perature of 19.0 °C with a jump of 4.1 °C. The chemical relaxation which occurred after a sudden temperature rise was followed at 500 nm by displaying the photomultiplier output on a Tektronix 549 storage oscilloscope. Relaxation curves were photographed, and the developed negatives traced on a computerized digitizer to calculate relaxation times. At least four determinations of relaxation time were measured for each solution.

All other kinetic and spectroscopic techniques were essentially the same as those described previously.[12] The spectral determination of the flavylium ion–anhydro base equilibrium position (pK_5^a, curve A of Figure 2) was carried out by placing a stock solution (1×10^{-4} M) of the ion in 0.1 M HCl in one syringe of a stopped-flow apparatus and various buffer solutions also containing 0.1 M NaOH in the other syringe. The absorbance value at 500 nm obtained on mixing (5–10 ms) was recorded. Curves B and C of Figure 2 were obtained by recording the absorbance at 500 and 440 nm, respectively, at a time corresponding to 6–8 half-lives of transformation ii (see Figure 3) after adjustment of the pH of the stock flavylium ion solution in 0.1 M HCl. Reacidification experiments were carried out by adding the stock acid solution to a dilute buffer solution also containing 0.1 M NaOH and, after a time corresponding to 6–8 half-lives of transformation ii, by mixing this in the stopped-flow apparatus with an appropriate HCl solution. Rate constants for transformation ii (Figure 3) were obtained by addition of the stock acid solution to an appropriate buffer, observing the decrease in absorbance at 500 nm associated with anhydro base disappearance. Rate constants for transformation iii were obtained at pH <9 by following at 500 nm the further disappearance of anhydro base and at pH >9 by following at 350 nm the appearance of *trans*-chalcone. In all experiments exposure to ambient light was kept at a minimum. The cis → trans isomerization is greatly accelerated even by room light.

Acknowledgment. Continued financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. The assistance of Dr. A. Ahwal and Professor A. J. Kresge in the running of the temperature-jump experiments is also acknowledged.

Registry No. F^+, 15896-53-4; AB, 15896-55-6; BZ, 82522-50-7; cC, 82522-51-8; tC, 82522-52-9; cC^-, 82522-53-0; BZ^-, 82522-54-1.

Frontier-Controlled Pericyclic Reactions of a Powerful Electron-Attracting Fused-Ring Cyclopentadienone

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Received November 6, 1981

2-Oxo-1,3-bis(ethoxycarbonyl)-2*H*-cyclopenta[*i*]acenaphthylene (**1a**) reacts readily with dienophile to give [4 + 2] π cycloadducts that lose carbon monoxide spontaneously to afford tetrasubstituted 1,3-cyclohexadiene derivatives. The cycloadducts with conjugated cyclic olefins undergo facile Cope rearrangement. Adducts with nonconjugated olefins are transformed into intramolecular double Diels–Alder adducts on heating. A proposed pathway for the pericyclic reaction of **1a** with cycloheptatriene is supported by an X-ray crystallographic study of the structure of the syn-endo [2 + 4] π cycloadduct. The cycloaddition reactions of **1a** are discussed in terms of frontier molecular orbital (FMO) theory. Molecular mechanics calculations indicate that strain release in the norbornen-7-one system fused to the acenaphthylene ring is important in the decarbonylation reaction and the Cope rearrangement of the primary Diels–Alder adducts of **1a**.

Interest in the chemistry of cycloaddition has led to a continuing search for new reactive components that can be used in carbon skeleton construction. Previously, we have studied pericyclic reactions of cyclopentadienones, such as 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1e**)[1] and phencyclone (**1f**),[2] with cyclic unsaturated compounds (Chart I). We have recently found that 2-oxo-1,3-bis(ethoxycarbonyl)-2*H*-cyclopenta[*i*]acenaphthylene (**1a**)[3a] undergoes cycloaddition to cyclooctatetraene to give an endo [4 + 6] π cycloadduct,[2c] which is the first example of an isolable cycloadduct derived from cyclooctatetraene. There are few reports of cycloaddition reactions of acecyclone derivatives such as **1a**–**d**, except for the synthetic interest[3b] in polycyclic aromatic hydrocarbons with the acenaphthylene skeleton. We here report on some cycloadditions of **1a**, discussed in terms of frontier molecular orbital (FMO) theory,[4] based on kinetics, MO calculations, force-field calculations, and X-ray crystallographic data.

Chart I

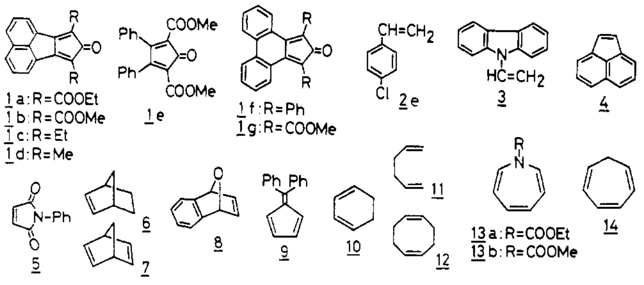

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Table I. FMO Energy Levels[a] of Cyclopentadienones 1 and Dienophiles Involving Medium Membraned Ring, Unsaturated Compounds by the CNDO/2 MO Method[b]

	1b	1d	1e[c]	1f[d]	2d[d]	13b[c]	14
LUMO	−0.18	0.43	0.06	−0.22	2.84	2.51	2.82
HOMO	−9.87	−9.10	−11.5	−9.50	−11.4	−10.5	−11.4

[a] In electronvolts. [b] Reference 10. [c] Reference 1a. [d] Reference 2a.

Table II. Second-Order Rate Constants and Relative Rates for Cycloaddition Reactions of 1a with Para-Substituted Styrenes 2a-h

	2a	2b	2c	2d	2e	2f	2g	2h
substituent (X)	NMe_2	OMe	Me	H	Cl	Br	CN	NO_2
$\sigma_p^{+\,a}$	−1.7	−0.778	−0.311	0.0	0.114	0.150	0.659	0.790
$k_2 \times 10^3$, $M^{-1}\ s^{-1}$	74.4	2.32	0.78	0.28	0.32	0.34	0.18	0.25
$\log k_2\ (X)/k_2\ (H)$	2.42	0.92	0.44	0.0	0.05	0.08	−0.19	−0.06

[a] Brown-Okamoto value.

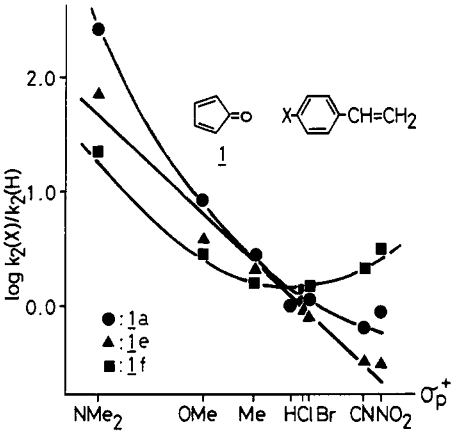


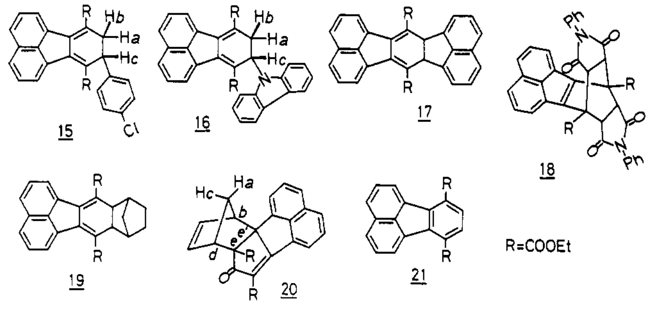
Figure 1. Plots of log $k_2(X)/k_2(H)$ against σ_p^+ for the cycloaddition reactions of **1a** (●), **1e** (▲), and **1f** (■) with para-substituted styrenes **2a–h**.

Results

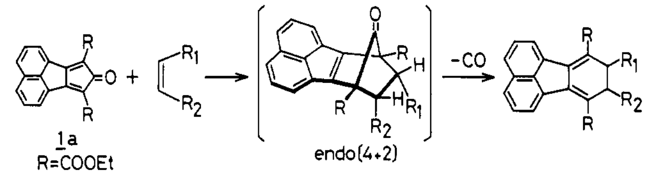
On the basis of previous studies,[1,2] we concluded that the ideal cyclopentadienone for a potent 4π-synthon should have a planar structure with electron-attracting substituents, such as alkoxycarbonyl groups. Accordingly, we wished to study cycloadditions of cyclopentadienone **1g** but found that this compound exists as a dimer that does not dissociate and does not undergo cycloadditions. Investigation of the analogous compounds **1a–d** revealed that only **1a** was suitable for our purpose; the solubility of **1b** is too low, and **1c** and **1d** form abnormal [2 + 2] π dimers that dissociate only at elevated temperatures.[5]

As shown in Table I, the FMO energy difference (HOMO–LUMO) in **1b** is very narrow, and the energy levels are within those of the dienophiles. The interaction between the LUMO of **1b** and the HOMO of a dienophile should predominate over that between the HOMO of **1b** and the LUMO of a dienophile. This prediction of reactivities based on MO calculations is compatible with kinetic data, which indicate that **1a** participates in an inverse cycloaddition in Sustmann's classification[6] of Diels–Alder reactions. In previous papers[1b,2a] we showed that the reactions of **1e** and **1f** can be rationalized as inverse and neutral Diels–Alder reactions, respectively. To investigate the reactivity of **1a**, which has electron-withdrawing substituents like **1e** and a fused ring system like **1f**, we carried out kinetic measurements of its cycloaddition with a series of para-substituted styrenes **2a–h**. The second-order rate constants (k_2) and the relative rates [log k_2 (X)/k_2 (H)] are shown in Table II. The substituent effects of **1a** and **2a–h** on the reaction rates were examined by plotting the relative rates against σ_p^+,[2a,7] (Figure 1),

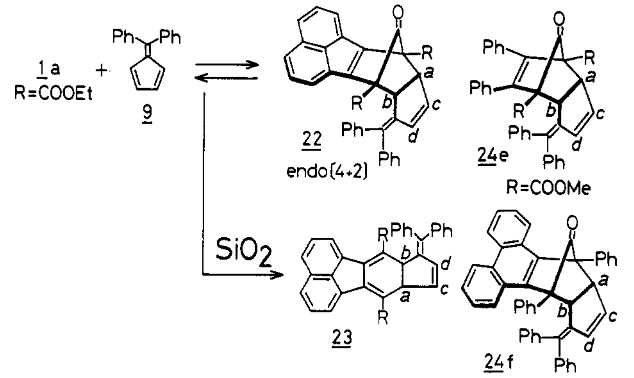
Chart II



Scheme I



Scheme II



Scheme III

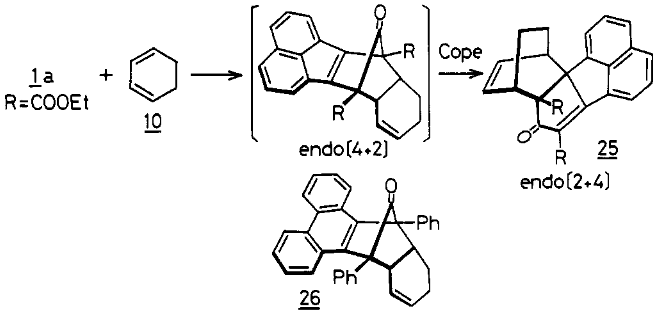


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Table III. Reaction Conditions, IR Spectra, and Physical Constants of the Cycloadducts 15-33

olefin	mole ratio of 1a/olefin	reaction condt temp, °C	reaction condt time, h	product (%)	IR ν_{max},[a] cm^{-1} (C=O)	mp, °C	MS, *m/e* (M$^+$)
2e	1:10	rt[b]	10	**15** (67)	1725, 1715[c]	oil	456
3	1:1	60	1.5	**16** (85)	1714	181-183	
4	1:2	80	0.5	**17** (87)	1708	212-215	
5	1:1	rt	29	**18** (77)	1780, 1750, 1730	>300	666
6	1:10	rt	13	**19** (71)	1722	119-120	442
7	1:2	50	2.5	**20** (10)	1742, 1718, 1700	79-86.5 dec	414
				21 (48)	1730	119-121	346
8	1:1	rt	1	**21** (80)	1730	119-121	
9	1:10	rt	10	**22** (85)	1800, 1738	181-183	
	1:10[d]	rt	6	**24e** (93)	1797, 1740, 1734	192-194	
	1:10[e]	rt	4	**24f** (92)	1787	269.5-271.5	
10	1:1	50	2	**25** (89)	1732, 1715, 1708	158-159	
	1:1[e]	50	6	**26** (95)	1776	257-259	
11	1:10	80	40	**27** (22)	1740, 1730[c]	oil	
				28 (56)	1740, 1730	90.5-92.5	
12	1:10	140	16	**29** (86)	1730	206-210 dec	
13a	1:2	80	40	**30a** (78)	1740, 1715, 1708	161-163	513
	1:4[f]	80	28	**30c** (69)	1718, 1695	157-159	
14	1:10	rt	108	**31a** (57)	1780, 1735	170-175	
				33a (24)	1738, 1710	184-185	
	1:10[f]	80	39	**31c** (21)	1760	156-161	
				33c (25)	1690	175-178	

[a] In Nujol. [b] Room temperature. [c] Neat. [d] 1e/olefin. [e] 1f/olefin. [f] 1c/olefin.

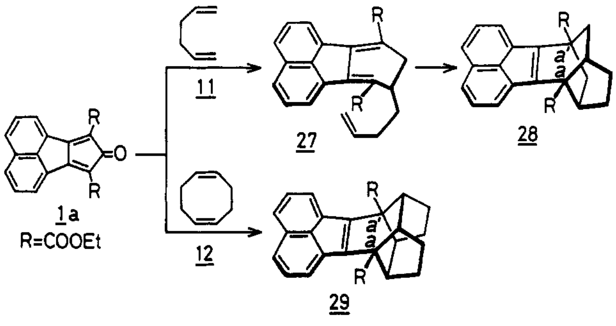
which indicated an inverse behavior similar to that of **1e**.[1b] These data indicate that **1a** has a very low LUMO energy level and should be a good 4π acceptor for olefins.

Reactions of 1a with Dienophiles 2–12. Reaction of **1a** with an equimolar amount or an excess of olefins **2–12** (Chart I) gave decarbonylated 1:1 adducts in high yields in all cases except **5** (Chart II). In these reactions, **1a** acts as a 4π component, and thermal decarbonylation or aromatic Cope rearrangement of the primary adducts occurs in all cases except **9** (Schemes I–III). The reaction conditions and properties of the cycloadducts **15–29** are shown in Table III, and their NMR data are given in Tables IV and V.

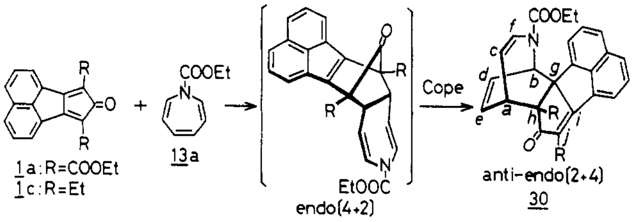
Reaction of **1a** with **9** gave a quantitative yield of the endo [4 + 2] π cycloadduct **22** (Scheme II), which had an IR absorption band at 1800 cm^{-1} due to a strained-ring carbonyl group.[1c] The ^{1}H NMR spectrum of **22** exhibited an anisotropic influence of the olefin signals of the diphenylfulvene moiety centered at δ 5.80 (H_c and H_d) because of the acenaphthylene ring-current effect. These data suggest the endo [4 + 2] π structure for **22**, in contrast to the nonplanar cyclopentadienone structure of **1e** (δ 6.24 and 6.67). Reaction of **1a** with **9** in the presence of silica gel gave the decarbonylated adduct **23**.

Cycloaddition of **1a** with **10** at 50 °C in benzene for 2 h afforded the rearrangement product **25** (Scheme III). On the other hand, heating a mixture of **1f** and **10** in benzene at 50 °C for 6 h gave the primary adduct **26**, which did not undergo Cope rearrangement on heating in chlorobenzene at 120 °C for 5 h. The destruction of the aromaticity of the phenanthrene ring in **26** seems to be energetically unfavorable.[2b] In the cycloadditions of **1a** with cyclic conjugated polyenes, the initial [4 + 2] π adduct immediately underwent Cope rearrangement to the [2 + 4] π adduct.

Scheme IV



Scheme V



Double Diels–Alder Reaction. Annelation of one double bond of the 1,5-acyclic diene **11** with **1a** at 80 °C produced a 1,3-cyclohexadienyl group, which was then available for an intramolecular Diels–Alder reaction with the remaining double bond of the diene to form isotwistene **28** in 56% yield (Scheme IV). The ^{13}C NMR spectrum of **28** showed four kinds of sp^3 carbon atoms, in support of this structure (Table V). Likewise, addition of **1a** to **12** at 140 °C produced **29** in 86% yield (Scheme IV). The ^{13}C NMR spectrum was consistent with **29** and showed two types of sp^3 carbon atoms (Table V). In the ^{1}H NMR spectrum, the methine protons appeared as a broad singlet at δ 2.54 (Table IV). It appears that an interesting use of **1a** is in the facile assembly of polycyclic carbocycles by means of the double Diels–Alder reaction.

Cycloaddition Reactions of 1a and 1c with 13a and 14. Reactions of **1a** and **1c** with **13a** in benzene at 80 °C gave only anti-endo [2 + 4] π cycloadducts **30a** and **30c**

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(7) The magnitude of the slope, ρ value, is assumed to be an indication of the narrowness of the HOMO–LUMO energy gap. According to MO calculation data shown in Table I, the ρ value of phencyclone **1f** is expected to be the highest. Contrary to the expectation, in the cycloaddition reaction of **1** with electron-rich styrenes **2a–c**, the ρ value of **1f** is smaller than that of **1e**. However, this is accountable for the decrease of the apparent second-order rate constants due to the charge-transfer complexation with donor olefins under measured conditions.[2d]

Table IV. ^{1}H NMR Spectral Data[a] for Cycloadducts 15-33

compd	chemical shifts, δ[b]
15[c]	1.12, 1.32 (t, 6 H, 2 CH_3), 2.96 (dd, 1 H, H_a, $J_{ab} = 8$, $J_{ac} = 8$), 3.24 (dd, 1 H, H_b, $J_{bc} = 8$), 4.24 (dd, 1 H, H_c), 4.16, 4.32 (q, 4 H, 2 CH_2), 7.22, 7.34 (AB q, 4 H, aromatic H), 7.44-7.90 (m, 4 H, aromatic H), 8.32, 8.58 (d, 2 H, aromatic H, $J = 8$)
16[c]	0.44, 1.28 (t, 6 H, 2 CH_3), 3.18 (dd, 1 H, H_a, $J_{ab} = 18$, $J_{ac} = 10$), 3.34 (dd, 1 H, H_b, $J_{bc} = 14$), 3.76, 4.28 (q, 4 H, 2 CH_2), 6.30 (dd, 1 H, H_c), 7.08-8.20 (m, 13 H, aromatic H), 8.65 (d, 1 H, aromatic H, $J = 7.5$)
17[c]	1.43 (t, 6 H, 2 CH_3), 4.52 (q, 4 H, 2 CH_2), 5.34 (s, 2 H, methine H), 7.07-7.92 (m, 10 H, aromatic H), 8.16 (d, 2 H, aromatic H, $J = 8$)
18[c]	1.44 (t, 6 H, 2 CH_3), 4.04 (s, 4 H, methine H), 4.56 (q, 4 H, 2 CH_2), 6.32 (m, 4 H, phenyl H), 6.24-6.40 (m, 4 H, aromatic H), 7.00-7.92 (m, 10 H, aromatic H), 8.82 (d, 2 H, aromatic H, $J = 7$)
19[c]	1.40 (t, 6 H, 2 CH_3), 1.40-1.84 (m, 6 H, methylene H), 2.32 (br s, 2 H, methine H), 3.24 (s 2 H, methine H), 7.40-7.80 (m, 4 H, aromatic H), 8.00 (d, 2 H, aromatic H, $J = 7$)
20[c]	0.74, 1.42 (t, 6 H, 2 CH_3), 1.96 (d, 1 H, H_a, $J_{ac} = 10$), 2.60 (br s, 1 H, H_b), 2.66 (d, 1 H, H_c), 3.72 (m, 1 H, H_d), 3.92, 4.38 (q, 4 H, 2 CH_2), 6.00, 6.44 (dd, 2 H, olefin H, $J = 5.5, 3.5$), 7.32-7.86 (m, 4 H, aromatic H), 8.04, 8.52 (d, 2 H, aromatic H, $J = 8$)
21[c]	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, $J = 7.5$)
22[d]	1.17, 1.41 (t, 6 H, 2 CH_3), 3.75, 4.47 (q, 4 H, 2 CH_2), 4.39 (m, 1 H, H_a, $J_{ab} = 7.5$), 4.82 (d, 1 H, H_b), 5.80 (m, 2 H, H_c, H_d, $J_{cd} = 5.5$), 6.13 (m, 2 H, aromatic H), 6.97 (m, 2 H, aromatic H), 7.20-8.12 (m, 12 H, aromatic H)
24e[d]	3.09 (t, 6 H, 2 CH_3), 4.34 (splitted d, 1 H, H_a, $J_{ab} = 8$), 4.58 (d, 1 H, H_b), 6.24 (dd, 1 H, H_c, $J_{cd} = 6$, $J_{ac} = 3$), 6.67 (dd, 1 H, H_d, $J_{ad} = 1.5$), 6.84-7.60 (m, 20 H, aromatic H)
24f[d]	4.66 (splitted d, 1 H, H_a, $J_{ab} = 7$), 4.83 (d, 1 H, H_b), 5.70 (m, 1 H, H_c, $J_{cd} = 5.5$, $J_{ac} = 2$), 5.74 (m, 1 H, H_d), 6.40-7.88 (m, 26 H, aromatic H), 8.80 (d, 2 H, aromatic H, $J = 8$)
25[e]	0.48, 1.40 (t, 6 H, 2 CH_3), 1.24-1.60 (m, 2 H, methylene H), 2.16-2.56 (m, 2 H, methylene H), 2.22, 3.64 (m, 2 H, methine H), 3.68, 4.36 (q, 4 H, 2 CH_2), 6.08-6.46 (m, 2 H, olefin H), 7.20-7.82 (m, 4 H, aromatic H), 8.02, 8.55 (d, 2 H, aromatic H, $J = 7$)
26[e]	0.64-1.08 (m, 1 H, methylene H), 1.40-1.88 (m, 2 H, methylene H), 2.00-2.36 (m, 1 H, methylene H), 3.44-3.88 (m, 2 H, methine H), 5.52-5.84 (m, 1 H, olefin H), 5.90-6.16 (splitted d, 1 H, olefin H, $J = 10, 2$), 6.80-8.00 (m, 16 H, aromatic H), 8.66 (d, 2 H, aromatic H, $J = 8$)
27[f]	1.30 (t, 6 H, 2 CH_3), 1.47-2.27 (m, 4 H, methylene H), 2.83 (m, 3 H, methylene H, methine H), 4.33 (q, 4 H, 2 CH_2), 4.77-5.17, 5.40-6.00 (m, 2 H, olefin H), 7.17-7.83 (m, 4 H, aromatic H), 8.27, 8.48 (d, 2 H, aromatic H, $J = 6$)
28[f]	1.27 (t, 6 H, 2 CH_3), 1.50-2.45 (m, 8 H, methylene H), 2.57 (br s, 2 H, methine H), 4.37 (q, 4 H, 2 CH_2), 7.17-7.80 (m, 6 H, aromatic H)
29[f]	1.34 (t, 6 H, 2 CH_3), 1.68-2.10 (m, 8 H, methylene H), 2.54 (br s, 4 H, methine H), 4.44 (q, 4 H, 2 CH_2), 7.12-7.84 (m, 6 H, aromatic H)
30a[g]	0.38 (t, 3 H, CH_3), 1.08, 1.42 (t, 6 H, 2 CH_3), 3.44 (q, 2 H, CH_2), 3.58 (dd, 1 H, H_a, $J_{ac} = 8$, $J_{ae} = 8$), 3.84, 4.42 (q, 4 H, 2 CH_2), 4.48, 4.66 (d, 1 H, H_b, $J_{bd} = 7$), 5.54 (dd, 1 H, $J_{cf} = 8$), 5.84 (dd, 1 H, H_d, $J_{de} = 7$), 6.56 (dd, 1 H, H_e), 6.70, 6.82 (d, 1 H, H_f), 7.36-7.84 (m, 4 H, aromatic H), 8.05, 8.62 (d, 2 H, aromatic H, $J = 8$)
30c[g]	0.28, 1.12 (t, 6 H, 2 CH_3), 0.36 (t, 3 H, CH_3), 1.84, 2.54 (q, 4 H, 2 CH_2), 2.96 (dd, 1 H, H_a, $J_{ac} = 8$, $J_{ae} = 8$), 3.44, 3.87 (q, 2 H, CH_2), 4.25, 4.44 (d, 1 H, H_b, $J_{bd} = 8$), 5.28 (dd, 1 H, H_c, $J_{cf} = 8$), 5.76 (dd, 1 H, H_d, $J_{de} = 8$), 6.50 (dd, 1 H, H_e), 6.77, 6.85 (dd, 1 H, H_f), 7.40-7.92 (m, 6 H, aromatic H)
31a[h]	1.28 (t, 6 H, 2 CH_3), 1.44 (m, 1 H, H_a, $J_{ab} = 14$), 1.66 (m, 1 H, H_b, $J_{bc} = 5$), 3.54 (dd, 2 H, H_c, $H_{c'}$, $J_{cd} = 5.5$), 4.28, 4.36 (q, 4 H, 2 CH_2), 6.16 (m, 2 H, H_d, $H_{d'}$), 6.38 (m, 2 H, H_e, $H_{e'}$), 7.20-7.92 (m, 6 H, aromatic H)
31c[h]	0.90 (t, 6 H, 2 CH_3), 1.22 (dd, 1 H, H_a, $J_{ab} = 12$, $J_{ac} = 6$), 1.64 (dd, 1 H, H_b, $J_{bc} = 5$), 2.12 (q, 4 H, 2 CH_2), 2.94 (dd, 2 H, H_c, $H_{c'}$), 6.04 (br s, 4 H, H_d, $H_{d'}$, H_e, $H_{e'}$), 7.40-7.86 (m, 6 H, aromatic H)
33a[h]	0.88, 1.50 (t, 6 H, 2 CH_3), 3.59 (m, 1 H, H_a), 3.75, 4.50 (q, 4 H, 2 CH_2), 4.70 (m, 1 H, H_b), 5.43 (m, 2 H, olefin H), 6.20 (m, 2 H, olefin H), 7.45-8.12 (m, 4 H, aromatic H), 8.56, 8.84 (d, 2 H, aromatic H, $J = 7$)
33c[h]	0.26, 1.12 (t, 6 H, 2 CH_3), 1.88, 2.48 (q, 4 H, 2 CH_2), 2.00 (m, 1 H, H_a), 2.28 (m, 2 H, H_b, H_c), 2.92 (m, 1 H, H_d), 5.46 (m, 2 H, H_e, H_f), 6.12 (m, 2 H, H_g, H_h), 7.40-7.90 (m, 6 H, aromatic H)

[a] Solvent $CDCl_3$. [b] J values are given in hertz. [c] See Chart II for atom labels. [d] See Scheme II for atom labels. [e] See Scheme III for atom labels. [f] See Scheme IV for atom labels. [g] See Scheme V for atom labels. [h] See Scheme VI for atom labels.

Table V. ^{13}C NMR Spectral Data[a] for Cycloadducts of 1a,c with Various Olefins

compd	chemical shifts, δ
15[b]	34.80 (t, C_a), 41.43 (d, C_c), 166.93, 167.11 (s, ester C=O)
20[b]	48.16, 56.60 (d, C_b, C_d), 50.98 (t, C_a), 69.20, 70.61 (s, C_e, $C_{e'}$), 161.89, 169.98 (s, ester C=O), 197.69 (s, C_f)
25[c]	19.28, 23.73 (t, methylene C), 35.33, 42.36 (d, methine C), 63.57, 65.92 (s, C_c, $C_{c'}$), 162.07, 168.63 (s, ester C=O), 199.57 (s, C_d)
28[d]	30.41 (t, methylene C), 39.84, 42.66 (d, methine C), 43.89, 57.48 (s, C_a, $C_{a'}$), 173.78, 174.20 (s, ester C=O)
29[d]	24.67 (t, methylene C), 46.14 (d, methine C), 56.60 (s, C_a, $C_{a'}$)
30a[e]	33.57 (d, C_a), 55.90, 56.48 (d, C_b), 66.09 (s, C_g), 71.84 (s, C_h), 136.87 (s, C_i), 161.77, 167.28 (s, ester C=O), 186.67 (s, C_j), 197.98 (s, enone C=O)
30c[e]	36.80 (d, C_a), 56.54, 57.13 (d, C_b), 64.16 (s, C_g), 66.04 (s, C_h), 139.69 (s, C_i), 172.14 (s, C_j), 211.11 (s, enone C=O)
31a[f]	25.14 (t, C_a), 42.36 (d, C_c, $C_{c'}$), 65.86 (s, C_f, $C_{f'}$), 192.77 (s, bridged C=O)

[a] Solvent $CDCl_3$. [b] See Chart II for atom labels. [c] See Scheme III for atom labels. [d] See Scheme IV for atom labels. [e] See Scheme V for atom labels. [f] See Scheme VI for atom labels.

(Scheme V and Table III). In the ^{1}H NMR spectra of **30a** and **30c**, the methyl and methylene signals of the ethoxycarbonyl group were complex bands owing to restricted rotation about the N—C=O bond of the urethane group. The signals of the methine protons adjacent to the nitrogen atom (H_b and H_f) were split (Tables IV and V), indicating

Table VI. Calculated Coefficients of 1,3,5-Cycloheptatriene 14 by the CNDO/2 MO Method[a]

	position					
	1	2	3	4	5	6
LUMO	0.29	−0.22	−0.45	0.45	0.22	−0.29
HOMO	0.37	0.24	−0.39	−0.39	0.24	0.37

[a] Reference 10.

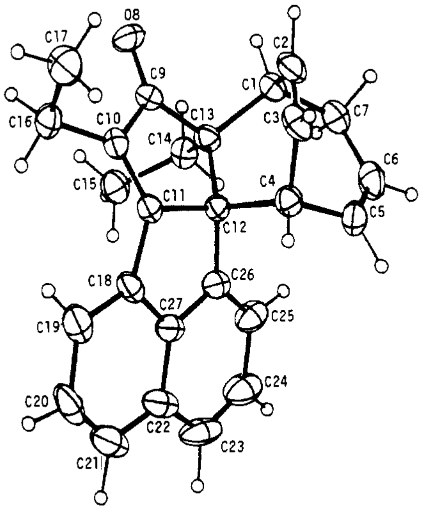

Figure 2. ORTEP diagram of **33c** to indicate the numbering sequence used in this paper for the 27 independent non-hydrogen atoms.

nonequivalence resulting from the partial-bond character of the N–C bond.

Reactions of **1a** and **1c** with **14** gave the exo [4 + 6] π adducts **31a** and **31c**, as well as the rearrangement products **33a** and **33c** from the endo [4 + 2] π adducts **32a** and **32c** (Scheme VI and Table III). The IR spectrum of **31a** showed a carbonyl band at 1780 cm^{-1}, suggesting the presence of a bridged carbonyl group. The ^{13}C NMR spectrum of **31a** (δ 25.14, 42.36, and 65.86) suggested a symmetrical structure, as did the ^1H NMR spectrum. The ^1H NMR spectra of **33** were difficult to analyze because of the large number of overlapping resonances. The first-order rate constant for the Cope rearrangement was 1.24×10^{-4} s^{-1}. Cycloadditions of **1e** and **1f** with **14** at 80 °C gave no rearrangement products.[8,9]

Inspection of the HOMO coefficients of **14** suggests that the initial cycloaddition gives exo [4 + 6] π adduct **31** and endo [4 + 2] π adduct **34** and that **34** subsequently undergoes Cope rearrangement to anti-endo [2 + 4] π adduct **35** (Table VI).[11]

Molecular Structure of 33c. In order to elucidate the structure of **33** and to confirm the reaction pathway proposed, we carried out a crystallographic analysis; the X-ray study was done on **33c** because well-formed crystals of **33a** could not be obtained. An ORTEP diagram[13] of **33c** is shown in Figure 2, giving the numbering sequence used in this section; each atom is represented as an ellipsoid with 20% probability. The X-ray data confirm the syn-endo [2 + 4] π structure with a syn orientation of the carbonyl group to the methylene group. The ring system is moderately strained: interbond angles at the sp^2 carbons (C_1–C_2–C_3, 117.7°; C_4–C_5–C_6, 124.0°; C_5–C_6–C_7, 127.2°) deviate by 2.3, 4.0, and 7.2°, respectively, from the unstrained angles of 120°. The sp^3 carbons show similar deviations from the tetrahedral angle of 109.5°. The C_4–C_{12}, C_1–C_{13}, and C_{12}–C_{13} bond lengths of 1.59, 1.57, and 1.57 Å are longer than the usual value of 1.54 Å.

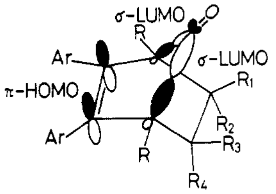

Figure 3. Three-system interactions for decarbonylation reaction.

To clarify the origin of the bond lengthening, empirical force-field (molecular mechanics) calculations were carried out by Allinger's MMI/MMPI force-field method,[14] but the calculations did not reproduce these values (C_4–C_{12}, 1.54 Å; C_1–C_{13}, 1.54 Å; C_{12}–C_{13}, 1.55 Å), indicating that steric repulsions were not responsible for the bond lengthening. These long bond distances might be caused by "through-bond" interaction between π systems.[1c,15]

The C_6–C_7 (C_{sp^2}–C_{sp^3}) length of 1.472 Å is 0.035 Å shorter than the calculated value of 1.507 Å, a difference four times the estimated standard deviation of the X-ray measurement. The most likely explanation is that the expansion of the C_1–C_7–C_6 (117.3°) and C_5–C_6–C_7 (127.2°) angles, which deviate from the normal values of 109.5 and 120°, respectively, causes a rehybridization of C_6 and C_7.[15b]

The upfield shift of the methyl protons (3 H_{15}) at δ 0.26 in the ^1H NMR spectrum of **33c** (Figure 2) can be explained by the anisotropic ring-current effect of the naphthalene system. The displacements of the hydrogen atoms attached to C_{15} from the plane of the naphthalene ring are 2.6, 3.4, and 3.8 Å, respectively. The conjugated enone system is nonplanar with a single-bond length (C_{11}–C_{18}) between the naphthalene and enone groups of 1.474 Å, and O_8, C_9, C_{10}, and C_{11} deviating by 0.16, 0.77, 1.15, and 1.81 Å, respectively, from the plane of the naphthalene ring.

These results provide strong evidence for the suggested pathway[16] for formation of the syn-endo [2 + 4] π adduct **33a** and rule out the possibility of a pathway via endo [4 + 2] π adduct **34a**, which occurs with azepine **13a**.[1a]

Discussion

The high reactivity of **1a** as a 4π acceptor in reactions with olefins derives from its low-lying LUMO and the effective secondary orbital interaction caused by the pla-

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[8] Sasaki, T.; Kanematsu, K.; Iizuka, K. *J. Org. Chem.* **1976**, *41*, 1105–1112.

[9] In the cycloaddition reaction of **1e** with cycloheptatriene **14** at 80 °C, exo [4 + 6] π adduct and endo [4 + 2] π adduct were obtained.[2c]

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[11] The FMO prediction is incompatible with the X-ray result. This might be interpreted by the sterically favorable secondary orbital interaction with the hyperconjugating methylene group of **14** resulting from the π-symmetry combinations of localized σ and σ^* CH bonds.[12] The CNDO/2 MO calculation of **14** reveals that the HOMO coefficient of the methylene proton (0.28) is large enough to stabilize the secondary orbital interaction.

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[16] Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4143–4145. On the basis of spectroscopic evidence, Houk et al. reported that in the cycloaddition reaction of 2,5-dimethyl-3,4-diphenylcyclopentadienone with **14**, a syn-type product, like **33**, was formed from an endo [4 + 2] π adduct, like **32**, via Cope rearrangement.

Scheme VI

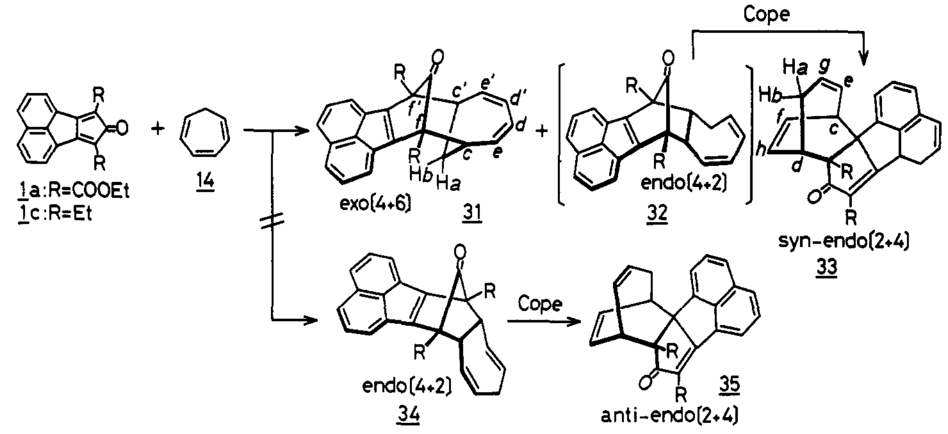

Chart III

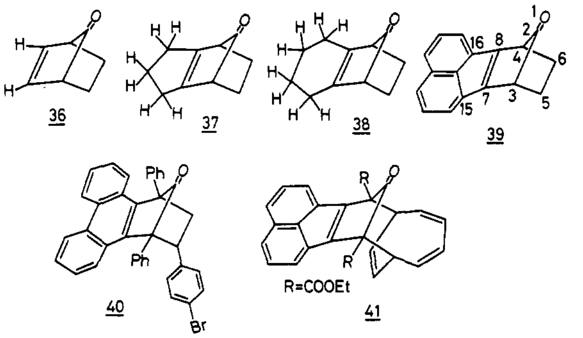

Table VII. Calculated and Observed Geometries and Strain Energies of the Bicyclo[2.2.1]hepten-7-one System

	36	37	38	39[a]	40	41
bond distance of C_7-C_8,[b] Å	1.341	1.334	1.338	1.335	1.366	1.347
bond angle, C_3-C_2-C_4	98.5	99.8	99.2	100.7	99.2	107.2
bond angle, C_3-C_7-C_{15}	125.4	137.0	126.1	140.4	128.3	136.9
strain energy,[c] kcal/mol	24	30	25	33		
method	MMI	MMI	MMI	MMPI	X-ray[d]	X-ray[e]

[a] The calculated geometry of 37 by the MMPI method was grossly consistent with the geometry expected from the X-ray results of 40[2a] and 41.[2c] [b] See Chart III for atom labels. [c] The calculated total strain energies of 36–38 by the MMI method are 23.7, 34.6, and 25.6 kcal/mol, respectively. The strain energies of the norbornen-7-one skeletons of 37–39 were simply estimated by adding the sum of the difference of the bending energies around the C_7–C_8 double bond between the molecule in question and the ring to be condensed to the total strain energy of 36. [d] See ref 2a. [e] See ref 2c.

Table VIII. Second-Order Rate Constants[a] for Cycloaddition of Cyclopentadienones[b] (1a,e,f) with *N*-Vinylcarbazole[c] 3 at 34.1 °C in Various Solvents

solvent	E_T, kcal/mol	1a	1e	1f
benzene	34.5	7.56		2.67
chlorobenzene	37.5	6.41	5.19	2.39
chloroform	39.1	13.1	6.21	2.57
benzonitrile	42.0	10.1		3.71
dimethylformamide	43.8	17.7		5.95
acetonitrile	46.0	44.4		

[a] M^{-1} s^{-1} × 10^4. [b] 1 × 10^{-3} M. [c] 1 × 10^{-1} M.

narity of its ring system. The facile decarbonylation of the primary [4 + 2] π adducts presents a striking contrast to the adducts formed in cycloaddition reactions of other cyclopentadienones, such as **1e** and **1f**. Decarbonylation of bicyclo[2.2.1]hepten-7-ones is generally of consequence only above 150 °C,[17] except for *endo*-cyclopropane derivatives, which involves scission of a bent σ bond.[18] The activation energy for decarbonylation of the endo adduct of cyclopentadienone and norbornene is 28 kcal mol^{-1}.[19] Decarbonylation is thought to be accelerated by favorable donor–acceptor interaction. The FMO view on this rate enhancement is that the interactions of the LUMO of the ketonic bridged σ bonds with the HOMO of the double bond are assisted by the electronegative alkoxycarbonyl group, as shown in Figure 3.[4] The most likely explanation for the decarbonylation in the formation of **23** from **1a** and **9** (Scheme II) is that silica gel acts as a weak acid that is not so acidic that a proton is transferred to the substrate, but that is able to from a hydrogen bond with it, resulting in a decreased electron density at the carbonyl carbon. Such a carbonyl group should act as a strong acceptor, allowing favorable HOMO–LUMO interactions.

The high rate of decarbonylation we observe[20] cannot be accounted for solely by FMO interactions. An important factor appears to be strain release in the bicyclo[2.2.1]hepten-7-one system of the primary adduct. The molecular mechanics calculation for **39** (Chart III) reveals that the calculated geometry is grossly consistent with the one deduced from the X-ray results.[2a,c] Inspection of these data, together with the MMI data for the related model compounds, indicates that the fusion of the acenaphthylene ring to the bicyclo[2.2.1]hepten-7-one system causes a considerable increase in the strain energy, derived from distortion of the external C_3–C_7–C_{15} angle, which is expanded to about 140° from the normal value of 125° (Table VII). The strain energy of **39** is estimated to be about 30 kcal mol^{-1}, sufficient to induce decarbonylation.[19] The increase in steric congestion around the bridged carbonyl group by attachment of two ethoxycarbonyl groups at the 3,4-positions of **39** might lead to a high rate of decarbonylation owing to F strain.[1c]

We believe that the facile decarbonylation of the endo [4 + 2] π adduct is related to the high strain in the bicy-

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[20] The decarbonylation rate of the endo [4 + 2] π adduct of **1a** and *n*-butyl vinyl ether (k_1 = 2.24 × 10^{-5} s^{-1} at 34.1 °C) is comparable to the decarbonylation rate[17] (k_1 = 1.19 × 10^{-5} s^{-1} at 150 °C) for the analogous cycloadduct of tetracyclone and ethylene.

clo[2.2.1]hepten-7-one system and to the favorable donor–acceptor interactions. The [3,3] sigmatropic rearrangement of the endo [4 + 2] π adducts is also considered to be affected by strain. These adducts could not be isolated even under mild reaction conditions, except for **22**. The large rate constant for the rearrangement of adduct **32** to the syn-endo [2 + 4] π adduct **33** (Scheme VI) supports the involvement of strain release.

In the cycloaddition reaction of **1a** with **3**, we could not observe a decrease in the second-order rate constant (k_2) with an increase in the dienophile concentration responsible for charge-transfer complexation,[2d] but we did observe a considerable solvent effect for a concerted cycloaddition (Table VIII). If a zwitterion was formed as a reaction intermediate, a much larger rate increase would have been seen in going from a nonpolar to a polar reaction medium. The small influence of solvent polarity on the rate leads us to conclude that the reaction follows, at least in part, a concerted course involving an unsymmetrical, charge-separated transition state.

The only endo [4 + 2] π adduct we were able to isolate (**22**) easily underwent reversion to starting materials on heating in benzene at 80 °C and did not undergo Cope rearrangement and decarbonylation. The absence of Cope rearrangement is attributed to interference of the orbital interaction necessary for this rearrangement with steric repulsion between the two phenyl groups and the acenaphthylene system. The lack of decarbonylation results from an unfavorable orbital interaction between the LUMO of the ketonic bridged σ bond and the HOMO of the double bond. The orbital symmetry of the latter is altered by through-bond interaction, which may elongate the newly formed σ bonds in the cycloaddition, leading to the retro-Diels–Alder reaction.

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were taken with a JASCO IR A-1 grating spectrophotometer. The ^{1}H NMR spectra were taken with a JEOL PS-100 instrument for solutions in deuteriochloroform with Me_4Si 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 Me_4Si. Mass spectra were obtained with a JEOL JMS-O1SG 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. All new products gave correct elemental analyses. Thin-layer chromatographic analyses were performed with a Iatroscan TH-10 analyzer with a flame-ionization detector. A Hitachi EPS-3T spectrophotometer was used to measure the rates of addition or decarbonylation. All the calculations were performed on the FACOM M-190 and M-200 computers in the computer center of Kyushu University.

Cyclopentadienones. 2-Oxo-1,3-disubstituted-2*H*-cyclopenta[*i*]acenaphthylene (**1a** and **1c**),[3a] 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1e**),[21] and phencyclone (**1f**)[22] were prepared according to the established methods. Compounds **1b** and **1d** are model compounds for MO calculations. We attempted to prepare phencyclone derivative (**1g**) according to the same method as phencyclone (**1f**),[22] but we could not obtain **1g** as monomer because it was a nondissociating dimer.

1g: mp >300 °C; yield 38%; IR (Nujol) 1795 (bridged C=O), 1740, 1760 (ester C=O), 1720 (enone C=O) cm^{-1}; mass spectrum, *m/e* 692 (M$^+$).

Materials. Compounds **2e–7**, **9**, **10** (Nakarai Chemicals Co.), **11**, **12** (Wako Pure Chemical Industries Co.), and **14** (Tokyo Kasei Organic Chemicals Co.) were used after distillation and after recrystallization. Compounds **5**,[23] **8**,[24] and **13**[25] were prepared according to the reported methods.

Cycloaddition Reactions of 1a with Various Olefins. General Procedure of Cycloaddition. A solution of **1a** and an excess amount of dienophile was stirred at a given temperature until the deep violet color had faded away. The mixture was diluted with methanol, and the precipitated solid was filtered off and purified by recrystallization. In the cycloadditions of **1a** with cycloheptatriene **14** and *N*-(ethoxycarbonyl)azepine **13a**, the products were purified by chromatography on silica gel with *n*-hexane–benzene. When acecyclone derivative **1c** was allowed to react with olefins, a more severe reaction condition was necessary for dissociation. In such a case, the reaction was carried out in refluxing benzene. The results are summarized in Tables III–V.

In the cycloaddition reaction of **1a** with diphenylfulvene **9**, the presence of silica gel in the reaction mixture brought about the decarbonylation to give the decarbonylated 1:1 adduct **23** and unidentified red pigment. Compound **23** was obtained as a yellow powder: mp 189–190.5 °C; IR (Nujol) 1732, 1714 (ester C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 and 1.43 (t, 6 H, 2 CH_3), 3.73 and 4.48 (q, 4 H, 2 CH_2), 4.35 (splitted d, 1 H, J_{ab} = 8.5 Hz, J_{ac} = 2 Hz, J_{ad} = 3 Hz), 5.09 (d, 1 H, H_b), 6.08 (dd, 1 H, H_c, J_{cd} = 6 Hz), 6.59 (dd, 1 H, H_d), 7.20–7.79 (m, 15 H, aromatic H), 8.62 (d, 1 H, aromatic H, J = 8 Hz).

Rates of Cycloaddtion of 1a to Para-Substituted Styrenes 2a–h. The para-substituted styrenes were prepared as previously described.[2a] A chlorobenzene solution (4 mL) containing **1a** (1×10^{-3} M) and styrene (1×10^{-1} M) was prepared. We maintained pseudo-first-order conditions by using a 100:1 ratio of styrene to **1a** in chlorobenzene solvent. We followed the rate at a given temperature by the loss of the long-wavelength absorbance of the chromophore of **1a** in the visible spectrum at 530 nm by using a 10 × 10 mm quartz cell, which was sealed with a ground glass stopper and thermostated with flowing water at constant temperature with a Yamato Model BH-41 constant bath equipped with a circulating water pump. The data are summarized in Table II.

Decarbonylation Rate of the Endo [4 + 2] π Cycloadduct of 1a and *n*-Butyl Vinyl Ether. The rate study was carried out by the method as described above with a large excess of dienophile in chlorobenzene. After the disappearance of the long-wavelength absorption of **1a** due to completion of the cycloaddition, the increase of the dihydrofluoranthene absorption at 400 nm was followed. Calculations made in the usual way gave a first-order rate constant (k_1) of 2.24×10^{-5} s^{-1} at 34.1 °C.

Rearrangement Rate of the Endo [4 + 2] π Cycloadduct of 1a and Cycloheptatriene 14. A mixture containing 0.1 g of **1a** and 1 mL of cycloheptatriene **14** in 3 mL of chloroform was allowed to stand at room temperature for 12 h. The solvent was removed under vacuum without heating, and the residue was taken up in ethanol. We followed the UV spectral change of the extract at 47.8 °C by measuring the increase of the absorbance at 340 nm due to an enone moiety to give a first-order-rate constant (k_1) of 1.24×10^{-4} s^{-1}.

X-ray Crystallographic Study of Syn-Endo [2 + 4] π Cycloadduct 33c. Suitable single crystals of **33c** were obtained by slow crystallization from a benzene–ethanol solution. A crystal of the compound **33c** with approximate dimensions of 0.45 × 0.3 × 0.3 mm was mounted on a glass fiber with epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis.

We determined unit cell parameters and the orientation matrix on a Syntex $P\bar{1}$ four-circle diffractometer equipped with a graphite monochromator and using Mo $K\alpha$ radiation.

Fifteen reflections were used in the least-squares refinement of the lattice parameters and orientation matrix. The cell parameters obtained were a = 15.345 (4), b = 11.646 (3), c = 10.626 (7) Å, β = 92.979 (4)°, and V = 1896 (1) Å^3. The calculated density of 1.543 g cm^{-3} for four formula units per cell agrees with the experimental density of 1.532 g cm^{-3} measured by the flotation

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method with a mixture of H_2O and KI. Systematic absences for the $h0l$ reflections with $h = 2n + 1$ and for the $0k0$ reflections with $k = 2n + 1$ are consistent with the space group $P2_1/a$.

Intensity data were collected by θ–2θ scans to a limit of $2\theta = 50°$ with X-ray source and monochrometor settings identical with those used for determination of the unit cell parameters. A variable scan rate from 24.0 to 4.0 min^{-1} was used. Three reflections monitored at regular intervals during the data collection showed no significant variation in intensity.

Of 3429 independent reflections, 1497 were treated as observed $[I > 2.3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption. Observed structure factors were converted into normalized structure factor amplitude, $|E|$ values, by use of the scale factor and overall temperature factor obtained from Wilson's statistics.[26] The structure was solved by the direct method by use of the MULTAN[27] program. An E map calculated with 258 signed E's ($|E| \geq 1.7$), which gave a figure of merit of 1.150, revealed the positions of all the non-hydrogen atoms. Nine cycles of block-diagonal least-squares of minimizing of $\sum(|F_o| - k|F_c|)^2$ by varying the positions and anisotropic vibrational amplitudes of the non-hydrogen atoms led to $R = 0.10$.

A difference Fourier map calculated at this stage revealed peaks of density appropriate to all hydrogen atoms. After adding the hydrogens and refining the values with anisotropic U's for non-hydrogen atoms and isotropic U's for hydrogen atoms, we obtained a final R of 0.051. In final refinements the following weights were used for the observed reflections: $w = 1.0$ for $F_o < 40.0$, $w = 1600/F_o^2$ for $F_o \geq 40.0$. The atomic scattering factors were taken from the literature.[28]

All the calculations were carried out with the Universal Crystallographic Computation Program System (UNICS II).[29]

Method of Molecular Orbital (MO) and Empirical Force-Field Calculations. The MO calculations were carried out by the CNDO/2 MO method.[10] Values for atomic distances and bond angles in **1b** and **1d** were taken from the X-ray results of the syn-endo [2 + 4] π cycloadduct **33c** of **1c** and cycloheptatriene **14**. In **1b**, the 1- and 3-methoxycarbonyl substituents were rotated by 60°[1a] out of the plane of cyclopentadienone.

The geometry of cycloheptatriene **14** was assumed to be in the tub conformation, and distances and angles were taken from the electron diffraction results.[30] The calculated coefficients of 1,3,5-cycloheptatriene **14** are listed in Table VI.

The empirical force-field calculations were carried out with Allinger's MMI/MMPI force-field method.[14]

Computer programs (CNDO/2 MO and MMI/MMPI) were locally modified for use on a FACOM M-200 computer and for damped SCF calculation.

Acknowledgment. The authors are grateful to Professor E. Ōsawa (Faculty of Science, Hokkaido University) for providing his modified version of the force-field program (MMI/MMPI) for use on a HITAC-100H. We also thank Y. Tahara for experimental assistance with the reaction of **1c** with cycloheptatriene and *N*-(ethoxycarbonyl)azepine.

Registry No. **1a**, 57830-24-7; **1e**, 16691-79-5; **1f**, 5660-91-3; **2a**, 2039-80-7; **2b**, 637-69-4; **2c**, 622-97-9; **2d**, 100-42-5; **2e**, 1073-67-2; **2f**, 2039-82-9; **2g**, 3435-51-6; **2h**, 100-13-0; **3**, 1484-13-5; **4**, 208-96-8; **5**, 941-69-5; **6**, 498-66-8; **7**, 121-46-0; **8**, 573-57-9; **9**, 2175-90-8; **10**, 592-57-4; **11**, 592-42-7; **12**, 111-78-4; **13a**, 2955-79-5; **14**, 544-25-2; **15**, 82469-18-9; **16**, 82482-29-9; **17**, 82482-30-2; 18, 82469-19-0; **19**, 82469-20-3; **20**, 82469-21-4; 21, 20852-12-4; **22**, 82469-22-5; **24e**, 82469-23-6; **24f**, 82469-24-7; **25**, 82469-25-8; **26**, 82469-26-9; **27**, 82469-27-0; **28**, 82469-28-1; **29**, 82469-29-2; **30a**, 82469-30-5; **30c**, 82482-31-3; **31a**, 82469-31-6; **31c**, 82469-32-7; **33a**, 82469-33-8; **33c**, 82469-34-9; **36**, 694-71-3; **37**, 82469-35-0; **38**, 82469-36-1; **39**, 82469-37-2; **40**, 62336-07-6; 41, 78512-92-2.

Supplementary Material Available: Tables of bond lengths (Table IX), bond angles (Table X), anisotropic thermal parameters for the nonhydrogen atoms (Table XI), coordinates for hydrogen atoms (Table XII), and elementary analyses of **15**–**33** (Table XIII) (5 pages). Ordering information is given on any current masthead page.

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Effect of Ring Size and Methyl Substituents on LiBr-Catalyzed Rearrangements of Aryloxiranes

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Received March 2, 1982

A series of indene 2,3-oxides and 3,4-dihydronaphthalene 1,2-oxides with methyl substituents on the oxirane ring was prepared, and the lithium bromide/acetonitrile catalyzed isomerization of these compounds to the corresponding 2-keto derivatives was examined. The presence of methyl substituents on the oxirane ring at the α carbon greatly enhanced the reactivity of the oxiranes relative to that of the unsubstituted compounds, while the presence of substituents at the β carbon reduced their reactivity. The effect of ring size was examined via a competition experiment involving indene 2,3-oxide and 3,4-dihydronaphthalene 1,2-oxide. The results of these studies suggest that the reagent can be used for selective transformations of aryloxiranes.

Studies by several groups[1] have established that the metabolism of a variety of carcinogenic aromatic hydrocarbons results in the formation of highly reactive diol epoxides, which have been shown to be strongly mutagenic, cytotoxic, and tumorigenic.[2] The powerful biological activity of these compounds has prompted several studies of the stereoelectronic factors that influence the solvolysis

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