Tropothione Undergoes Cycloadditions in a Way Different from Tropone: A Comparative Study of Their Reactivities on Cycloaddition to Fulvene[1]

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Abstract: Tropothione, which is valence isoelectronic with tropone, reacts concertedly with fulvenes to give 1:1 [8 + 2] cycloadducts. The product configuration is sharply different from that of the initially formed [6 + 4] cycloadduct between tropone and fulvene. The reaction mechanisms are studied kinetically and by molecular orbital calculations. The obtained endo form of the [8 + 2] product is found to arise from the secondary orbital interaction in the course of the intrinsic reaction coordinate.

Despite the extensive studies of both thiocarbonyl[3] and [7]-annulenone (troponoid)[4] compounds, little is known about their combined systems, [7]annulenethiones, because of their instability. We have reported the synthesis and isolation of tropothione[5] (**1**) as thermally unstable crystals and the novel properties of the related compounds.[6] Fundamental physical properties of **1** are quite different from those of tropone (**2**).[7] Structural similarities between **1** and **2** allow an interesting comparison of their reactivities since tropone is a typical compound for a variety of cycloadditions[4] including [6 + 4][8] and [8 + 2][9] reactions. Houk et al. reported that tropone reacted with 6,6-dimethylfulvene to give a novel double [6 + 4]-type adduct[10] (**3**) via an initially formed [6 + 4] cycloadduct[11] (**4**) (Scheme I).

We have communicated a study of the cycloaddition of tropothione with cyclopentadiene (**5**) (Scheme IIb).[7b] In fact, we have found theoretically that the [8 + 2] cycloaddition is a facile process by the use of a model reaction system, tropothione and ethylene.[12]

In contrast to the [6 + 4] cycloaddition[13] between **2** and **5** in Scheme IIa, **1** reacts with **5** to afford an [8 + 2] cycloadduct (**6**) in Scheme IIb and the reaction proceeds with high stereo- and regioselectivities in a concerted manner. In view of this contrast, it is tempting to examine the cycloaddition between **1** and fulvene to determine whether the [8 + 2] or [6 + 4] cycloadduct is formed. This is because fulvene works flexibly as a 2π,[14] 4π,[15] or 6π[16] moiety in cycloadditions.[17] In this work, a mechanistic study of the tropothione–fulvene reaction focuses on the following points.

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(1) Dedicated to Professor Klaus Hafner on the occasion of his 66th birthday [especially called "Ka-koh" (double-six-age cellebration) in the Japanese language] and a life-long career in the study of "Hafner's Hydrocarbons" including fulvene chemistry. For his biography and work, see: Kreher, R. P. *Chem.-Ztg.* **1987**, *111*, 375–381 and references therein.

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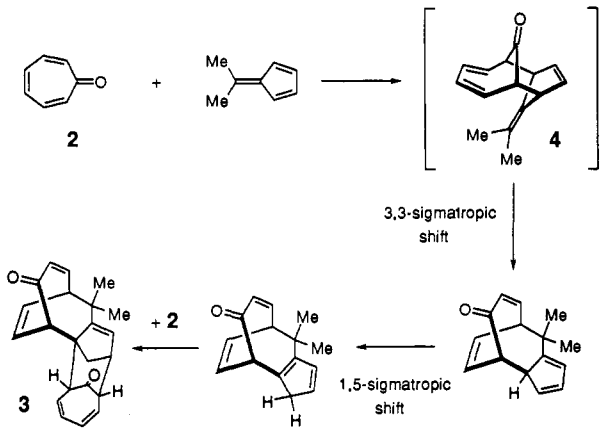
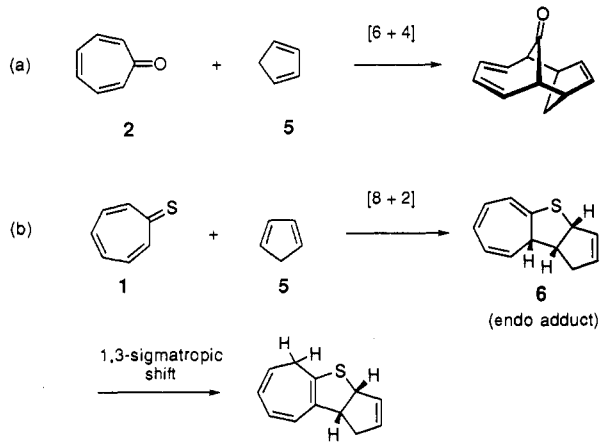
Scheme I. Double [6 + 4] Cycloaddition between Tropone and 6,6-Dimethylfulvene



Scheme II. Cycloaddition between Tropone (**2**) or Tropothione (**1**) and Cyclopentadiene



One is the source of symmetry-allowed [6 + 4] and [8 + 2] selectivities. The other is that of exo and endo selectivities in an [8 + 2] cycloaddition. It will be shown that the frontier-orbital interaction at the initial stage of the intrinsic reaction coordinate of cycloadditions plays a decisive role.

Experimental Results and Discussion

Reactions of tropothione (**1**) with 6,6-dimethylfulvene[18] and 6,6-diphenylfulvene[19] afforded the corresponding 1:1 cycloadducts **7a** and **7b**, respectively (Scheme III). The absence of significant amounts of other products in the reaction was proved by high-performance liquid chromatographic (HPLC) analysis and

Scheme III. Cycloaddition between Tropothione and 6,6-Dimethyl- or 6,6-Diphenylfulvene

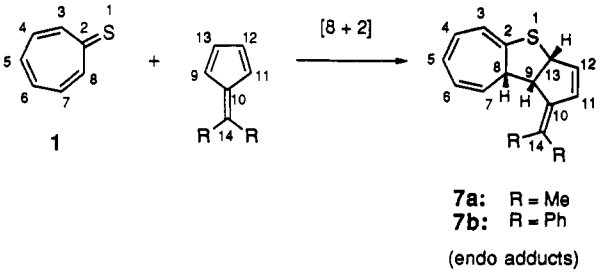


Table I. Experimental Rate Constants for Cycloaddition of Tropothione (**1**) to 6,6-Dimethylfulvene in Two Solvents[a]

chloroform[b]		benzene[b]	
T (K)	k^c (s^{-1})	T (K)	k^c (s^{-1})
298.1 ± 0.1	0.314×10^{-5}	302.9 ± 0.1	0.352×10^{-5}
303.1 ± 0.1	0.465×10^{-5}	308.1 ± 0.1	0.454×10^{-5}
307.9 ± 0.1	0.683×10^{-5}	313.1 ± 0.1	0.774×10^{-5}
313.0 ± 0.1	1.069×10^{-5}	317.9 ± 0.1	1.031×10^{-5}
318.1 ± 0.1	1.539×10^{-5}	323.0 ± 0.1	1.560×10^{-5}

[a] Determined spectroscopically for the reactions. [b] The concentration of tropothione (**1**) is 5×10^{-2} M in all experiments. [c] The pseudo-first-order rate constants due to the excess concentration of 6,6-dimethylfulvene (20 times that of **1**).

Table II. Experimental Activation Parameters for Cycloaddition of Tropothione (**1**) to 6,6-Dimethylfulvene

	chloroform	benzene
E_a (kcal mol^{-1})	15.2 (11.7)[a]	14.8 (11.5)
log A (s^{-1})	5.60 (4.56)	5.18 (4.13)
$\Delta S^{\ddagger}$ [b] (eu)	−33.0 (−37.8)	−34.9 (−39.6)
$\Delta H^{\ddagger}$ [b] (kcal mol^{-1})	14.5 (11.1)	14.2 (11.0)
$\Delta G^{\ddagger}$ [b] (kcal mol^{-1})	24.7 (22.8)	24.9 (23.2)

[a] Values in parentheses are for the reaction between tropothione (**1**) and cyclopentadiene (**5**). Reference 7b. [b] 308 K.

spectral monitoring (400-MHz ^{1}H NMR) at temperatures of 25 and 50 °C. Elemental analyses and mass spectral data showed that **7a** and **7b** are 1:1 adducts. NMR spectroscopies (^{13}C and ^{1}H) proved the structure of the products using comparison of the nuclear Overhauser effect (NOE) observed with those expected for the various possible isomers of 1:1 adducts.

To establish the reaction mechanisms, we carried out kinetic studies of the cycloaddition reactions at different temperatures in solvents with different polarities under pseudo-first-order reaction conditions in which the molarity of 6,6-dimethylfulvene was 20 times greater than that of tropothione (**1**). The reactions were followed by observing the decrease in the absorptivity of the UV maximum of **1** at 380 nm. Tables I and II give the resulting reaction rates and activation parameters. These $\Delta S^{\ddagger}$ values are comparable with those between −40 and −30 eu obtained for cycloadditions of mobile systems.[20] The activation energy (E_a = 14.8–15.2 kcal mol^{-1}) indicates that this cycloaddition is comparable to those (E_a = 8–18 kcal mol^{-1}) for Diels–Alder reactions.[20] The values strongly suggest that the reactions proceeded as concerted cycloadditions through the highly oriented compact transition state (TS) of a 10π peripheral system. The cis–cis configuration of the adducts (**7a** and **7b**) suggests that the

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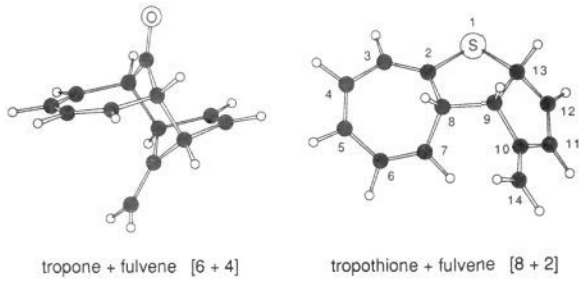

Figure 1. Geometries of two cycloadducts optimized by the PM3 method.[24] Atom numberings of the [8 + 2] endo adduct are the same as those in Scheme III. Empty circles denote hydrogen atoms.

reactions proceed in a suprafacial–suprafacial manner of the endo approach type. Hence, we can conclude that the cycloadduct **7a** is formed from the reaction of tropothione (**1**) with 6,6-dimethylfulvene via a concerted $[_\pi 8_s + _\pi 2_s]$ path.

Molecular Orbital Calculations

To elucidate the [6 + 4]–[8 + 2] and exo–endo (in [8 + 2]) selectivities, we carried out MO calculations for cycloadditions of tropone (**2**) and tropothione (**1**) to the parent fulvene. Figure 1 shows geometries of [6 + 4] and [8 + 2] cycloadducts for understanding their stereochemistry. In the endo [8 + 2] adduct detected here, the seven-membered ring moiety is nonplanar and shows a slight ring strain imposed on the cyclohexatriene fragment. Figure 2 shows PM3 TS geometries of [6 + 4] and [8 + 2] cycloadditions. The PM3 activation energies at the top show that tropone (X = O) prefers [6 + 4] to [8 + 2], as expected in the Scheme I. On the contrary, as observed in the previous section, tropothione (X = S) prefers [8 + 2] to [6 + 4] cycloaddition by both PM3 and STO-3G* calculations. Among the four TS structures, only that of the X = S [8 + 2] has a character such that fulvene is an electron acceptor. This result suggests that the highest occupied molecular orbital (HOMO) of tropothione has a key role in the [8 + 2] reaction.

Starting from the STO-3G* TS, we have sought the intrinsic reaction coordinates (IRCs) of three tropothione–fulvene cycloadditions.[21] One is the [8 + 2] endo reaction observed here. The other two, [8 + 2] exo and [6 + 4], are *model* reactions for comparison. These are not detected experimentally. Figure 3 exhibits energy changes along the three IRCs. Activation energies show the reactivity order, [8 + 2] endo > [8 + 2] exo > [6 + 4]. At s of ca. −1.5 Bohr·amu$^{1/2}$ in the [8 + 2] endo energy curve, the energy ascent is depressed. The somewhat bent curve of the [8 + 2] endo shows that the sharply increasing energy owing to steric crowding is relaxed by some kind of the secondary interaction. The singularity at $s \approx -1.5$ Bohr·amu$^{1/2}$ may be related to the orbital interaction because MO overlaps suddenly become large as two molecules come closer to each other. Figure 4 presents geometric changes along the IRCs. In contrast to the significant difference of adduct geometries in Figure 1, orientations of two molecules in [6 + 4] and [8 + 2] endo paths are similar at $s = -2.997$ Bohr·amu$^{1/2}$. That is to say, there is only a slight difference between these paths. At $s = -2.997 \rightarrow 0$ Bohr·amu$^{1/2}$ of the [8 + 2] endo, the C(6)···C(14) distance is almost invariant, 3.470 → 3.441 Å, whereas the reaction center distance C(8)···C(9) is decreased considerably (2.904 → 2.279 Å). The C(6)···C(14) region seems to be of the secondary orbital interaction. From the early stage to the TS, tropothione (**1**) is

(21) PM3 fails to reproduce the [8 + 2] exo–endo selectivity. That is, the exo TS is better than the endo TS, which is inconsistent with the experimental result. A similar defect in PM3 has also appeared in Figure 2. At two [8 + 2] geometries of X = O and X = S, the C···O distance (1.985 Å) is almost equal to the C···S one (1.992 Å). In view of standard covalent lengths, 1.43 Å (C–O) and 1.81 Å (C–S), this equality is clearly incorrect. PM3 and AM1 tend to overestimate the C–S strength, which leads to the sterically crowded and unstable [8 + 2] endo TS.

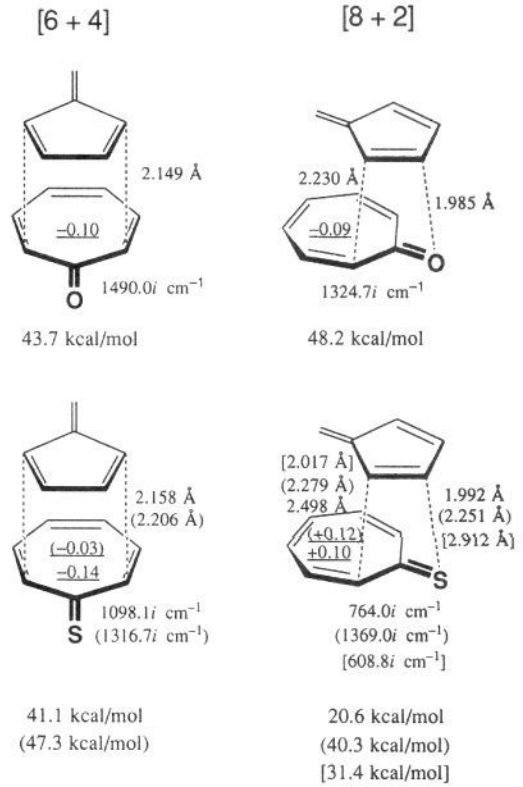

Figure 2. Transition-state (TS) structures of [6 + 4] and [8 + 2] cycloadditions between C_7H_6X and fulvene optimized with the PM3 method. X = O is tropone (**2**), and X = S is tropothione (**1**). For X = S, numbers in parentheses are those of RHF/STO-3G*. For [8 + 2] X = S, RHF/3-21G* data almost optimized (see Computational Methods in the Experimental Section) are shown in square brackets. Imaginary frequencies in cm^{-1} indicate that obtained geometries are really of the TS. Energies in kcal mol^{-1} are calculated activation energies, which are evidently overestimated due to rough computational methods as was discussed in the tropothione–ethylene model system.[12] Underlined numbers are electronic charges shifted from fulvene to C_7H_6X. Therefore, negative values show that C_7H_6X is an electron acceptor.

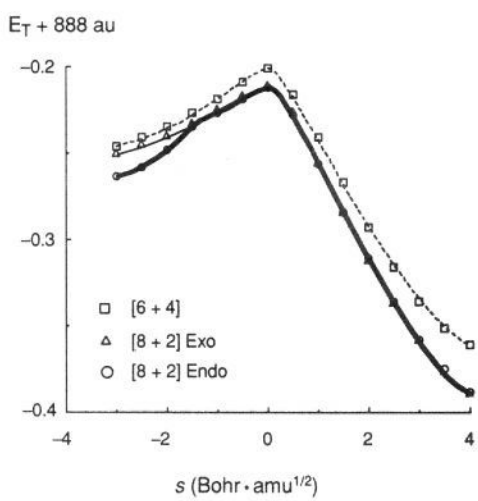

Figure 3. STO-3G* potential energy profiles along the intrinsic reaction coordinate of three cycloadditions between tropothione (**1**) and fulvene. STO-3G* activation energies of [6 + 4], [8 + 2] exo, and [8 + 2] endo are 47.3, 40.9, and 40.3 kcal mol^{-1}, respectively.

an electron donor to fulvene in [8 + 2] exo and endo additions. Noteworthy is the donor–acceptor reversal in the [6 + 4] reaction. At $s = -2.997$ Bohr·amu$^{1/2}$, tropothione is a donor, while as already shown in Figure 2, it is an acceptor at the TS. Thus, the

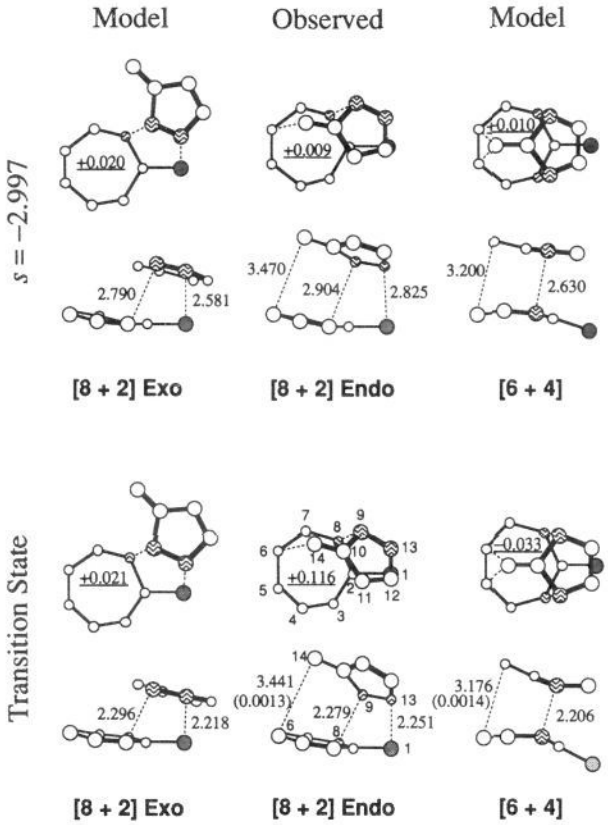

Figure 4. Geometries of an early stage (s = −2.997 Bohr·amu$^{1/2}$) and the TSs of three cycloadditions between tropothione (**1**) and fulvene optimized with RHF/STO-3G*. [6 + 4] and [8 + 2] endo TS data are the same as those in Figure 2. Almost the same notations as those in Figure 2 are used. Numbers in parentheses stand for C(14)···C(6) atom–atom bond populations (positive, bonding) for the secondary orbital interactions. Dark circles denote the sulfur atoms, and waved circles show reaction-center carbon atoms. Twelve hydrogen atoms are omitted for clarity.

dominant frontier molecular orbital (FMO) interaction at the early stage of any tropothione reaction should be HOMO (tropothione) → lumo (fulvene).

Discussions on Computed Data

In previous section, computations have shown correctly that tropothione (**1**) reacts with fulvene in an [8 + 2] manner while tropone (**2**) reacts in a [6 + 4] manner. The source of the [8 + 2] and [6 + 4] selectivity is explained in Figure 5. The HOMOs of both tropone (X = O) and tropothione (X = S) are symmetric π orbitals. However, their shapes are entirely different. When the HOMO of **2** (X = O) is viewed at the cut plane above the molecular plane, its shape is almost the same as the hexatriene HOMO and the extension on the oxygen atom is almost absent. On the contrary, the HOMO of **1** (X = S) is localized largely on the sulfur atom, and the cyclohexatriene moiety has a small extension. The HOMO shape in Figure 5 is sketched schematically in Figure 6 together with other frontier orbitals. The source of the [8 + 2] addition is the large lobe of the HOMO on the sulfur atom. The lobe makes the tropothione an electron donor at the early stage of the addition in the *model* [6 + 4] path as well as in the [8 + 2] exo and endo paths. The HOMO of **2** (practically hexatriene) cannot have the lobe. This leads to the [6 + 4] reaction.

In Figure 4, the [8 + 2] endo path is different only slightly from the [6 + 4] path. This difference is ascribed to the choice of main and secondary orbital interactions (full and broken arrows, respectively, for [8 + 2] endo in Figure 6a). When the broken arrow is switched to the full arrow between C(3)···C(11) and S(1)···C(13), the [6 + 4] orbital interaction is obtained. The C(6)···C(14) secondary orbital interaction in HOMO → lumo of Figure 6a is the main source of the [8 + 2] endo selectivity.

To demonstrate the role of the interaction, three atom–atom bond populations along the [8 + 2] endo IRC are shown in Figure 7a. The starting point of the sharp increase in the C(6)···C(14) population (s of ca. −1.5 Bohr·amu$^{1/2}$) is almost the same as the lightly bent point in Figure 3. The [8 + 2] endo energy curve in Figure 3 is depressed at $s \approx -1.5$ Bohr·amu$^{1/2}$ owing to the HOMO → lumo secondary orbital interaction. In Figures 6a and 7a, the reaction between tropothione (**1**) and fulvene has been discussed. It is a mechanistic question whether a similar interaction for the endo orientation is involved in the tropothione–cyclopentadiene reaction. The interaction is examined in Figures 6b and 7b. It is found that the 1s orbital of the methylene hydrogen in the cyclopentadiene may participate the interaction leading to the C(6)–H bonding density. Thus, the [8 + 2] endo orientation comes from the HOMO → lumo secondary orbital interaction in both cycloadditions. So far, the secondary orbital interaction was discussed only qualitatively.[22] This analysis has demonstrated, for the first time, that the secondary orbital interaction does work for the endo selectivity along the reaction path.

In Table II, activation energies of tropothione–dimethylfulvene are larger than those of tropothione–cyclopentadiene.[7b] The higher reactivity of cyclopentadiene is ascribed to the larger diene lobe of the lumo [the lobe of the C(14) site is absent] for the dominant S(1)···C(13) interaction.

Concluding Remarks

In contrast to the [6 + 4] cycloaddition between tropone and 6,6-dimethylfulvene,[10] an [8 + 2] addition has been observed between tropothione and the same fulvene. The stereochemical and kinetic data have shown that the [8 + 2] reaction occurs concertedly with endo selectivity. This experimental result has been interpreted in terms of the HOMO (tropothione) → lumo (fulvene) interaction. The primary reaction center is the sulfur p_π of the HOMO for [8 + 2], and the C(14)···C(6) secondary orbital interaction involved in HOMO → lumo along the IRC gives rise to the endo configuration.

Experimental Section

Reagents and Starting Material. The starting material, tropothione (**1**), was obtained by direct thiocarbonylation of tropone,[23] according to a previously reported procedure.[5] The freshly prepared solution of **1** used in this report was obtained immediately after the isolation of pure crystals of **1**. The above dilute solutions (0.01 M) have a half-life of 10 days at room temperature. 6,6-Dimethylfulvene[18] was freshly distilled. 6,6-Diphenylfulvene[19] was prepared according to a literature method and recrystallized. The solvents used for the preparation, isolation, and reactions of tropothione (**1**) were freshly distilled under nitrogen from appropriate drying agents and were all degassed. For column chromatography, Merck Kieselgel 60 (0.063–0.200 mm) was employed.

Instrumentation and Analytical Procedures. Melting points were determined on a Büchi 511 apparatus in open capillary tubes and are incorrected. Elemental analyses were performed at the Analytical Laboratory, Department of Chemistry, University of Tokyo, Hongo, Tokyo (for S), as well as at the Chemical Analysis Center, Saitama University (for C and H). IR spectra were recorded on a Hitachi 260–50 grating spectrometer. UV–visible spectra were taken with a Hitachi EPS-3T recording spectrometer using 1-cm quartz cells. Mass spectra were obtained with a JEOL DM-303 double-focusing spectrometer using a direct inlet, while the chamber temperature was maintained at 240 °C. The values of m/z in significant ions were reported with relative intensities in parentheses (percent of the base peak) for low-resolution analyses. NMR (^{13}C and ^{1}H) spectra were recorded on a Bruker AM-400 instrument

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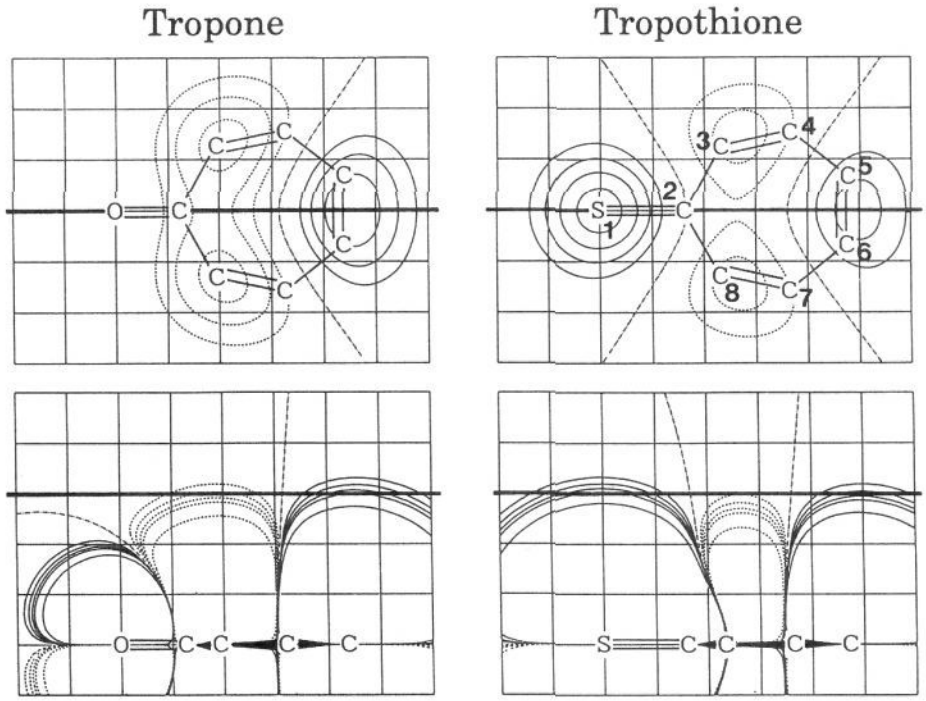

Figure 5. Shapes of the highest occupied molecular orbital (HOMO) of tropone (**2**) (C_7H_6X, X = O) and tropothione (**1**) (C_7H_6X, X = S). Interrupted lines denote nodal borderlines. Bold lines denote cut planes. On this chart, each unit equals 1 Å.

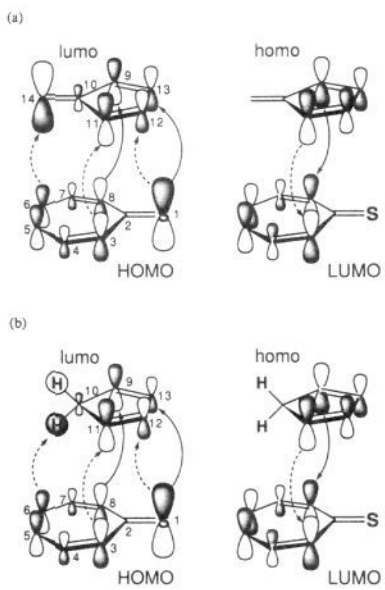

Figure 6. Frontier-orbital interactions for the [8 + 2] endo cycloaddition (a) between tropothione (**1**) and fulvene and (b) between **1** and cyclopentadiene. Full arrows indicate dominant charge-transfer (CT) interactions for the covalent-bond formation. Broken arrows show secondary CT interactions.

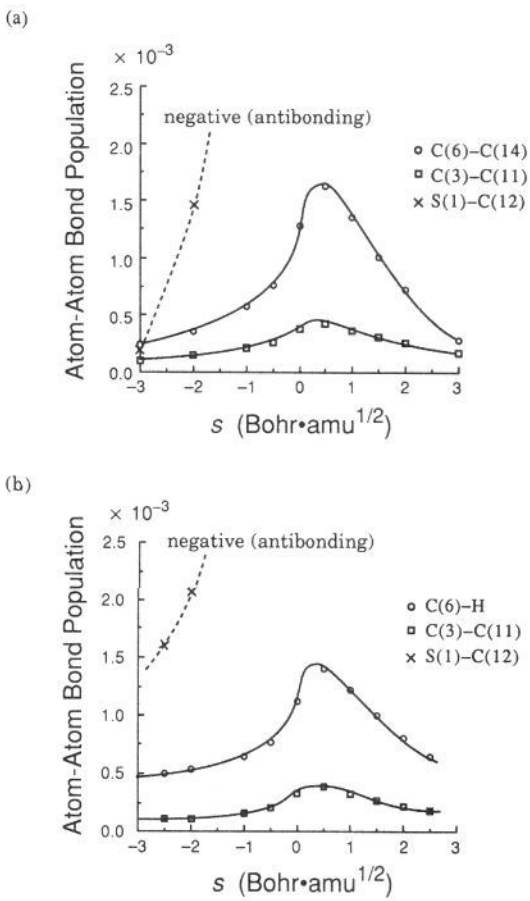

Figure 7. Atom–atom bond populations at three secondary CT interactions (broken arrows in Figure 6) along the [8 + 2] endo addition path (a) between tropothione (**1**) and fulvene and (b) between **1** and cyclopentadiene.

in $CDCl_3$ with tetramethylsilane as the internal standard. The assignments of NMR spectra are based on $^1H\{^1H\}$ homonuclear decoupling and $^{13}C\{^1H\}$ heteronuclear one- and two-dimensional NMR experiments. The analytical HPLC was performed on a Hitachi 655 using a Du Pont Zorbax SIL 4.6 × 250-mm i.d. stainless steel columns with hexane–AcOEt (0.05%) at a flow rate of 0.7 mL/min, and signal integration was achieved by using a Hitachi 655-31 integrator monitored at 280 nm. TLC analyses were performed on Merck Kieselgel 60 GF_{254} and Alminiumoxid 60 GF_{254} with a 0.2-mm layer thickness.

General Procedure for Cycloaddition Reactions of Tropothione (1) with Fulvenes. In a typical case, to a stirred deep red solution (240 mL) of tropothione (1.54 g, 12.6 mmol) was added with stirring a solution of a fulvene (10 equiv, 126 mmol) in 60 mL of benzene (or chloroform). The reaction mixture was stirred until the reaction was completed by the discharged color of the solution. The solvent removal in vacuo below 10 °C gave the cycloadduct. After medium-pressure column chromatography, the product was further purified by redistillation or recrystallization.

Cycloadduct 7a between Tropothione (1) and 6,6-Dimethylfulvene. The general procedure was followed using 6,6-dimethylfulvene[18] (13.4 g, bp 31–32 °C, 3 mmHg). The reaction mixture was stirred for 4 h at 10 °C. After removing the unreacted fulvene by distillation under vacuum (1 mmHg), medium-pressure column chromatography on silica gel with hexane as an eluent gave 2.33 g of the cycloadduct (81% isolated yield) as a pale yellow oil (bp 50.5–52 °C, 0.10 mmHg). An analytical sample was obtained by redistillation. **7a**: R_f = 0.23 (silica gel, hexane); IR (neat) ν_{max} 3005 (m), 2960 (m), 2910 (s), 2851 (m), 1581 (s), 1502 (s), 1441 (m), 1375 (s), 1086 (s), 822 (s), 790 (m), 739 (m), 719 (vs), 663 (m) cm^{-1}; UV–vis λ_{max} (EtOH) 233 (log ϵ 4.58), 250 (4.54), 315 nm (4.08); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 3 H, Me), 1.91 (s, 3 H, Me), 2.54 (dd, 1 H, $J_{8,9}$ = 9.7 $J_{7,8}$ = 5.9 Hz, H-8), 3.94 (dd, 1 H, $J_{8,9}$ = 9.7, $J_{9,13}$ = 8.0 Hz, H-9), 4.89 (dd, 1 H, $J_{6,7}$ = 9.1, $J_{7,8}$ = 5.9 Hz, H-7), 5.00 (ddd, 1 H, $J_{9,13}$ = 8.0, $J_{11,13}$ = 2.3, $J_{12,13}$ = 1.2 Hz, H-13), 5.83 (dd, 1 H, $J_{11,12}$ = 5.2, $J_{12,13}$ = 1.2 Hz, H-12), 6.06 (dd, 1 H, $J_{6,7}$ = 9.1, $J_{5,6}$ = 5.6 Hz, H-6), 6.10 (d, 1 H, $J_{3,4}$ = 6.1 Hz, H-3), 6.41 (dd, 1 H, $J_{4,5}$ = 10.8, $J_{5,6}$ = 5.6 Hz, H-5), 6.45 (dd, 1 H, $J_{11,12}$ = 5.2, $J_{11,13}$ = 2.3 Hz, H-11), 6.59 (dd, 1 H, $J_{4,5}$ = 10.8, $J_{3,4}$ = 6.1 Hz, H-4); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.72 [q, Me (δ 1.91)], 21.64 [q, Me (δ 1.71)], 50.91 (d, C-9), 51.42 (d, C-8), 59.51 (d, C-13), 111.95 (d, C-3), 122.57 (d, C-7), 124.67 (d, C-6), 126.07 (s, C-2), 126.45 (d, C-11), 130.86 (d, C-5), 131.00 (d, C-4), 133.36 (d, C-12), 137.59 (s, C-10 or C-14), 137.92 (s, C-14 or C-10); EI-MS (75eV) m/z (relative intensity) 229 (M^+ + 1, 7), 228 (M^+, 41), 122 (43), 121 (35), 106 (100), 91 (71), 78 (50); HRMS calcd mass for $C_{15}H_{16}S$ 228.0973, found 228.0989. Quantitative difference NOE experiment: irr δ 2.54 (H-8), enhanced δ 3.94 (26%, H-9); irr δ 3.94 (H-9), enhanced δ 2.54 (18%, H-8), δ 5.00 (12%, H-13); irr δ 5.00 (H-13), enhanced δ 3.94 (13%, H-9), δ 5.83 (24%, H-12); irr δ 1.71 (Me), enhanced δ 3.94 (13%, H-9), δ 4.89 (12%, H-7). Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06; S, 14.04. Found: C, 78.78; H, 7.08; S, 14.12.

Cycloadduct 7b between Tropothione (1) and 6,6-Diphenylfulvene. The general procedure was followed using 6,6-diphenylfulvene[19] (29.0 g), and keeping the temperature at 80 °C, not 10 °C, for 4 h gave 3.77 g of the adduct (85% isolated yield) after medium-pressure column chromatography [silica gel, hexane–ethyl acetate (19:1)]. An analytical sample was obtained by recrystallization from cyclohexane (colorless needles, mp 151–152 °C). **7b**: R_f = 0.51 [silica gel, hexane–ethyl acetate (19:1)]; IR (KBr) ν_{max} 3020 (m), 2950 (w), 1599 (w), 1581 (s), 1495 (s), 1442 (s), 1378 (m), 1228 (m), 1212 (m), 1090 (m), 829 (s), 774 (s), 755 (s), 720 (vs), 707 (vs) cm^{-1}; UV–vis λ_{max} (EtOH) 231 (log ϵ 4.43), 284 nm (4.42); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (dd, 1H, $J_{8,9}$ = 9.7, $J_{7,8}$ = 6.0 Hz, H-8), 3.83 (dd, 1 H, $J_{8,9}$ = 9.7, $J_{9,13}$ = 7.1 Hz, H-9), 4.98 (dt, 1 H, $J_{9,13}$ = 7.1, $J_{12,13}$ = $J_{11,13}$ = 2.1 Hz, H-13), 5.17 (dd, 1 H, $J_{6,7}$ = 9.1, $J_{7,8}$ = 6.0 Hz, H-7), 6.02 (dd, 1 H, $J_{11,12}$ = 5.7, $J_{12,13}$ = 2.1 Hz, H-12), 6.04 (d, 1 H, $J_{3,4}$ = 6.7 Hz, H-3), 6.18 (dd, 1 H, $J_{6,7}$ = 9.1, $J_{5,6}$ = 5.6 Hz, H-6), 6.43 (dd, 1 H, $J_{4,5}$ = 10.8, $J_{5,6}$ = 5.6 Hz, H-5), 6.54 (dd, 1 H, $J_{11,12}$ = 5.7, $J_{11,13}$ = 2.1 Hz, H-11), 6.55 (dd, 1 H, $J_{4,5}$ = 10.8, $J_{3,4}$ = 6.7 Hz, H-4), 7.16–7.35 (complex m, 10 H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 52.68 (d, C-9), 52.90 (d, C-8), 59.10 (d, C-13), 112.16 (d, C-3), 122.62 (d, C-7), 125.16 (d, C-6), 126.63 (d, C-5), 127.04 (d, Ph), 127.09 (d, Ph), 128.11 (d, 2C, Ph), 128.15 (d, 2C, Ph), 128.83 (d, 2C, Ph), 129.68 (d, 2C, Ph), 131.29 (d, C-4 or C-11), 132.68 (d, C-11 or C-4), 136.06 (s, Ph), 137.25 (d, C-12), 137.70 (s, Ph), 141.71 (s, C-2), 142.30 (s, C-10 or C-14), 142.47 (s, C-14 or C-10); EI-MS (75 eV) m/z (relative intensity) 353 (M^+ + 1, 8), 352 (M^+, 25), 230 (100), 229 (49), 122 (15), 121 (14), 78 (14); HRMS calcd mass for $C_{25}H_{20}S$ 352.1286, found 352.1278. Quantitative difference NOE experiment: irr δ 2.20 (H-8), enhanced δ 3.83 (35%, H-9); irr δ 3.83 (H-9), enhanced δ 2.20 (26%, H-8), δ 4.98 (28%, H-13); irr δ 4.98 (H-13), enhanced δ 3.83 (27%, H-9), δ 6.02 (26%, H-12). Anal. Calcd for $C_{25}H_{20}S$: C, 85.18; H, 5.72; S, 9.10. Found: C, 85.04; H, 5.77; S, 9.19.

Kinetic Data Collection. The rates of cycloaddition between tropothione (1) and 6,6-dimethylfulvene were followed spectrophotometrically by monitoring the disappearance of the absorbance of tropothione at 380 nm. The reaction was carried out under an argon atmosphere in the dark, and their course was followed to greater than 90% completion. Typically, a solution of 6,6-dimethylfulvene (100 mmol) in 5 mL of benzene (or chloroform) was added to a solution containing tropothione (5.0 mmol) in 95 mL of benzene (or chloroform). The initial absorption spectrum was measured after 5 s (mixing time). The pseudo-first-order rate constant k_{obsd} was obtained from the least-squares evaluation of the slope of the absorbance change in A_0/A_t with time, where A_0 and A_t are the absorbances (λ 380 nm) of tropothione at the initial time and time t, respectively. The kinetics studies were carried out at five different temperatures. In all cases, the fit in the pseudo-first-order plots was obtained with a correlation coefficient of 0.998 or better.

Computational Methods. PM3[24] semiempirical MO calculations in Figures 1 and 2 are performed by the MOPAC version 6.[25] RHF/STO-3G* ab initio MO calculations in Figures 2, 3, 4, and 7 are carried out by GAUSSIAN 92.[26] The STO-3G* intrinsic reaction coordinate in Figures 3 and 7 is determined by the method of Gonzalez and Schlegel.[27] A RHF/3-21G* transition-state (TS) search has been made by the use of various initial Z-matrices and force constants. However, the search by Z-matrices has not succeeded probably due to too many geometric parameters at RHF/3-21G*. Alternatively, we have tried the RHF/3-21G* TS search via Cartesian coordinates [opt = (Cartesian, TS)]. After over a 200-cycle optimization, an almost optimized (maximum displacement = 0.003 577, threshold = 0.001 800) geometry has been obtained and is shown in square brackets in Figure 2. Thus, calculations at higher levels than RHF/STO-3G* are quite difficult technically. Since the RHF/3-21G* geometry is similar to the RHF/STO-3G* one, the latter method seems to be qualitatively useful for analyzing the reaction mechanism. All the MO calculations were made on the CONVEX C-220 computer installed at the Information Processing Center of Nara University of Education and the CONVEX C-3420 computer at the Computer Center of Nara University, Japan.

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