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Syntheses and Cycloaddition Reactions of Thiaazulenocyclone and Thiaazulenocyclone 8,8-Dioxide[1]

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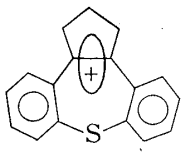
Thiaazulenocyclone (**2**) and thiaazulenocyclone 8,8-dioxide (**3**) were synthesized and their reactions were investigated. The reaction of **2** with N-phenylmaleimide and the reactions of **2** or **3** with acenaphthylene and norbornene provided the Diels–Alder endo adducts, but cycloaddition reactions of **2** or **3** with acetylenic dienophiles, maleic anhydride or benzyne yielded decarbonylated products derived from the [4+2] adducts. The adduct of **2** and N-phenylmaleimide was a mixture of two stereoisomers and was decarbonylated on heating.

The reactivities of **2** and **3** in the cycloaddition reactions were estimated by consideration of the frontier orbital interaction. The stereospecificity was mainly controlled by the steric and dipole-dipole interactions.

Keywords——thiaazulenocyclone; cycloaddition reaction; Diels–Alder reaction; retro Diels–Alder reaction; endo cycloproduct; dienophile; decarbonylation; frontier electron interaction

The syntheses and reactions of thiaazulenylium salts have been studied.[2] Theoretical calculation predicted that the 6-thiaazulenylium salt would be unstable and that its synthesis might be impossible.[3] We reported on the synthesis and reactivity of 2-thiaazulenylium salts.[4]

In order to synthesize the dibenzothiaazulenylium salt (**1**), 1,3-diphenyl-2,8-dihydrodibenzo[*e*, *h*]-8-thiaazulen-2-one (thiaazulenocyclone) (**2**)[5] was prepared.



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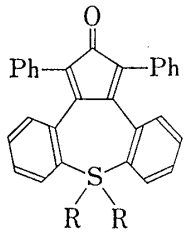


2 : R= :
3 : R=O

Chart 1

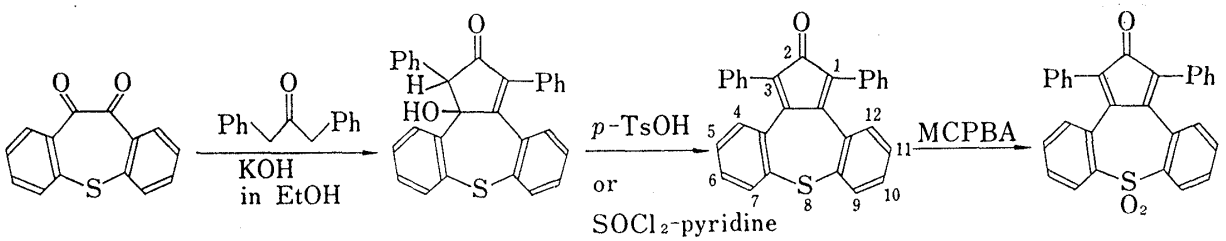
Cycloaddition reactions of cyclopentadienones and related compounds were recently investigated.[6] As is well known, cyclopentadienones are reactive dienes in the Diels–Alder reaction. Sasaki *et al.* reported on the cycloaddition reactions of phencyclone and its analogs.[7] Phencyclone is planar, but thiaazulenocyclone (**2**) and thiaazulenocyclone 8,8-dioxide (**3**) are not planar.

It was of interest to examine how the nonplanarity and electronic effects of the sulfide and sulfone groups affected the cycloaddition reactions with dienophiles. We now wish to describe the syntheses of **2** and **3** and their cycloaddition reactions with some electron-rich and electron-deficient dienophiles.

Results

Syntheses of Thiaazulenocyclone (2) and Thiaazulenocyclone 8,8-Dioxide (3)

10,11-Dihydrodibenzo[*b*, *f*]thiepin-10,11-dione (**4**)[8] reacted with dibenzyl ketone in the presence of KOH to give 1,3-diphenyl-1,2,8-trihydro-12b-hydroxydibenzo[*e*, *h*]-8-thiaazulen-2-one (**5**) as colorless prisms, mp 258°, in 64% yield. Dehydration of **5** with *p*-toluenesulfonic acid or thionyl chloride-pyridine gave **2** as violet needles, mp 246°, in 27% or 65% yield, respectively.



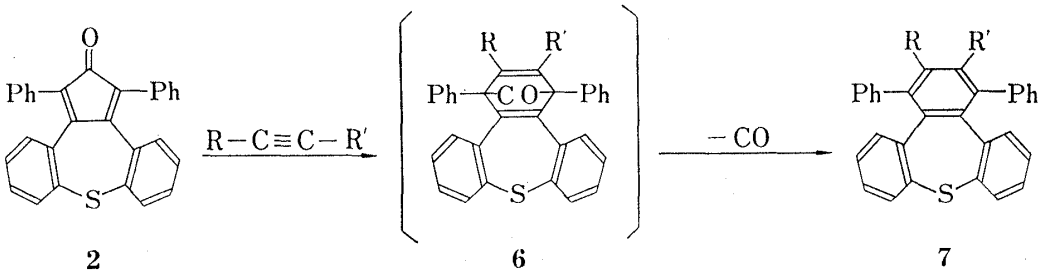
4 5 2 3

Chart 2

Compound **5** was oxidized with *m*-chloroperbenzoic acid to the dioxide **3**, violet needles, mp>300°, in 56% yield.

Cycloaddition Reactions of Thiaazulenocyclone (2)

With Acetylenic Derivatives——Compound **2** was heated with acetylenic compounds to give tribenzo[*b*, *d*, *f*]thiepins (**7a**—**d**) which were the decarbonylated compounds of the [4+2] adducts **6**. The ease of decarbonylation is attributable to aromatization of **6** to **7**.



2 6 7

a : R=R′=Ph
b : R=Ph, R′=H
c : R=R′=CO_2Me
d : R=CO_2Me, R′=H

Chart 3

With Electron-Deficient Olefins——The reaction of **2** with N-phenylmaleimide at 150° for 20 min gave a mixture of endo [4+2] adducts (**8a** and **8b**) in 73% yield. The IR spectrum showed an absorption of the strained five-membered carbonyl group at 1800 cm^{-1}. The NMR spectrum exhibited two methine singlets of **8a** and **8b** at δ 4.57 and 4.38, respectively, which might be deshielded by the anisotropy of the bridged carbonyl group. The chemical shifts are in good agreement with those of endo adducts.[7] The isomer ratio **8a**/**8b**=9 was determined from the intensities of the methine signals. On heating, the mixture was quantitatively decarbonylated to give a mixture of **9a** and **9b**. The NMR spectrum of the mixture of **9a** and **9b** showed that the intensity of the methine signal of **9a** at δ 4.70 decreased gradually at room temperature and that of **9b** at δ 4.31 increased. After several hours they reached an intensity ratio of 1:1. A mixture of **9a** and **9b** was formed directly in 88% yield by refluxing **2** and N-phenylmaleimide in xylene for 4 hr.

Reaction of **2** with maleic anhydride under reflux in xylene afforded a mixture of **10a** and **10b** in the ratio of **10a**/**10b**=7/3. The difference of the ratios, **9a**/**9b**=1 and **10a**/**10b**=7/3, may arise because maleic anhydride is smaller than N-phenylmaleimide and the steric interaction of maleic anhydride with the sulfur atom is less than that of N-phenylmaleimide. The mixture of **10a** and **10b** was refluxed with bromine in bromobenzene to afford a tribenzo[*b*, *d*, *f*]-thiepin derivative (**11**). No isomer could be found in the product by NMR measurement. This finding suggested that **10a** and **10b** were stereoisomers.

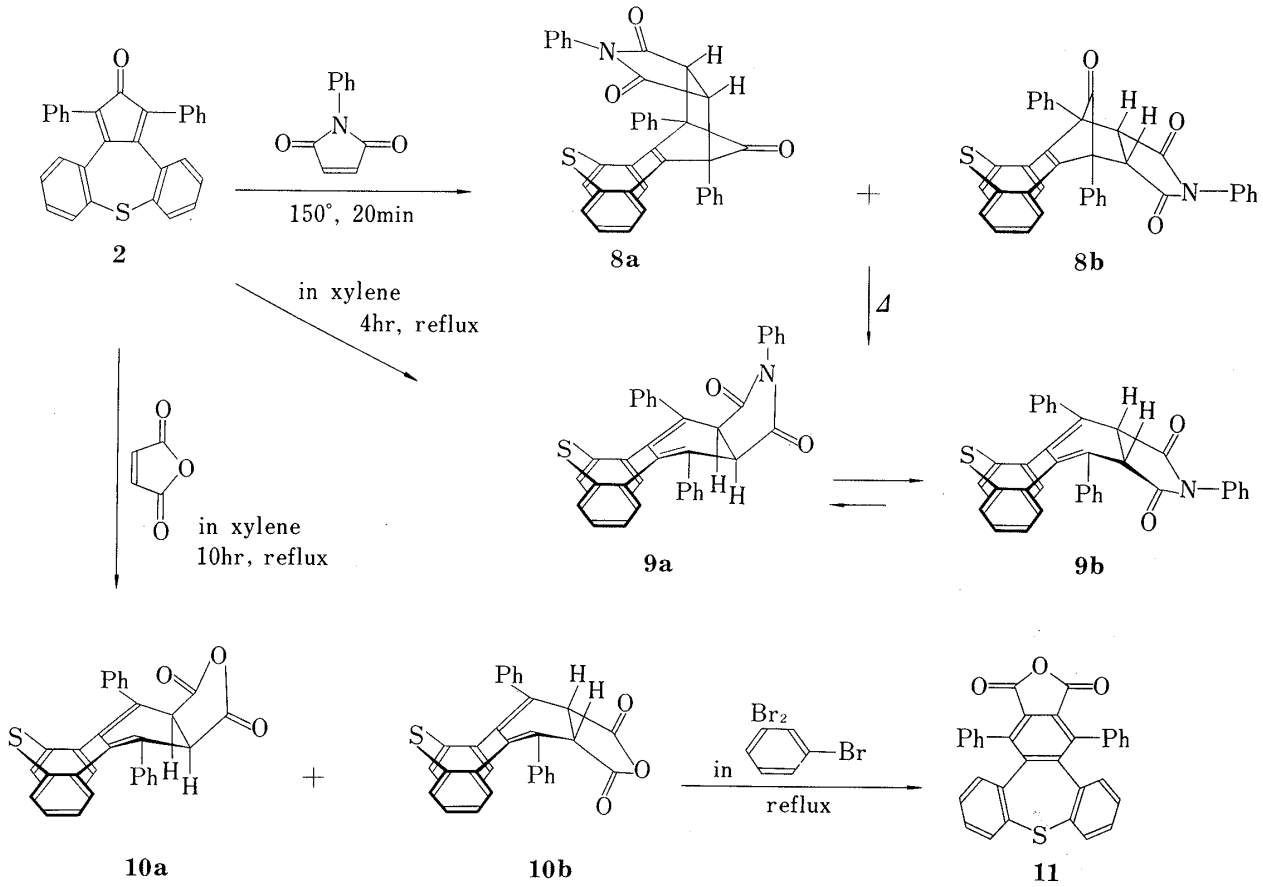


Chart 4

The structures of the compounds **8**—**10** were determined by comparing their NMR data with those of the cycloadducts which were formed by the reaction of phencyclone or azulenocyclone with dienophiles.[8]

Some other electron-deficient olefins such as *p*-benzoquinones, 1,4-naphthoquinone, tetracyanoethylene, and diphenylcyclopropenone did not react with **2**.

With Electron-Rich Olefins——The reaction of **2** with acenaphthylene gave a 1: 1 adduct **12** in 88% yield. Pyrolysis of **12** at 230° caused the retrogressive Diels–Alder reaction to form **2** and acenaphthylene, quantitatively. The IR spectrum of **12** showed a characteristic band at 1775 cm^{-1} due to the strained ring carbonyl group. Furthermore, a singlet at δ 4.80 due to two methine protons was remarkably deshielded by the bridged carbonyl group.

Norbornene reacted with **2** in boiling xylene for 13 hr to give the endo-exo [4+2] adduct (**14**) as colorless prisms in 79% yield.

Cyclohexene and cycloheptatriene did not react with **2**.

With Benzyne——Benzyne generated from 1-(2-carboxyphenyl)-3,3-dimethyltriazene[9] reacted with **2** in refluxing chlorobenzene for 6 hr to give the tribenzothiepin derivative **13** in 92% yield.

Cycloaddition Reactions of Thiaazulenocyclone 8,8-Dioxide (3)

We expected a difference in the mode of cycloaddition between thiaazulenocyclone (**2**) and thiaazulenocyclone 8,8-dioxide (**3**) owing to the differences in steric and electron-withdrawing effects.

With Acetylenic Derivatives——The cycloaddition reactions of **3** with diphenylacetylene and dimethyl acetylenedicarboxylate afforded tribenzo[*b*, *d*, *f*]thiepin derivatives (**16a** and **16b**, respectively). An intermediate [4+2] adduct (**15**) resulted in the cheletropic reaction to form **16**.

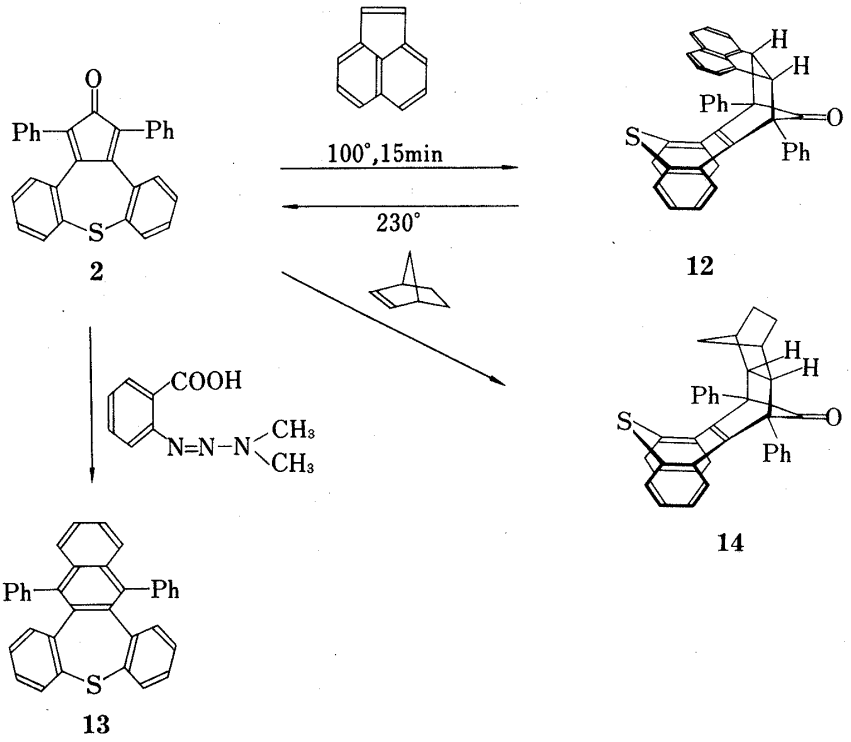


Chart 5

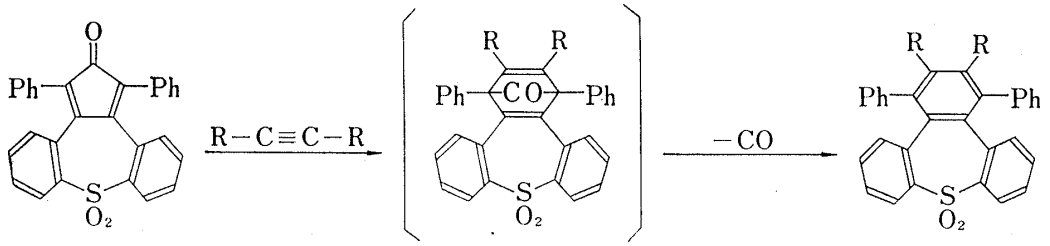


Chart 6

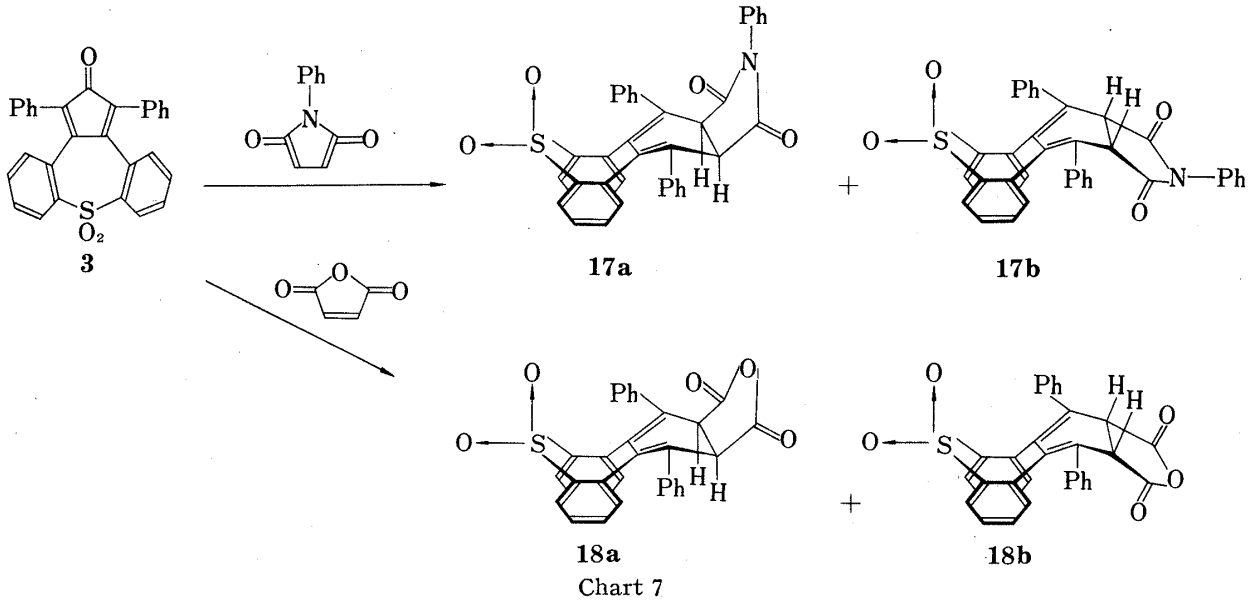


Chart 7

With Electron-Deficient Olefins——A solution of **3** and N-phenylmaleimide in xylene was refluxed for 3 hr to give a mixture of **17a** and **17b** in the ratio of 1:3. The NMR spectrum showed the signals of the methine protons of **17a** and **17b** as singlets at δ 4.63 and 4.24, respectively. The reaction of **3** with maleic anhydride was carried out in refluxing xylene for 8 hr. A mixture of **18a** and **18b** was obtained in the ratio of 3:2. The NMR spectrum exhibited two singlets at δ 5.25 and 4.73 due to the methine protons of **18a** and **18b**, respectively. The main products were **17b** from the reaction with N-phenylmaleimide and **18a** from the reaction with maleic anhydride. The significance of this result is discussed below.

With Electron-Rich Olefins——Acenaphthylene was heated with **3** at 100° for 5 min to give the endo [4+2] adduct **19** as colorless prisms, mp 241°, in 82% yield. The NMR spectrum showed the signal of two methine protons as a singlet at δ 5.01 and the IR spectrum exhibited a characteristic bridged-carbonyl absorption at 1770 cm^{-1}. No stereoisomer was detected in the product. On heating above the melting point, **19** underwent the retrogressive Diels–Alder reaction to form **3** and acenaphthylene. Norbornene was allowed to react with **3** in refluxing xylene for 3 hr, and **20** was obtained in 83% yield. The IR spectrum exhibited a carbonyl absorption at 1790 cm^{-1}.

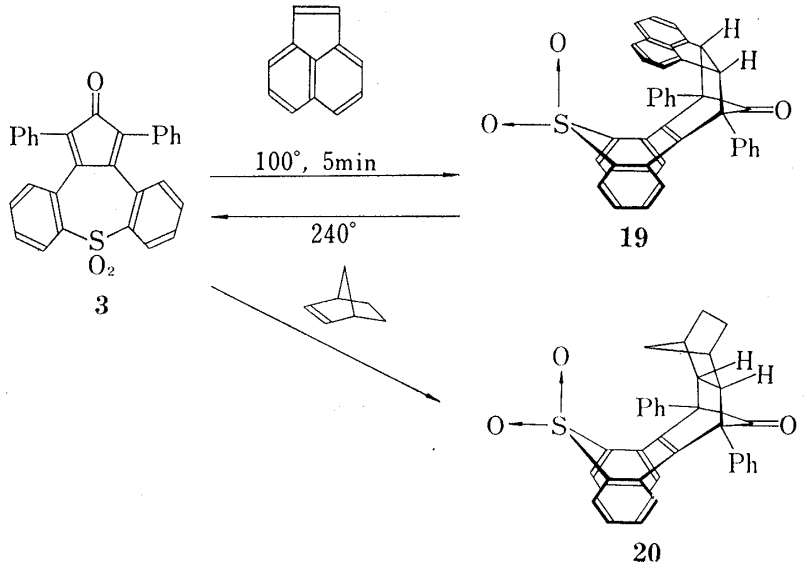


Chart 8

Discussion

Some common interactions such as secondary-orbital effect, geometrical primary effect, and steric and dipole-dipole interactions between reactants are important in relation to the stereoselectivity of cycloaddition. The thiaazulenocyclone (**2**) and thiaazulenocyclone 8,8-dioxide (**3**) are not planar, so steric and dipole-dipole interactions should largely control the stereospecificity. Among the four possible approaches A—D, the dipole-dipole interactions would favor endo approach (A and C), as depicted in Fig. 1. Furthermore, the steric interaction between dienophile and diene would favor the approach A. In the cycloaddition of **2** with N-phenylmaleimide, the product **8a** was formed *via* the approach A and the minor product **8b** was formed *via* the approach C. The [4+2] cycloadducts such as **12**, **13**, **19**, **20** were produced through the approach A.

The isomers of the products decarbonylated from the [4+2] cycloadducts undergo interconversion between the E and F forms (Chart 9) owing to ring inversion. The isomer ratios are presumably controlled by the steric interaction between X and Y as depicted in

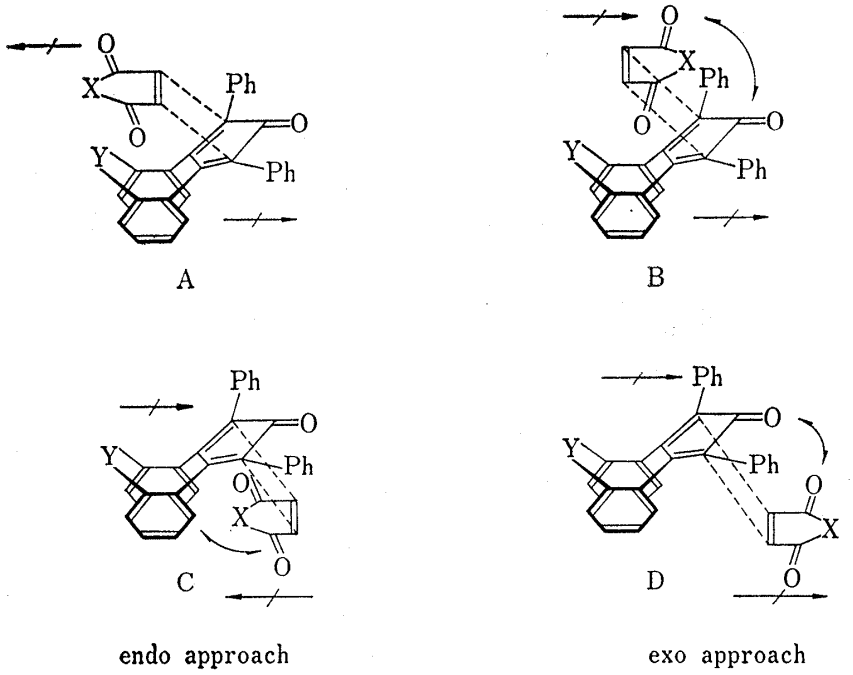


Fig. 1. Possible Approaches in the Cycloaddition Reactions of Thiaazulenocyclone and Thiaazulenocyclone 8,8-Dioxide with Dienophilies

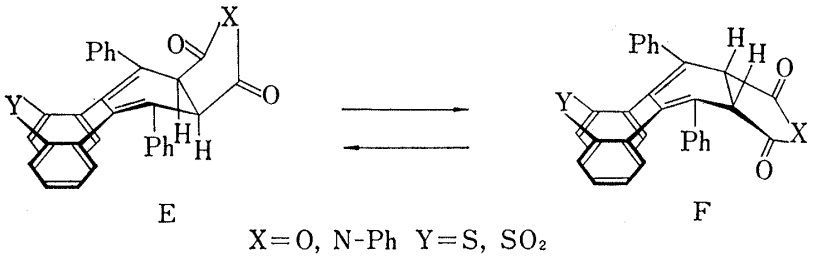


Chart 9

Chart 9. The isomer ratios (**10a**/**10b**=3/2, **18a**/**18b** =3/2, **9a**/**9b**=1, **17a**/**17b**=1/3) showed that the amount of the isomer F increased with increasing steric interaction.

Sasaki *et al.* isolated the [4+2] cycloadducts from the reactions of phencyclone with some dienophiles.[7] The adducts of phencyclone and dienophiles were stable and did not undergo decarbonylation or retrogressive Diels–Alder reaction. However, the reactions of **2** and **3** with acetylenic compounds, electron-deficient olefins and benzyne afforded the decarbonylated products, and the reactions with electron-rich olefins gave the [4+2] cycloadducts which underwent the retrogressive Diels–Alder reaction. The adducts of phencyclone and dienophiles are stabilized by the phenantherene moiety, but the adducts of **2** and **3** with dienophiles do not have such a stabilizing factor. Therefore, the latter underwent decarbonylation or the retrogressive reaction.

Compounds **2** and **3** were less reactive to olefinic dienophiles than phencyclone and less reactive to *p*-benzoquinone than azulenocyclone. The dioxide **3** was more reactive to electron-rich olefins than **2**, *i.e.*, compound **2** required refluxing for 13 hr, while **3** required refluxing for 4.5 hr for reaction with norbornene. The results can be explained by reference to Sasaki's

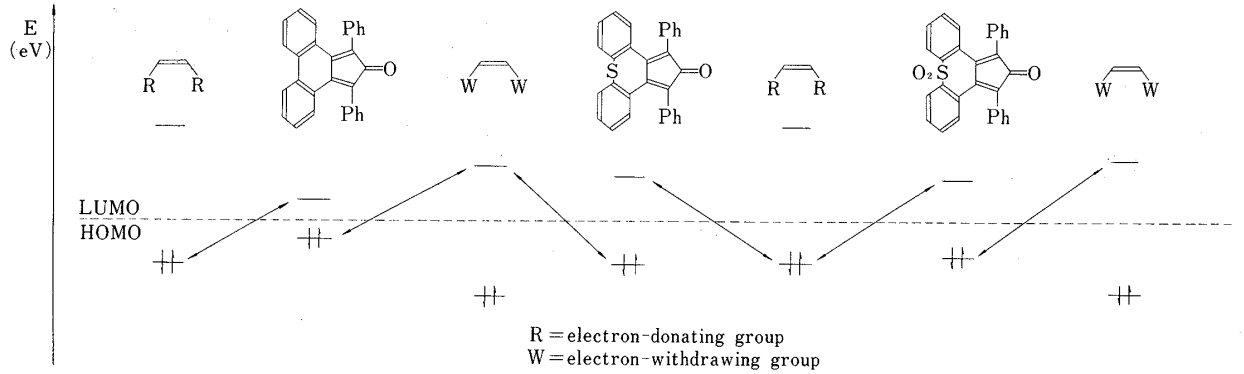


Fig. 2. Frontier Orbital Interactions forCyclopentadienones and Olefins

reports:[7] The energy gap between LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) of **2** and **3** is presumably larger than those of phencyclone and azulenocyclone. Therefore, the interactions of 2-HOMO and electron-deficient olefin-LUMO, and of 2-LUMO and electron-rich olefin-HOMO are weaker than those of phencyclone or azulenocyclone. Since **3** has an electron-withdrawing group, $-SO_2-$, the 3-LUMO energy level should be lower than that of 2-LUMO, and **3** is thus more reactive to electron-rich olefins than **2**.

Experimental

Melting points were measured on a Yanagimoto micro-melting-point apparatus and are uncorrected. NMR spectra were determined on a Hitachi R-20B spectrometer and chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard. IR spectra were determined on a JASCO model IRA-1 spectrometer. The EI mass spectra were measured on a JEOL JMS-D300 machine at an ionizing voltage of 70 eV.

1,3-Diphenyl-1,2,8-trihydro-12b-hydrodibenzo[*e,h*]-8-thiaazulen-2-one (**5**)——A solution of KOH (220 mg) in EtOH (10 ml) was gradually added to a solution of 10,11-dihydrodibenzo[*b,f*]thiepin-10,11-dione (**4**)[8] (17.23 g) in EtOH (800 ml) at room temperature, and the mixture was stirred for 2 hr. The white precipitate was collected by filtration, washed with cold EtOH and dried. Recrystallization from CH_2Cl_2–hexane gave colorless needles (22.7 g, 64%), mp 258°. *Anal.* Calcd for $C_{29}H_{20}O_2S$: C, 80.53; H, 4.66. Found: C, 80.26; H, 4.58. IR ν_{max}^{KBr} cm^{-1}: 3380 (OH), 1718 (CO). NMR (DMSO-d_6) δ: 6.95—7.90 (18H, m, ArH), 6.25 (1H, s, OH), 4.19 (1H, s, C_1–H). MS *m/e*: 432 (M^+).

Thiaazulenocyclone (**2**)——a) Thionyl chloride (4.40 g) was gradually added with stirring to an ice-cold suspension of **5** (8.00 g) in $CHCl_3$ (300 ml) and pyridine (5.85 g) was added to the mixture. After being stirred for 48 hr at room temperature, the mixture was diluted with water and extracted with $CHCl_3$. The extracts were washed with dilute HCl and saturated $NaHCO_3$ solution, then dried and concentrated. Recrystallization of the residue from CH_2Cl_2–hexane gave violet needles (4.97 g, 65%), mp 246°. *Anal.* Calcd for $C_{29}H_{18}OS$: C, 84.03; H, 4.38. Found: C, 84.31; H, 4.41. IR ν_{max}^{KBr} cm^{-1}: 1710 (CO). UV λ_{max}^{EtOH} nm: 213 ($\varepsilon=5.1\times10^4$), 2.68 ($3.3\times10^4$). MS *m/e*: 414 ($M^+$).

b) *p*-Toluenesulfonic acid (30 mg) was added to a solution of **5** (1.00 g) in benzene (150 ml). Water was removed as the benzene azeotrope. After refluxing for 1 hr, the reaction mixture was diluted with water and extracted with benzene. The extract was washed with saturated $NaHCO_3$ solution and water, then dried and concentrated. The residue was chromatographed on silica gel using CH_2Cl_2–hexane and recrystallized from CH_2Cl_2–hexane to give violet needles (0.26 g, 27%), mp 246°. The product was identified by comparison of its IR and NMR spectra with those of the sample synthesized by method a.

Thiaazulenocyclone 8,8-Dioxide (**3**)——*m*-Chloroperbenzoic acid (1.77 g) was added to a solution of **2** in CH_2Cl_2 (40 ml), and the mixture was stirred for 8 hr at room temperature. Saturated $NaHCO_3$ solution was added to the mixture. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2. The extracts were washed with water, dried and concentrated. The residual solid was recrystallized from CH_2Cl_2–hexane to give colorless needles (1.02 g, 56%), mp>300°. *Anal.* Calcd for $C_{29}H_{18}O_3S$: C, 78.01; H, 4.06. Found: C, 78.19; H, 4.08. IR ν_{max}^{KBr} cm^{-1}: 1710 (CO), 1330, 1160 (SO_2). NMR ($CDCl_3$) δ: 7.05—7.60 (16H, m, ArH), 7.98—8.20 (2H, m, ArH).

Reaction of 2 with Diphenylacetylene——A mixture of **2** (1.00 g) and diphenylacetylene (0.128 g) was fused at 200° for 2 hr. The cooled reaction mixture was recrystallized from $CHCl_3$ to give 1,2,3,4-tetraphenyltribenzo[*b,d,f*]thiepin (**7a**, 0.105 g, 76.8%) as colorless prisms, mp>300°. *Anal.* Calcd for $C_{42}H_{28}S$: C, 89.33; H, 5.00. Found: C, 89.40; H, 4.90. IR ν_{max}^{KBr} cm^{-1}: 3020, 1100, 730, 690.

Reaction of 2 with Phenylacetylene——A mixture of **2** (0.10 g) and phenylacetylene (0.074 g) was heated at 150° for 20 min. The reaction mixture was diluted with hexane. The resulting precipitate was filtered off and recrystallized from CH_2Cl_2–hexane to afford 1,2,4-triphenyltribenzo[*b*,*d*,*f*]thiepin (**7b**, 0.083 g, 70.1%) as colorless needles, mp 290°. *Anal.* Calcd for $C_{36}H_{24}S$: C, 88.49; H, 4.95. Found: C, 88.25; H, 4.89. IR ν_{max}^{KBr} cm^{-1}: 3050, 1600, 750, 735, 690. NMR ($CDCl_3$) δ: 6.60—7.80 (24H, m, ArH).

Reaction of 2 with Dimethyl Acetylenedicarboxylate——A solution of **2** (0.10 g) and dimethyl acetylenedicarboxylate (0.103 g) in xylene (20 ml) was heated under reflux for 2 hr. The solution was concentrated under reduced pressure and diluted with hexane. The resulting precipitate was filtered off and recrystallized from CH_2Cl_2–hexane to afford 2,3-dimethoxycarbonyl-1,4-diphenyltribenzo[*b*,*d*,*f*]thiepin (**7c**, 0.112 g, 87.6%) as colorless plates, mp 245°. *Anal.* Calcd for $C_{34}H_{24}O_4S$: C, 77.26; H, 4.58. Found: C, 77.01; H, 4.50. IR ν_{max}^{KBr} cm^{-1}: 1720 (CO). NMR ($CDCl_3$) δ: 3.52 (6H, s, CH_3), 6.55—7.80 (18H, m, ArH).

Reaction of 2 with Methyl Propiolate——A solution of **2** (0.10 g) and methyl propiolate (0.061 g) in xylene (10 ml) was heated under reflux for 2 hr. The solution was concentrated under reduced pressure and diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2–hexane to give 2-methoxycarbonyl-1,4-diphenyltribenzo[*b*,*d*,*f*]thiepin (**7d**, 0.086 g, 75.7%) as colorless prisms, mp 220°. *Anal.* Calcd for $C_{32}H_{22}O_2S$: C, 81.67; H, 4.71. Found: C, 81.37; H, 4.62. IR ν_{max}^{KBr} cm^{-1}: 1720 (CO). NMR ($CDlC_3$) δ: 3.51 (3H, s, CH_3), 6.50—7.80 (18H, m, ArH), 7.93 (1H, s, C_3–H).

Reaction of 2 with N-Phenylmaleimide——a) A mixture of **2** (0.10 g) and N-phenylmaleimide (0.083 g) was heated at 150° for 20 min. Water was added to the cooled mixture. The resulting mixture was extracted with $CHCl_3$. The extracts were washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was separated by preparative TLC using $CHCl_3$–benzene (1: 1) to give a mixture of **8a** and **8b** (0.103 g, 72.7%) as colorless prisms, mp 218—219°. *Anal.* Calcd for $C_{39}H_{25}NO_3S$: C, 78.84; H, 4.49; N, 2.46. Found: C, 78.44; H, 4.18; N, 2.27. IR ν_{max}^{KBr} cm^{-1}: 1800, 1720 (CO). NMR ($CDCl_3$) δ: 4.38, 4.57 (2H, s, methine H), 6.85—7.92 (23H, m, ArH). The intensity ratio of the methine signals at δ: 4.38 and 4.57 was 1: 9.

b) A solution of **2** (0.20 g) and N-phenylmaleimide (0.084 g) in xylene (7 ml) was heated under reflux for 4.5 hr. The solution was then concentrated under reduced pressure and diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2–hexane to give a mixture of **9a** and **9b** (0.23 g, 88.1%) as colorless prisms, mp 280—285°. *Anal.* Calcd for $C_{38}H_{25}NO_2S$: C, 81.55; H, 4.50; N, 2.50. Found: C, 81.60; H, 4.49; N, 2.27. IR ν_{max}^{KBr} cm^{-1}: 1780, 1720 (CO). NMR ($CDCl_3$) δ: 4.31, 4.70 (2H, s, methine H), 6.60—7.65 (23H, m, Ar H). The intensity ratio of the methine signals at δ: 4.31 and 4.70 was 1: 1.

Reaction of 2 with Maleic Anhydride——A solution of **2** (0.30 g) and maleic anhydride (0.076 g) in xylene (10 ml) was heated under reflux for 10 hr. The solution was evaporated to dryness under reduced pressure and the residue was recrystallized from $CHCl_3$ to give a mixture of **10a** and **10b** (0.283 g, 80.7%) as colorless needles, mp 292—295°. *Anal.* Calcd for $C_{32}H_{20}O_3S$: C, 79.32; H, 4.16. Found: C, 79.23; H, 4.09. IR ν_{max}^{KBr} cm^{-1}: 1860, 1785 (CO). NMR (DMSO-d_6) δ: 4.75, 5.23 (2H, s, methine H), 6.50—7.80 (18H, m, Ar). The intensity ratio of the methine signals at δ: 4.75 and 5.23 was 3: 7.

Reaction of a Mixture of 10a and 10b with Bromine——One drop of bromine was added to a solution of the mixture of **10a** and **10b** (0.10 g) in bromobenzene (10 ml). The mixture was heated under reflux for 1 hr and evaporated to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2–hexane to give **11** (0.08 g, 80%) as colorless needles, mp 290°. *Anal.* Calcd for $C_{32}H_{18}O_3S$: C, 79.65; H, 3.76. Found: C, 79.40; H, 3.64. IR ν_{max}^{KBr} cm^{-1}: 1830, 1770 (CO). NMR ($CDCl_3$) δ: 6.30—7.70 (18H, m, ArH).

Reaction of 2 with Acenaphthylene——A mixture of **2** (0.10 g) and acenaphthylene (0.055 g) was heated at 100° for 15 min. The reaction mixture was diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2–hexane to give **12** (0.116 g, 83%) as colorless plates, mp 230° (dec.). *Anal.* Calcd for $C_{42}H_{26}OS$: C, 87.17; H, 4.53. Found: C, 87.05; H, 4.59. IR ν_{max}^{KBr} cm^{-1}: 1775 (CO). NMR ($CDCl_3$) δ: 4.80 (2H, s, methine H), 5.87—8.42 (24H, m, ArH). On heating the product above its melting point, the retrogressive Diels–Alder reaction took place.

Reaction of 2 with Norbornene——A solution of **2** (0.20 g) and norbornene (0.05 g) in xylene (10 ml) was heated under reflux for 13 hr. The solution was concentrated under reduced pressure and diluted with hexane. The precipitated solid was filtered off and recrystallized from benzene–hexane to give **13** (0.194 g, 79%) as colorless prisms, mp 277—280°. *Anal.* Calcd for $C_{36}H_{28}OS$: C, 85.00; H, 5.55. Found: C, 84.90; H, 5.52. IR ν_{max}^{KBr} cm^{-1}: 1770 (CO).

Reaction of 2 with Benzyne——A solution of **2** (0.10 g) and 1-(2-carboxyphenyl)-3,3-dimethyltriazene (0.047 g) in chlorobenzene (10 ml) was heated for 6 hr. The solution was evaporated to dryness under reduced pressure. Hexane was added to the residue. The precipitated solid was filtered off and recrystallized from CH_2Cl_2-hexane to give **14** (0.104 g, 92%) as colorless needles, mp>300°. *Anal.* Calcd for $C_{34}H_{22}S$: C, 88.28; H, 4.80. Found: C, 88.16; H, 4.63. IR ν_{max}^{KBr} cm^{-1}: 3050, 740, 695. NMR ($CDCl_3$) δ: 6.29—8.32 (22H, m, ArH).

Reaction of 3 with Diphenylacetylene——A mixture of **3** (0.05 g) and diphenylacetylene (0.06 g) was heated at 200° for 2 hr. The cooled reaction mixture was diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2-hexane to give 1,2,3,4-tetraphenyltribenzo[*b*,*d*,*f*]thiepin 9,9-dioxide

(0.05 g, 76%) as colorless prisms, mp>300°. *Anal.* Calcd for $C_{42}H_{28}O_2S$: C, 84.54; H, 4.73. Found: C, 84.51; H, 4.65. IR ν_{max}^{KBr} cm^{-1}: 1330, 1170 (SO_2).

Reaction of 3 with Dimethyl Acetylenedicarboxylate——A solution of 3 (0.05 g) and dimethyl acetylenedicarboxylate (0.048 g) in xylene (5 ml) was heated under reflux for 4.5 hr. The solution was concentrated under reduced pressure and diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2–hexane to give 2,3-dimethoxycarbonyl-1,4-diphenyltribenzo[*b*,*d*,*f*]thiepin 9,9-dioxide (0.051 g, 81%) as colorless prisms, mp>300°. *Anal.* Calcd for $C_{34}H_{24}O_6S$: C, 72.84; H, 4.31. Found: C, 72.84; H, 4.25. IR ν_{max}^{KBr} cm^{-1}: 1730, 1240 (CO), 1325, 1165 (SO_2). NMR ($CDCl_3$) δ: 3.51 (6H, s, CH_3), 6.60—7.70 (16H, m, ArH), 7.80—8.01 (2H, m, ArH).

Reaction of 3 with N-Phenylmaleimide——A solution of 3 (0.10 g) and N-phenylmaleimide (0.042 g) in xylene (3.5 ml) was heated under reflux. The solution was diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2–hexane to give a mixture of **17a** and **17b** (0.129 g, 98%) as colorless needles, mp 295—300°. *Anal.* Calcd for $C_{38}H_{25}NO_4S$: C, 77.14; H, 4.26; N, 2.37. Found: C, 77.18; H, 4.23; N, 2.09. IR ν_{max}^{KBr} cm^{-1}: 1780, 1710 (CO), 1330, 1165 (SO_2). NMR ($CDCl_3$) δ: 4.24, 4.63 (2H, s, methine H), 6.70—7.92 (23H, m, ArH). The intensity ratio of the methine signals at δ: 4.24 and 4.63 was 3: 1.

Reaction of 3 with Maleic Anhydride——A solution of 3 (0.10 g) and maleic anhydride (0.022 g) in xylene (3.5 ml) was heated under reflux for 8 hr. The solution was diluted with hexane. The precipitated solid was filtered off and recrystallized from CH_2Cl_2–hexane to afford a mixture of **18a** and **18b** (0.107 g, 93%) as colorless prisms, mp 240—244°. *Anal.* Calcd for $C_{32}H_{20}O_5S$: C, 74.40; H, 3.90. Found: C, 74.36; H, 3.84. IR ν_{max}^{KBr} cm^{-1}: 1860, 1790 (CO), 1330, 1170 (SO_2). NMR (DMSO-d_6) δ: 4.73, 5.25 (2H, s, methine H), 6.40—8.10 (18H, m, ArH). The intensity ratio of the methine signals at δ: 4.73 and 5.25 was 2: 3.

Reaction of 3 with Acenaphthylene——A mixture of 3 (0.10 g) and acenaphthylene (0.051 g) was fused at 100° for 15 min. The reaction mixture was diluted with hexane. The precipitate was filtered and recrystallized from CH_2Cl_2–hexane to afford **19** (0.11 g, 82%) as colorless prisms, mp 241°. *Anal.* Calcd for $C_{42}H_{26}O_3S$: C, 82.25; H, 4.38. Found: C, 81.96; H, 4.39. IR ν_{max}^{KBr} cm^{-1}: 1770 (CO), 1312, 1165 (SO_2). NMR ($CDCl_3$) δ: 5.01 (2H, s, methine H), 6.05—6.52 (4H, m, ArH), 6.88—7.60 (16H, m, ArH), 8.03—8.45 (4H, m, ArH).

Reaction of 3 with Norbornene——A solution of 3 (0.20 g) and norbornene (0.047 g) in xylene (10 ml) was heated under reflux for 4.5 hr, when the violet color of the original solution had disappeared. The solution was evaporated to dryness under reduced pressure. The residue was washed with hexane and recrystallized from $CHCl_3$–hexane to afford **20** (0.201 g, 83%) as colorless prisms, mp>300°. *Anal.* Calcd for $C_{36}H_{28}O_3S$: C, 79.97; H, 5.22. Found: C, 79.77; H, 5.12. IR ν_{max}^{KBr} cm^{-1}: 1790 (CO), 1330, 1165 (SO_2).

References and Notes

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