9; **24**, 76773-69-8; **25**, 573-57-9; **26**, 76773-70-1; **27**, 76821-84-6.