

warm to 25 °C during 1 h. Dilution with 1:1 ether-pentane (10 mL) followed by washing with 10% HCl, twice with saturated Na₂CO₃, once with brine, and filtration through Na₂SO₄ gave after removal of solvent and preparative TLC with 50% ether-pentane (*R_f* 0.05-0.53) 198 mg of a mixture of (*Z*)- and (*E*)-**24**, X = H and SePh (87% yield based on 1-(3-furyl)-4-(phenylseleno)-5-hexyn-1-one): IR 3580, 3100, 1765(sh), 1720, 1620, 1550, 1530, 1490 cm⁻¹.

A sample of stereochemically pure (*E*)-**24** (X = H) was prepared by deselenation of the mixture prepared above by using the same procedure as for the conversion of **12** to **14** (1 PhSeNa/NEt₃/MeOH; 2 H₂O₂): NMR (CDCl₃, 270 MHz) δ 0.69 (d, *J* = 6.9 Hz, 3 H), 1.11 (d, *J* = 6.9 Hz, 3 H), 2.1 (m, 3 H), 2.38 (br q, *J* = 7 Hz, 2 H), 3.95 (symm m, 4 H), 4.24 (d, *J* = 2.2 Hz, 1 H), 6.22 (dt, *J* = 15.6, 1.5 Hz, 1 H), 6.32 (m, 1 H), 7.05 (dt, *J* = 15.6, 7.0 Hz, 1 H), 7.4 (m, 2 H).

1-(3-Furyl)-4,8-dimethyl-7-hydroxy-1,6-nonandione, 1-Ethylene Ketal. An oven-dried flask was flushed with N₂, and 741 mg of CuI (3.88 mmol) was added, followed by 40 mL of ether and 0.29 mL of dimethyl sulfide. This was cooled to 0 °C, and MeLi (~1 M, 8 mL) was added until a clear yellow solution was obtained. After 15 min, the solution was cooled to -78 °C and 350 mg of enones **24** in 2.5 mL of ether was added. The resulting bright yellow solution was stirred at -78 °C for 2 h and then decanted into 15 mL of 10% HCl. The solid was removed by filtration (and washed with ether), and the acid layer was extracted three times with ether. The combined organic extracts were shaken with basic NH₄Cl-NaOH (pH 8.5) and brine. After filtration through Na₂SO₄, the ether was evaporated. The residue was taken up into 2.4 mL of MeOH and 0.3 mL of PhSH, and 0.4 mL of NEt₃ was added. After being stirred for 1.25 h, the reaction mixture was diluted with 5% NaOH and extracted four times with 1:1 ether-pentane. The extracts were combined, washed with brine, and dried over Na₂SO₄. Solvent removal followed by preparative TLC with 45% ether-pentane gave a broad band centered at *R_f* 0.30, containing 160 mg of the desired ketal (66% yield, ~2:1 mixture of diastereomers): NMR (CDCl₃) δ 0.5-1.45 (m, ~11 H including d, *J* = 7 Hz, at 0.70, 0.91, and 1.10), 1.6-2.5 (m, ~7 H), 3.43 (d, *J* = 6 Hz, 1 H), 3.9 (m, 5 H), 6.37 (m, 1 H), 7.43 (m, 2 H); IR 3480, 2960, 2880, 1705, 1500, 1420, 1385, 1365, 1175, 1115, 1050, 1020 cm⁻¹; MS M⁺ 310.1780 (calcd for C₁₇H₂₆O₅, 310.1780); major fragments 310 (0.1), 210 (3.4), 195 (2.2), 149 (3.0), 147 (7.4), 139 (100), 123 (6.8), 95 (59.5), 83 (9.9), 73 (13.3), 71 (18.6), 55 (24.2).

1-(3-Furyl)-4,8-dimethyl-7-hydroxy-1,6-nonandione ((±)-7-Hydroxymyoporone and Its Epimer). The ketal (220 mg, 0.71 mmol) was dissolved in 1.6 mL of THF, and 2.4 mL of 50% aqueous HOAc was added. The resulting solution was stirred at 21 °C for 7 h, diluted with 20 mL of saturated NaHCO₃, and extracted five times with ether-pentane (1:1). The extracts were washed with 1 mL of brine and filtered through Na₂SO₄. Solvent removal left 185 mg of semisolid crude material. Examination of the NMR showed that the ketal was >90% hydrolyzed (crude yield was 88%). Recrystallization from 50% ether in pentane (three times) gave small white crystals, mp 70.5-71.5 °C.

Anal. Calcd for C₁₅H₂₂O₄: C, 67.64; H, 8.33. Found: C, 67.61; H, 8.30.

The proton and carbon NMR spectra of the crude product showed the presence of an ~70:30 mixture of isomers which could not be separated by TLC. The NMR spectra are summarized and compared with those of authentic 7-hydroxymyoporone in Table II (supplementary material). The synthetic mixture did not show any separate carbon resonances for the isomers in CDCl₃ solvent at 15.04 MHz, but in C₆D₆ at 25.16 MHz all except two of the aliphatic resonances showed peaks in approximately a 70:30 ratio. The 270-MHz proton spectra in benzene also showed a number of split signals. In each case the minor signal was identical with that of authentic (+)-7-hydroxymyoporone.

6-Phenyl-2-hexynol. LDA (2.05 mL, 1 M) was added to a cooled (-78 °C) THF (4 mL) solution of 0.28 mL (2 mmol) of 1-(phenylseleno)-1-propyne under N₂. After 10 min, 0.285 mL (2.02 mmol) of 3-phenylpropyl iodide was added and stirred for 1 h, and the reaction mixture was worked up. The crude 3-(phenylseleno)-6-phenyl-1,2-hexadiene (NMR δ 1.79 (quintet, *J* = 7 Hz, 2 H), 2.2 (m, 2 H), 2.56 (t, *J* = 7 Hz, 2 H), 4.57 (t, *J* = 2 Hz, 2 H), 7.0-7.7 (m, 10 H)) was oxidized without further purification. It was dissolved in 6 mL of CH₂Cl₂ and 0.2 mL of pyridine. Water (0.5 mL) and H₂O₂ (30%, 0.5 mL) were added to the solution, and it was vigorously stirred to initiate the reaction. Once the oxidation had started, the reaction mixture was stirred at moderate speed for 0.5 h and then worked up as usual. The concentrated filtrate gave 0.235 g (68% yield) of 6-phenyl-2-hexynol upon preparative TLC: NMR δ 1.78 (quintet, *J* = 7 Hz, 2 H), 2.16 (br t, *J* = 7 Hz, 2 H), 2.69 (t, *J* = 7 Hz, 2 H), 3.54 (s, 1 H), 4.15 (t, *J* = 1.5 Hz, 2 H), 7.1 (m, 5 H); IR 3380, 3030, 2940, 2220, 1602 cm⁻¹; MS M⁺ 174.1041 (calcd for C₁₂H₁₄O, 174.1045).

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Supplementary Material Available: Experimental details for runs 4, 6, 8, and 10 (Table I), for the crossover experiment and the preparation of 3-(trifluoromethyl)phenyl propargyl selenide and deuterated phenyl propargyl selenide, for the determination of the regioselectivity for the methylation of **1** and **5a**, and for the preparation and reactions of 3-(methylthio)-1-nonyne and ¹H and ¹³C spectral data for 7-hydroxymyoporone and epi-7-hydroxymyoporone (7 pages). Ordering information is given on any current masthead page.

Frontier-Controlled Pericyclic Reactions of Cyclooctatetraene with Cyclopentadienones. First Example of Exo [4 + 6]π Cycloadduct by Effective Secondary Orbital Control and Its Molecular Structure

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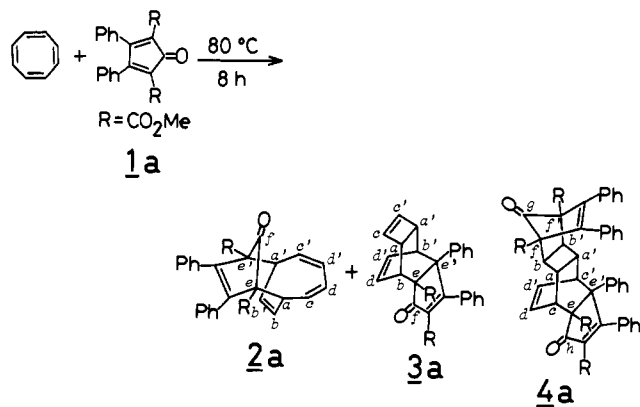
Contribution from the Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi, Higashi-ku, Fukuoka 812, Japan.
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Abstract: Pericyclic reactions of cyclooctatetraene with 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**), 2-oxo-1,3-bis(ethoxycarbonyl)-2*H*-cyclopenta[*i*]acenaphthylene (**1b**), and 2-oxo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthrene (**1c**) were investigated. The cycloaddition reactions of cyclooctatetraene with **1a** and **1b** afforded the novel exo [4 + 6]π cycloadducts together with bis-Diels-Alder cycloadducts. The configuration of the exo [4 + 6]π cycloadduct was assigned by the spectral data and verified by X-ray crystallography. The reactions are discussed on the kinetic and molecular orbital calculation data together with X-ray structural determination of the exo [4 + 6]π and bis-Diels-Alder cycloadducts.

Cyclooctatetraene has played an outstanding role in many aspects of theoretical and synthetic chemistry. As a medium-ring

polyene, it undergoes a wide variety of reactions which are often accompanied by skeletal transformations, and it is the progenitor

Scheme I



of a large number of interesting species.

In the past decade, the chemistry of cyclooctatetraene has received considerable attention and several reviews have appeared.¹ Cycloaddition reactions of cyclooctatetraene with electron-deficient 2 π components, wherein cyclooctatetraene plays the role of 4 π donor based on the dynamic properties with isomerization to bicyclo[4.2.0]octa-2,4,7-triene, are extensively studied. There are few reports on the cycloaddition reactions of cyclooctatetraene with 4 π components such as tetrachlorocyclopentadienone ketal² and 2,5-dimethyl-3,4-diphenylcyclopentadienone (**1d**),³ affording the cycloadducts with the valence bond isomer. In the cycloaddition reactions of cyclooctatetraene with octachlorofulvalene,^{4a} and with 2,5-bis(methoxycarbonyl)tetrazine,^{4b} the structures of the products are not known. So far as we know, there are no reports on the concerted cycloaddition of cyclooctatetraene itself with unsaturated compounds.

We have recently elucidated that 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) and 2-oxo-1,3-diphenyl-2H-cyclopenta[*l*]phenanthrene (phencyclone) (**1c**) show the high reactivity and selectivity toward various olefins involving conjugated medium-ring polyenes.⁵

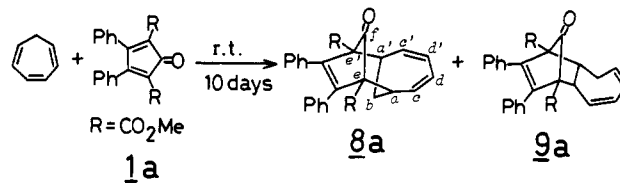
In this connection, we have recently communicated the isolation of the novel exo [4 + 6] π cycloadduct (**2a**)⁶ from 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) and cyclooctatetraene.

Here we report our studies of the pericyclic reactions of cyclooctatetraene with various cyclopentadienones based on the kinetic and molecular orbital calculation data together with X-ray structural determination of the exo [4 + 6] π and bis-Diels-Alder cycloadducts.

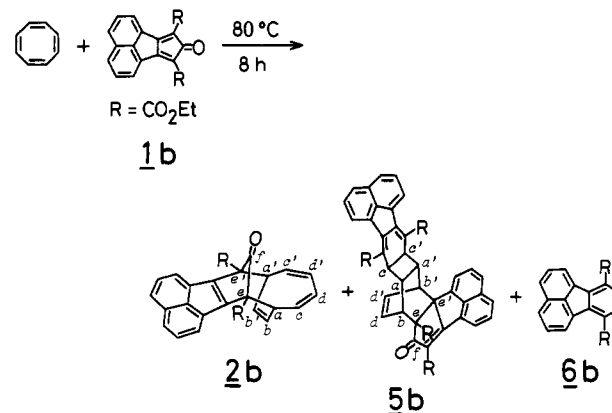
Results

Cycloaddition Reactions of Cyclooctatetraene with 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (1a). Heating a mixture of **1a** and cyclooctatetraene in benzene at 80 °C for 8 h resulted in the formation of two types of 1:1 cycloadduct, exo [4 + 6] π cycloadduct (**2a**) (46%) and endo [2 + 4] π cycloadduct (**3a**) (9%), together with 2:1 adduct (**4a**) (35%) (see Scheme I). The 1:1 and 2:1 nature were shown by mass spectrometry and elemental analyses. The structure of **2a** is mainly assigned on the basis of the ¹³C NMR spectrum, in which the bridgehead carbons (δ 71.5 and 40.7) suggest the symmetrical structure. Comparison of the ¹³C NMR spectral patterns of the adduct (**2a**) is grossly similar to the exo [4 + 6] π cycloadduct (**8a**) from

Scheme II



Scheme III



cycloheptatriene and **1a** indicating the skeletal resemblance to each other (see Scheme II and Experimental Section). The ¹H NMR data of the double resonance technique⁷ displayed the bridgehead protons at δ 3.88 strongly coupled with adjacent vinyl protons appeared at δ 6.04 excluding the possibility of another structure such as **10** (see Scheme VI); irradiation of the aliphatic proton multiplet at δ 3.88 led to collapse of the two-proton quartet at δ 5.74 into a sharp singlet indicating the absence of coupling between the protons at δ 5.74 and the other four olefinic protons centered at δ 6.04. The exo nature of the adduct (**2a**) was deduced from the chemical shift of H_c (H_{c'}) and H_d (H_{d'}) characteristic of exo diene protons observed in **8a** and the fact that H_b (H_{b'}) at δ 5.74 has suffered an upfield shift relative to that at δ 5.96 of the adduct⁷ derived from cyclooctatetraene and 4-phenyl-1,2,4-triazoline-3,5-dione, which might be shielded by the phenyl ring current. The IR spectrum of **2a** also supports this assignment showing a characteristic carbonyl band at 1768 cm⁻¹ to suggest the presence of a bridged carbonyl group of exo [4 + 6] π cycloadduct which absorbs at lower frequency than that of bicyclo[2.2.1]hepta-7-one moiety in **4a** (1806 cm⁻¹). Furthermore, the stereostructure of **2a** was confirmed by the X-ray analytical data of the analogous exo [4 + 6] π cycloadduct (**2b**) from 2-oxo-1,3-bis(ethoxycarbonyl)-2H-cyclopenta[*l*]acenaphthylene (**1b**)⁸ and cyclooctatetraene as described below.

The minor compound (**3a**) is readily assigned the endo [2 + 4] π adduct, which showed an enone carbonyl absorption at 1710 cm⁻¹ and four olefinic protons at δ 5.76, 5.86 (H_c and H_{c'}) and 6.34 (H_d and H_{d'}) and four bridgehead protons at δ 3.52 (H_b and H_{b'}) and 2.28 (H_a and H_{a'}) (see Scheme I).

The IR spectrum of **4a** showed a characteristic carbonyl band at 1804 cm⁻¹ suggesting the presence of a bridged carbonyl group and showed an enone carbonyl absorption at 1713 cm⁻¹. The ¹³C NMR spectrum of **4a** presented two carbonyl carbons at δ 191.3 and 197.9 and four ester carbonyl carbons at δ 163.1, 166.3, 167.1, and 168.3. These facts support the belief that **4a** is a bis-Diels-Alder adduct. The configuration of the cyclobutane moiety in the adduct (**4a**) was determined by the crystallographic data of the analogous 2:1 cycloadduct (**7c**) from phencyclone (**1c**) and cyclooctatetraene as described below.

With 2-Oxo-1,3-bis(ethoxycarbonyl)-2H-cyclopenta[*l*]acenaphthylene (1b). Heating cyclooctatetraene with **1b** in

(1) (a) Schröder, G. "Cyclooctatetraene"; Verlag Chemie: GmbH, Weinheim/Bergstr, 1965. (b) Paquette, L. A. *Tetrahedron* **1975**, *31*, 2855-2883. (c) Fray, G. I.; Saxton, R. G. "The Chemistry of Cyclooctatetraene and Its Derivatives"; Cambridge University Press: New York, 1978.

(2) Fray, G. I.; Smith, D. P. S. *J. Chem. Soc. C* **1969**, 2710-2716.

(3) Houk, K. N.; Luskus, L. J. *J. Org. Chem.* **1977**, *42*, 4151-4153.

(4) (a) Mark, V. *Chem. Commun.* **1973**, 910-911. (b) Avram, M.; Dinulescu, I. G.; Marica, E.; Nenitzescu, C. D. *Chem. Ber.* **1962**, *95*, 2248-2253.

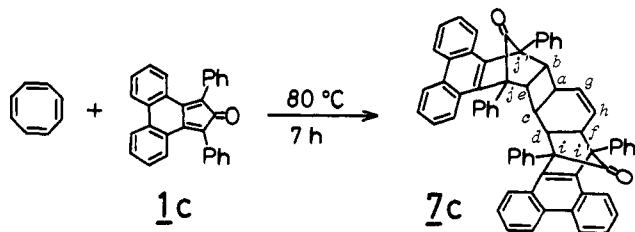
(5) (a) Yasuda, M.; Harano, K.; Kanematsu, K. *J. Org. Chem.* **1980**, *45*, 659-664. (b) *Ibid.* **1980**, *45*, 2368-2372 and references cited therein. (c) Harano, K.; Yasuda, M.; Ban, T.; Kanematsu, K. *Ibid.* **1980**, *45*, 4455-4462.

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(7) Evin, A. B.; Miller, R. D.; Evanga, G. R. *Tetrahedron Lett.* **1968**, 5863-5865.

(8) Allen, C. F. H.; Allan, J. V. *J. Org. Chem.* **1952**, *17*, 845-854.

Scheme IV



benzene at 80 °C for 8 h gave 1:1 cycloadduct (**2b**) (16%) and 2:1 adduct (**5b**) (62%) (see Scheme III).⁹ Comparison of the ¹³C NMR spectral patterns of the adduct (**2b**) shows they are in good agreement with those of the adduct (**2a**). The ¹³C NMR spectrum of **2b** displayed the bridgehead carbons (δ 66.3 and 42.1) suggesting the symmetrical structure. In the ¹H NMR spectrum of **2b**, the similar long-range coupling between the protons H_a and H_b (or H_{a'} and H_{b'}) as shown in that of **2a** is observed. The exo nature of **2b** is deduced from the fact that H_b (H_{b'}) at δ 5.22 has suffered a considerable upfield shift compared to that at δ 5.74 of **2a**, shielded apparently by naphthalene ring current. The IR spectrum of **2b** displayed a characteristic carbonyl band at 1765 cm⁻¹ to suggest the presence of a bridged carbonyl group of exo [4 + 6] π cycloadduct.

A more conclusive proof of structure for **2b** seems to be desirable because the reaction constitutes the first example of a [4 + 6] π cycloaddition involving cyclooctatetraene as the 6 π component. An X-ray crystallographic structure determination was carried out as described below.

The ¹³C NMR spectrum of **5b** presented an enone carbon at δ 198.9 and four ester carbons at δ 162.0, 166.9, 167.1, and 168.0. The IR spectrum of **5b** showed an enone carbonyl absorption at 1715 cm⁻¹ and two ester carbonyl absorptions at 1740 and 1725 cm⁻¹.

With Phencyclone (1c). The reaction of cyclooctatetraene with **1c** in benzene at 80 °C for 7 h gave a single adduct (**7c**) (85%) (see Scheme IV). The IR spectrum of **7c** showed a characteristic carbonyl band at 1781 cm⁻¹ suggesting the presence of a bridged carbonyl group. The ¹³C NMR spectrum (δ 196.8 and 201.7) of **7c** suggests that **7c** is a 2:1 cycloadduct of an unsymmetrical structure. The ¹H NMR spectrum was difficult to analyze precisely because of the existence of an extraordinary upfield shift of the neighboring methine proton to the double bond. A rigorous proof of the endo nature of **7c** could not be accomplished, since no Cope rearrangement occurs upon heating even at 120 °C for 3 days.

In order to elucidate the complete stereostructure of **7c**, the crystal structure analysis was carried out as described below.

Description of the Molecular Structures. Exo [4 + 6] π Cycloadduct (**2b**). We have performed an X-ray crystallographic analysis of **2b** since well-formed crystals are not available for **2a**. An ORTEP diagram¹⁰ of **2b** is shown in Figure 1, and the numbering sequence of **2b** in this paragraph is illustrated in it, where each atom is represented as an ellipsoid with 20% probability. As can be seen in the ORTEP drawing (Figure 1), the molecular structure of **2b** was confirmed as exo [4 + 6] π cycloadduct. The tricyclo[6.2.2.1]tridecan-11-one moiety is less strained than the tricyclo[6.2.1.1]dodecan-11-one moiety of the exo [4 + 6] π adduct (**18**) from **1a** and *N*-(ethoxycarbonyl)azepine.^{5c} The bond angle of C-CO-C of **18** is 102.9 \pm 0.6°, and this angle of **2b** is 107.2 \pm 0.2°. These agree with the IR absorption bands for the corresponding carbonyl of **18** and **2b** at 1770 and 1765 cm⁻¹ and the ¹³C NMR data of carbonyl carbons of **18** and **2b** at δ 193.8 and 196.3, respectively. The C₃-C₂₇ and C₆-C₃₀ bond lengths of 1.57 and 1.58 Å are longer than the usual value of 1.54 Å. These long

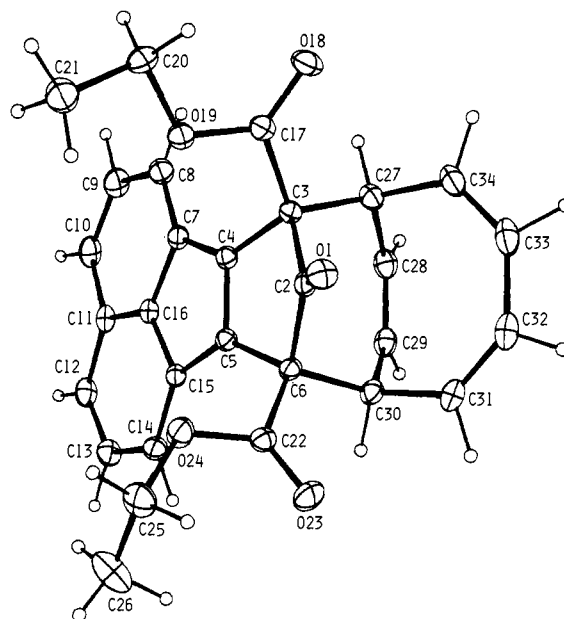


Figure 1. ORTEP diagram of **2b** to indicate the numbering sequence used in this paper for the 34 independent nonhydrogen atoms.

bond distances might be caused by "through-bond" interaction between π systems.¹¹ As seen in Figure 1, the upfield shift of olefinic protons (H₂₈ and H₂₉) at δ 5.22 in the ¹H NMR spectrum of **2b** can be explained by the anisotropic ring current effect of the acenaphthylene moiety. The displacements of the atoms (H₂₈ and H₂₉) from the plane of the acenaphthylene are 3.43 and 3.50 Å, respectively. The dihedral angles of C₄-C₃-C₁₇-O₁₉ and O₂₄-C₂₂-C₆-C₅ are 38.2 and 32.7°, respectively. The plane through atoms C₃₁, C₃₂, C₃₃, and C₃₄ is almost planar. The angle between the plane through atoms C₂₇, C₂₈, C₂₉, and C₃₀ and the plane through atoms C₃₁, C₃₂, C₃₃, and C₃₄ is near 107°.

Bis-Diels-Alder Cycloadduct (7c). In order to elucidate the complete stereostructure of the cycloadduct and to account for the spectroscopic data, crystallographic analysis was carried out.

The configuration of the adduct **7c** with the numbering sequence in this paragraph is illustrated in Figure 2, where each atom is represented as an ellipsoid with 20% probability.

As can be seen in the computer-generated drawing (Figure 2), the molecular structure of **7c** was confirmed as the 2:1 cycloadduct. The overall geometry and bonding makes this adduct (**7c**) a most interesting structure, wherein adjacent phenanthrene rings in the adduct are in a syn arrangement with respect to the H₃₃ and H₃₄ of the bicyclo[4.2.0]oct-2-ene moiety, and the bicyclo[2.2.1]heptan-7-one moieties are strained considerably, and these angles are reduced to 98.4 and 101.1°, respectively. This agrees with the IR absorption band for the carbonyl absorption at 1781 cm⁻¹. The C₃-C₃₁, C₆-C₃₂, C₃₅-C₃₉, and C₃₆-C₄₂ bond lengths, 1.58, 1.57, 1.59, and 1.57 Å, respectively, are longer than the usual value of 1.54 Å. These long bond distances might be mainly caused by large steric repulsions between the planes of the phenanthrene ring moiety. As shown in Figure 2, the extraordinary upfield shift of H₃₃ at δ 0.80 in the ¹H NMR spectrum of **7c** can be explained by the anisotropic ring current effect of phenanthrene moieties. The dihedral angles of C₁₁-C₁₂-C₁₃-C₁₄ and C₄₇-C₄₈-C₄₉-C₅₀ are 4.8 and 5.3°, respectively. With regard to the cyclohexane moiety, the six-membered ring is almost planar as well as the four-membered one, and the dihedral angle between the plane through atoms C₃₁, C₃₂, C₃₃, and C₃₄ and the plane through atoms C₃₃, C₃₄, C₃₅, C₃₆, C₃₇, and C₃₈ is near 120°.

Discussion

As shown in Table I, in the light of lower energy of the lowest unoccupied molecular orbital (LUMO), the cyclopentadienones

(9) Additional product is **6b**, mp 119–121 °C, 14%. The formation mechanism is obscure at this stage.

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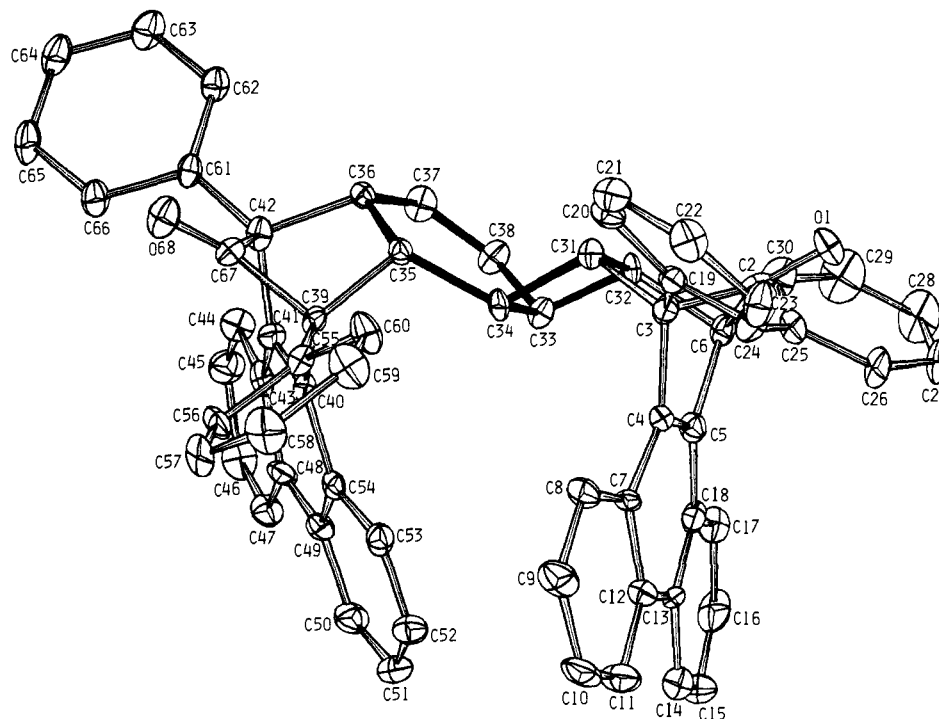


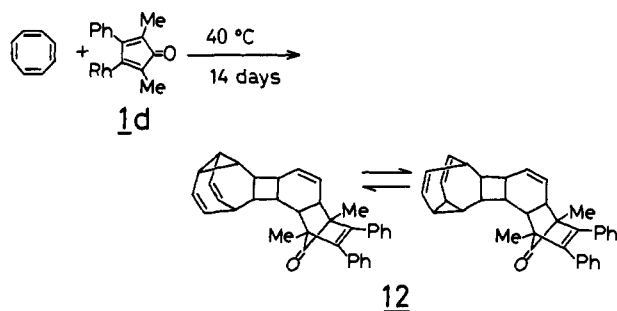
Figure 2. ORTEP drawing of 7c to indicate the numbering sequence used in this paper for the 68 independent nonhydrogen atoms.

Table I. FMO Energy Levels of Cyclopentadienones (1a-d) and Related Compounds by CNDO/2 MO Method

	1a	1b	1c	1d	cyclooctatetraene	bicyclo[4.2.0]octa-2,4,7-triene	cycloheptatriene
LUMO ^a	0.06	-0.18	-0.22	0.66	2.44	3.18	2.82
HOMO ^a	-11.50	-9.87	-9.50	-10.65	-10.74	-10.57	-11.40

^a In eV.

Scheme V



should be readily trapped by electron-rich dienophiles such as cyclooctatetraene and cycloheptatriene with higher energy of the highest occupied molecular orbital (HOMO). The CNDO/2 MO¹³ calculation indicates a 0.6–0.9 eV lowering of the LUMO for 1a–c as compared to 2,5-dimethyl-3,4-diphenylcyclopentadienone (1d),

(12) (a) Fujimoto, H.; Inagaki, S.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 2670–2671 and references cited therein. (b) Houk, K. N. "Pericyclic Reactions"; Academic Press: New York, 1977; pp 248–255.

(13) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970. The calculations reported here carried out by the CNDO/2 MO method on the model near the actual geometry. A complete description of the geometries of cyclopentadienones used in the calculations is given in the previous paper^{5a,b} in this series. Three-dimensional coordinates of cyclooctatetraene taken from the X-ray^{14a} and electron-diffraction^{14b} results and bicyclo[4.2.0]octa-2,4,7-triene are optimized by using Allinger's MMPI force field. Computer programs (CNDO/2 and MMPI) were locally modified versions for damped SCF calculation.

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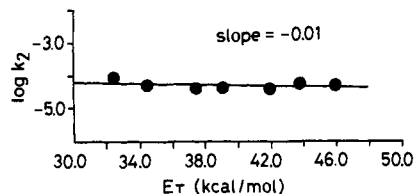


Figure 3. Plot of $\log k_2$ vs. E_T value for the cycloaddition reaction.

which has often been used as a trapping reagent in the cycloaddition reaction predicting that 1a–c show high reactivity to cyclooctatetraene in comparison with 1d, and a remarkable donor property for cyclooctatetraene as compared with cycloheptatriene. Indeed, Houk reported that cyclooctatetraene dimerizes more rapidly than 1d undergoes cycloaddition to cyclooctatetraene to give the adduct (12).³ Our results are in a sharp contrast to Houk's observations (see Scheme V). The difference could be explained satisfactory in terms of the frontier orbital control¹² with predominant donor–acceptor interaction between the HOMO (cyclooctatetraene) and the LUMO (cyclopentadienone) assisted by narrow frontier molecular orbital (FMO) separation.

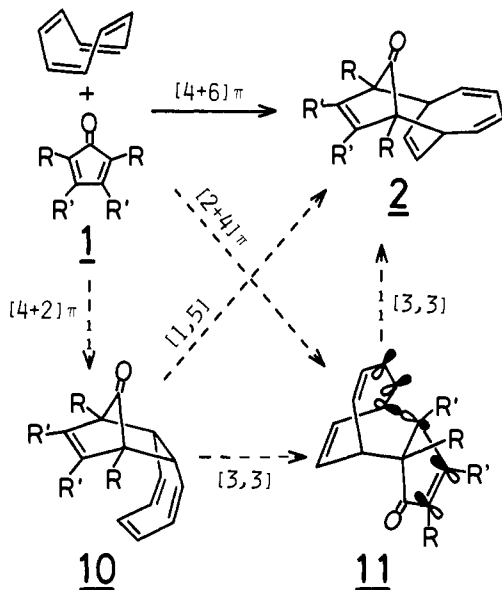
With phencyclone (1c), cyclooctatetraene seems to react formally with the valence tautomer acting as a dienophile to give the adduct of structure 7c. Similar additions take place with 1a and 1b, although the initial reaction is followed by Cope rearrangement to give products of structure 4a and 5b.

In the cases of 1a and 1b, direct addition to cyclooctatetraene itself also occurs to give exo [4 + 6] π cycloadducts (2a,b). As far as we know, there are no reports concerned with the [4 + 6] π cycloadduct from the frontier-controlled pericyclic reaction of cyclooctatetraene. This case is a first example of novel exo [4 + 6] π cycloadduct which could not be originally supposed by taking into consideration only the nonplanar conformation (tub structure).^{1b}

Table II. Rate Constants (k_2) for Cycloaddition Reactions of **1a** with Cyclooctatetraene in Various Solvents at $47.8 \pm 0.1^\circ\text{C}$

solvent	E_T , kcal mol ⁻¹ (25 °C)	$k_2 \times 10^5$ (L mol ⁻¹ s ⁻¹)
CH ₃ CN	46.0	4.94
(CH ₃) ₂ NCOH	43.8	6.04
C ₆ H ₅ CN	42.0	4.04
CHCl ₃	39.1	4.19
C ₆ H ₅ Cl	37.5	4.15
C ₆ H ₆	34.5	4.28
CCl ₄	32.5	8.72

Scheme VI



The E_T values of Dimroth, based on the bands of solvatochromism of pyridinium *N*-phenylbetaines, were used as a scale of solvent ionizing power in studying the effect of solvent on the rate of reaction.^{5b} As illustrated in Figure 3, plots of $\log k_2$ vs. E_T values show a linear relationship ($\log k_2 = aE_T + b$). The magnitude of the slope a has been used as a measure of the sensitivity of a reaction to the ionizing power of the medium. The a value is only -1.0×10^{-2} , sensitivity to ionizing power being very low as compared with those of typical concerted reactions.^{5b} The little response to variation of the polarity of the solvent rules out a dipolar intermediate suggested in the cycloaddition reaction of cyclooctatetraene with tetracyanoethylene^{1b} (see Table II).

For the formation of the $[4 + 6]\pi$ cycloadduct (**2**) in the thermal condition, two different pathways shown in Scheme VI are possible, one involving sigmatropic rearrangements ($[3,3]$ or $[1,5]$) of the adducts (**10** and **11**) and other direct cycloaddition of **1a** (4π) to cyclooctatetraene (6π). The pathway via the $[3,3]$ sigmatropic rearrangement may be excluded by consideration of the orientation of interacting orbitals in compound **11** as depicted in Scheme VI and the thermal stability³ of the analogous compound derived from **1d** and cycloheptatriene. The probability of the $[1,5]$ sigmatropic rearrangement is also excluded in view of the reaction conditions and absence of any intermediate which can be detected by thin-layer chromatographic analyzer when the reaction is carried out in controlled conditions. The reaction might proceed through the latter pathway.¹⁶

Figure 4 shows transition states for *exo* $[4 + 6]\pi$ and *endo* $[4 + 2]\pi$ cycloaddition, respectively. The cycloaddition of **1a** with cyclooctatetraene gives the *exo* $[4 + 6]\pi$ cycloadduct (**2a**) rather

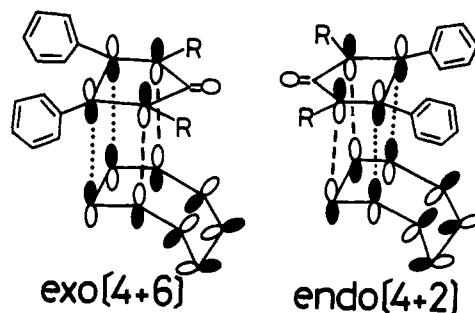
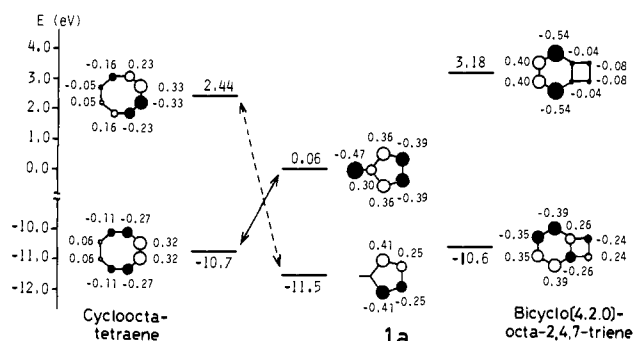
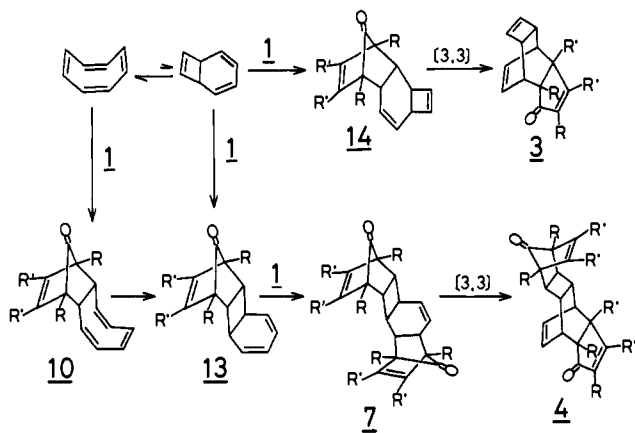
Figure 4. Transition states of the cycloaddition reaction of **1a** with cyclooctatetraene.

Figure 5. FMO energy levels and coefficients by the CNDO/2 MO method.

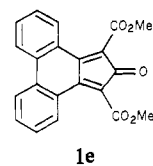
Scheme VII



than the *endo* $[4 + 2]\pi$ cycloadduct (**10a**), because steric repulsion of the *endo* adduct between the phenyl protons and cyclooctatetraene protons may be larger than that of the *exo* adduct. In case of **1c**, the steric repulsion is larger than those of **2a,b**.¹⁷ This agrees with the experimental result that the reaction of **1c** with cyclooctatetraene could not afford the *exo* $[4 + 6]\pi$ cycloadduct.

In general, $[4 + 6]\pi$ addition gives the *exo* adduct rather than the *endo* adduct, because the secondary orbital interactions of the frontier orbitals are antibonding. It is to be noted that these *exo* $[4 + 6]\pi$ adducts (**2a,b**) are the first model compounds in which

(17) Unfortunately, further attempts to effect the cycloaddition reactions of 2-*exo*-1,3-bis(methoxycarbonyl)-2*H*-cyclopenta[1]phenanthrene (**1e**) with cyclooctatetraene were unsuccessful since the preparation failed.



(16) The total energies for the reaction of **1a** with cyclooctatetraene calculated by the previous method^{3c} suggest that the *exo* adduct formation (-8596.17 eV) is quite energetically favorable as well as the *endo* adduct one (-8596.28 eV). This may be attributed to the effective secondary effect of **2a**.

Table III. ^1H NMR Data^a for the Cycloadducts from Cyclopentadienones (1a-c) and Cyclooctatetraene

compd no.	chemical shifts, δ ^b
2a ^c	3.64 (s, 6 H, 2 CH ₃), 3.88 (m, 2 H, H _a , H _{a'} , $J_{ab'} = 3$, $J_{ac} = 5$), 5.74 (dd, 2 H, H _b , H _{b'}), 6.04 (m, 4 H, H _c , H _{c'} , H _d , H _{d'}), 6.96-7.28 (m, 10 H, aromatic H)
2b ^d	1.20 (t, 6 H, 2 CH ₃), 3.90 (m, 2 H, H _a , H _{a'} , $J_{ab} = 6$, $J_{ab'} = 3$, $J_{ac} = 7$), 4.26 (q, 4 H, 2CH ₂), 5.22 (dd, 2 H, H _b , H _{b'}), 6.14 (m, 4 H, H _c , H _{c'} , H _d , H _{d'}), 7.40-7.92 (m, 6 H, aromatic H)
3a ^c	2.28 (m, 2 H, H _a , H _{a'}), 3.52 (m, 2 H, H _b , H _{b'}), 3.46, 3.60 (s, 6 H, 2 CH ₃), 5.76, 5.86 (m, 2 H, H _c , H _{c'}), 6.34 (m, 2 H, H _d , H _{d'}), 6.90-7.40 (m, 10 H, aromatic H)
4a ^c	2.44 (dd, 2 H, H _a , H _{a'} , $J_{aa'} = 6$, $J_{ab} = 2$), 3.04 (br s, 2 H, H _b , H _{b'}), 3.32 (s, 3 H, CH ₃), 3.40, 3.64 (m, 2 H, H _c , H _{c'}), 3.60 (s, 6 H, 2CH ₃), 3.66 (s, 3 H, CH ₃), 6.20, 6.74 (m, 2 H, H _d , H _{d'}), 6.92-7.40 (m, 20 H, aromatic H)
5b ^d	0.44, 0.74, 1.42, 1.56 (t, 12 H, 4 CH ₃), 2.50 (m, 2 H, H _a , H _{a'}), 3.12 (br s, 2 H, H _b , H _{b'}), 3.28 (m, 2 H, H _c , H _{c'}), 3.66, 3.98, 4.38, 4.48 (q, 8 H, 4 CH ₂), 6.40, 6.70 (m, 2 H, H _d , H _{d'}), 7.06-8.06 (m, 10 H, aromatic H), 8.24-8.60 (m, 2 H, aromatic H)
6b	1.48 (t, 6 H, 2 CH ₃), 4.54 (q, 4 H, 2 CH ₂), 7.56-8.00 (m, 6 H, aromatic H), 8.64 (d, 2 H, aromatic H, $J = 8$)
7c ^e	0.80 (m, 1 H, H _a), 2.34 (m, 1 H, H _b), 2.88 (m, 1 H, H _c), 3.40 (m, 1 H, H _d), 3.48 (m, 1 H, H _e), 3.90 (m, 1 H, H _f), 5.08 (m, 1 H, H _g), 5.96 (m, 1 H, H _h), 6.70-8.56 (m, 28 H, aromatic H)

^a Solvent CDCl₃. ^b J values are given in Hz. ^c See Scheme I for atom labels. ^d See Scheme III for atom labels. ^e See Scheme IV for atom labels.

Table IV. ^{13}C NMR Data^a for the Cycloadducts from Cyclopentadienones (1a-c) and Cyclooctatetraene

compd no.	chemical shift, δ
2a ^b	40.7 (d, C _a , C _{a'}), 71.5 (s, C _e , C _{e'}), 169.0 (s, ester C), 198.6 (s, C _f)
2b ^c	42.1 (d, C _a , C _{a'}), 66.3 (s, C _e , C _{e'}), 169.1 (s, ester C), 196.3 (s, C _f)
3a ^b	34.5, 38.1 (d, C _a , C _{a'}), 38.4, 38.6 (d, C _b , C _{b'}), 61.1, 66.9 (s, C _e , C _{e'}), 163.2, 168.8 (s, ester C), 198.5 (s, C _f)
4a ^b	34.0, 34.9 (d, C _a , C _{a'}), 38.4, 42.0 (d, C _b , C _{b'}), 42.4, 42.5 (d, C _c , C _{c'}), 61.5, 67.1 (s, C _e , C _{e'}), 68.7, 69.0 (s, C _f , C _{f'}), 163.1, 166.3, 167.1, 168.3 (s, ester C), 191.3 (s, C _g), 197.9 (s, C _h)
5b ^c	36.2 (d, C _a , C _{a'}), 40.3, 45.4 (d, C _b , C _{b'}), 46.5, 48.3 (d, C _c , C _{c'}), 63.2, 64.6 (s, C _e , C _{e'}), 162.0, 166.9, 167.1, 168.0 (s, ester C), 198.9 (s, C _f)
7c ^d	32.7 (d, C _b , C _e), 36.5, 39.0 (d, C _c , C _d), 40.7, 43.0 (d, C _a , C _f), 64.3, 66.1 (s, C _i , C _j), 66.5, 67.0 (s, C _j , C _{j'}), 196.8 (s, C _k), 201.7 (s, C _j)

^a Solvent CDCl₃. ^b See Scheme I for atom labels. ^c See Scheme II for atom labels. ^d See Scheme IV for atom labels.

the secondary orbital interactions are bonding, i.e., in phase as depicted in Figure 4. When 1a was allowed to react with cyclooctatetraene at room temperature, the yield of exo [4 + 6] π cycloadduct (2a) raised to 74%. These facts suggest that the formation of the exo [4 + 6] π cycloadduct could be kinetically controlled and thermodynamically stable.

With regard to the formation of bis-Diels-Alder adducts (4a and 5b), in principle, the initial addition of the diene component could occur either to cyclooctatetraene itself or to its valence tautomer as shown in Scheme VII. The pathway via bicyclo[4.2.0]octa-2,4,7-triene may not be important because of the low concentration^{18a} of bicyclo[4.2.0]octa-2,4,7-triene and the unfavorable FMO interaction as shown in Figure 5, and the rearrangement product (3) presumably derived from this interaction could be isolated in a low yield. On the contrary to the case of bicyclo[4.2.0]octa-2,4,7-triene, cycloocta-1,3,5-triene equilibrates with bicyclo[4.2.0]octa-2,4-diene in high concentration at moderate temperature (10.8% at 60 °C).^{18b} Thus, cyclopentadienone (1) may react with cyclooctatetraene directly to form endo [4 + 2] π cycloadduct (10) leading to 13 via intermolecular Diels-Alder reaction. These facts suggest that the precursors of 2:1 adducts have structure 13. The subsequent addition to 13 must be fast in comparison with its rate of formation, since the intermediate 13 could not be isolated.

In the case of 7c, no Cope rearrangement occurs upon heating. The difficulty of the Cope rearrangement in 7c is undoubtedly the result of the large steric repulsion between the phenanthrene moieties as shown in Figure 2 and the stability of the adduct (7c).^{5b}

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. The UV spectra were determined with a Hitachi EPS-3T spectrophotometer. The ^1H NMR spectra were taken with a JEOL PS-100 instrument for solutions in deuteriochloroform with Me₄Si as an internal standard; chemical shifts are expressed in δ values. The ^{13}C NMR data were recorded on a JEOL FX-100 and refer to solutions in deuteriochloroform, as concomitant standard,

downfield chemical shifts being computed relative to Me₄Si. The IR spectra were taken with a JASCO IR A-1 infrared spectrophotometer. Mass spectra were obtained with a JEOL JMS-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150-200 °C. Thin-layer chromatographic analyses were performed with a Iatroscan TH-10 analyzer with a flame ionization detector.

Cycloaddition Reaction of Cyclooctatetraene with 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (1a). A solution of 1a (0.50 g) and a tenfold excess of cyclooctatetraene (1.63 mL) in benzene was heated at 80 °C for 8 h. The solvent was then evaporated under reduced pressure and the residue was chromatographed on silica gel, using benzene/ethyl acetate (20/1). The first fractions gave 2a (0.30 g, 46%) as colorless prisms: mp 189-198 °C dec; IR (Nujol) 1768 (bridged C=O), 1740 (ester C=O) cm⁻¹; mass spectrum m/e 452 (M⁺). Anal. (C₂₉H₂₄O₅) C, H. The second fractions gave 3a (0.06 g, 9%) and colorless powder: mp 225-228 °C; IR (Nujol) 1740, 1720 (ester C=O), 1710 (enone C=O) cm⁻¹. Anal. (C₂₉H₂₄O₅) C, H. And the third fractions gave 4a (0.20 g, 35%) as colorless powder: mp 257-258 °C; IR (Nujol) 1806 (bridged C=O), 1745, 1740, 1735 (ester C=O) cm⁻¹; mass spectrum m/e 800 (M⁺). Anal. (C₂₉H₂₄O₅) C, H. The ^1H and ^{13}C NMR spectral data are summarized in Tables III and IV.

With 2-Oxo-1,3-bis(ethoxycarbonyl)-2H-cyclopentadienylphenylene (1b). A solution of 1b (0.40 g) and a tenfold excess of cyclooctatetraene (1.30 mL) in benzene was heated at 80 °C for 8 h. The solvent was then evaporated under reduced pressure and the residue was chromatographed on silica gel, using benzene. The first fractions gave 6b as pale yellow needles: mp 119-121 °C; IR (Nujol) 1730 (ester C=O) cm⁻¹; mass spectrum m/e 346 (M⁺). Anal. (C₂₂H₁₈O₄) C, H. The second fractions gave 2b (0.06 g, 16%) as yellow prisms: mp 169-172.5 °C; IR (Nujol) 1765 (bridged C=O), 1730 (ester C=O) cm⁻¹. Anal. (C₂₉H₂₄O₅) C, H. And the third fractions gave 5b (0.19 g, 62%) as yellow needles: mp 224-235 °C; IR (Nujol) 1740, 1735, 1725 (ester C=O), 1715 (enone C=O) cm⁻¹; mass spectrum m/e 772 (M⁺). Anal. (C₂₉H₂₄O₅) C, H. The ^1H and ^{13}C NMR spectral data are summarized in Tables III and IV.

With Phencyclone (1c). A solution of 1c (0.24 g) and a tenfold excess of cyclooctatetraene (0.70 mL) in benzene was heated at 80 °C for 7 h. The solvent was then evaporated under reduced pressure and the residue was recrystallized from benzene-methanol. The single product is 7c (0.23 g, 85%) as colorless prisms: mp 239-246 °C dec; IR (Nujol) 1781 (bridged C=O); mass spectrum m/e 868 (M⁺). Anal. (C₆₆H₄₄O₂:C₆H₆:CH₃OH) C, H. The ^1H and ^{13}C NMR spectral data are summarized in Tables III and IV.

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Cycloaddition Reaction of Cycloheptatriene with 1a. A solution of **1a** (0.20 g) and a twofold excess of cycloheptatriene (0.12 mL) in chloroform was allowed to stand at room temperature for 10 days. The solvent was then evaporated under reduced pressure and the residue was recrystallized from ethanol-petroleum ether to give exo [4 + 6] π cycloadduct (**8a**) (0.14 g, 57%) as colorless prisms: mp 189–193 °C; IR (Nujol) 1781 (bridged C=O), 1735 (ester C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.76 (d, 1 H, H_b , $J_{bb'} = 14$ Hz), 2.60 (m, 1 H, $H_{b'}$), 3.56 (s, 6 H, 2 CH_3), 3.68 (t, 2 H, H_a , H_c ; $J_{ab} = 5$, $J_{ac} = 6$ Hz), 5.98 (m, 2 H, H_d , H_d'), 6.30 (m, 2 H, H_e , H_e'), 6.96–7.50 (m, 10 H, aromatic H); ^{13}C NMR (CDCl_3) δ 25.0 (t, C_b), 41.5 (d, C_a , C_c), 71.5 (s, C_e , C_e'), 195.2 (s, C_f). Anal. ($\text{C}_{28}\text{H}_{24}\text{O}_5$) C, H.

Endo [4 + 2] π cycloadduct (**9a**) (0.05 g, 20%) was obtained from the filtrate as colorless powder: mp 172–177 °C; IR (Nujol) 1798 (bridged C=O), 1736 (ester C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 2.62, 2.72 (m, 2 H, methylene), 3.54, 3.76 (s, 6 H, 2 CH_3), 3.70 (m, 2 H, methine), 5.96–6.32 (m, 4 H, olefin), 6.82–7.40 (m, 10 H, aromatic H). Anal. ($\text{C}_{28}\text{H}_{24}\text{O}_5$) C, H.

Kinetics. The pseudo-first-order conditions were maintained by using a 100:1 ratio of cyclooctatetraene to **1a** in various solvents. The rate was followed at 47.8 ± 0.1 °C by measuring the decrease of the absorption at 450 nm, using a 1×10 mm quartz cell sealed with a ground glass stopper which was thermostated with flowing water at constant temperatures. Pseudo-first-order rate constants were determined by using infinity values taken after 10 half-lives. All spectra were calculated by means of a nonweighted least-squares program (see Table II). The results indicate that all of the reactions, involved in this reaction obeyed second-order rate law and proceed via nonionic transition states.

Diffraction Measurements. General Procedure. All measurements were made on a Syntex P1 automated diffractometer with graphite monochromated Mo K α (0.71069 Å) radiation. Crystal surveys and unit-cell selections were made for each compound by using the search, centering, and automatic indexing routines of the P1 system and 15 randomly selected reflections. The cell constants were found by a least-squares procedure, using the values of the Bragg angles of 15 reflections. Intensity data were collected by using θ - 2θ scans to a limit of $2\theta = 55^\circ$. The available scan rate from 24.0 to 4.0°/min was used, and three reflections were monitored after every measurement of 97 reflections. The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorptions.

Observed structure factors were converted into normalized structure factor amplitudes, $|E|$ values, by use of the scale factor and the overall temperature factor obtained from Wilson's statistics.¹⁹ The structure was solved by the direct method, using the MULTAN series of programs.²⁰ The atomic scattering factors were taken from the tables of Cromer and Waber.²¹

All structure-solving programs were from the computer center of Kyushu University with the Universal Crystallographic Computation Program System (UNICS II)²² and all calculations were performed on the FACOM M-200 computer.

Exo [4 + 6] π Cycloadduct (2b**).** Single crystals of the compound **2b** were prepared by slow evaporation of a benzene-ethanol solution at room temperature. Crystals of the compound **2b** are yellow parallelepipeds. The density was measured by flotation in an aqueous potassium iodide solution.

Statistical Wilson analysis of the data indicated a centrosymmetric distribution of intensities. The space group $P\bar{1}$ was selected from the number of molecules per unit cell ($Z = 2$) and was later confirmed in the course of the structure refinement. Crystals of the adduct **2b** are triclinic with the following unit-cell parameters: $a = 8.409$ (3), $b = 18.283$ (7), $c = 8.377$ (2) Å, $\alpha = 98.88$ (3), $\beta = 100.12$ (3), $\gamma = 112.39$ (3)°, $Dm = 1.310$ g cm^{-3} (KI), $Dc = 1.322$ g cm^{-3} , $V = 1137$ (1) Å³. Of 3548 independent reflections, 2800 were treated as observed ($I > 2.3\sigma(I)$).

An E map calculated with 443 signed E 's ($|E| \geq 1.5$), which gave the absolute figure of merit (ABS FOM) 1.194, revealed the positions of 34 of the all nonhydrogen atoms. Six cycles of block-diagonal least-squares minimizing $\sum(|F_o| - k|F_c|)^2$ by varying the positions and isotropic vibrational amplitudes of the C and O atoms led to $R = 0.12$. Nine further cycles of least-squares refinement of atomic parameters with anisotropic vibrational amplitudes converged to $R = 0.079$. At this stage, the positions of 24 hydrogen atoms were located on a subsequent difference Fourier map. The thermal parameters of the hydrogen atoms were assigned so that $B(\text{H}) = B(\text{C}) + 1.0$ Å². After adding the hydrogens, and refining with anisotropic U 's for all the C and O atoms, we obtained a final R of 0.0375.

Bis-Diels-Alder Cycloadduct (7c**).** Cubic crystals of **7c** grown from benzene/methanol solution were obtained. Of 3916 independent reflections, 2215 were treated as observed ($I > 2.3\sigma(I)$). The space group is $P\bar{1}$, with the following cell parameters: $a = 15.998$ (14), $b = 20.071$ (22), $c = 9.670$ (4) Å, $\alpha = 92.23$ (7), $\beta = 116.87$ (6), $\gamma = 105.83$ (8)°, $Z = 2$, $V = 2617$ (4) Å³, $Dc = 1.243$, and $Dm(\text{KI}) = 1.232$ g cm^{-3} .

Statistical Wilson analysis of the data did not indicate a definite nature of a centrosymmetric distribution of intensities, but the space group ($P\bar{1}$) was later confirmed by the successful solution and refinement of the structure. An overall temperature factor of 4.04 Å was obtained from a Wilson plot and used to calculate normalized structure factors.¹⁹ The difficulties were encountered in direct phasing. The difficulty was overcome by omitting the 1, 11, -8 reflection from the automatically selected origin fixing reflections because the number of the Σ_2 relation of it was very small. The resulting 352 E values larger than 1.7 were processed through the multiple solution tangent refinement method of Germain, Main, and Woolfson.²⁰ In addition to the three origin-fixing reflections (3, 3, -1; 6, 0, 7; 7, 8, -2) and one reflection (6, 6, -2) phased from the Σ_2 formula, five reflections (3, 12, 5; 4, -6, 6; 4, -4, 6; 9, -7, -1; 9, 11, -7) were allowed as an initial basis set. Of the 32 possibilities, the correct solution had the 14th highest figure of merit (0.9789) and yielded the 47 coordinates of 68 atoms of the molecule. At this stage, the positions of the remaining atoms (29 atoms), including a benzene molecule and a methanol one, were located on a subsequent difference Fourier map.

Many cycles of refinement with isotropic and then anisotropic temperature factors resulted in the discrepancy factor $R = 9.34\%$ for the observed reflections. The hydrogen atoms were placed in calculated positions and their contributions were included in structure-factor calculations, but they were not refined because of the very large number of variables (876) wherein the thermal parameters of the hydrogen atoms were assigned so that $B(\text{H}) = 3.5$ Å². Block diagonalized anisotropic refinement converged at $R = 6.65\%$.

Acknowledgment. The authors wish to thank Miss R. Hasegawa for experimental assistance of the reaction of **1a** with cycloheptatriene.

Supplementary Material Available: Tables of bond lengths (Tables V and VI), bond angles (Tables VII and VIII), final structure parameters for the nonhydrogen atoms (Tables IX and X), and coordinates for hydrogen atoms (Tables XI and XII) (8 pages). Ordering information is given on any current masthead page.

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