

Frontier-controlled Cycloaddition Reactions of Cyclopentadienones having Electron-donating or -attracting Substituents: Configuration of Adducts and Kinetic Studies

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The stereochemistry of the main adducts resulting from the cycloadditions of 2,5-dimethoxycarbonyl- and 2,5-diethyl-3,4-diphenylcyclopentadienones [CPC (1a) and EPC (1b)] with *para*-substituted styrenes (2a–h), norbornadiene (7), norbornene (8), 1,4-dihydro-1,4-epoxynaphthalene (9), maleic anhydride (10), and *N*-phenylmaleimide (11), was established as having the *endo* configuration. In order to define the substituent effects on the rate of the Diels–Alder reaction, a kinetic study of the reactivities of (1a, b) with a series of styrenes (2a–h) was carried out. The $\log k/k_H$ values for the cycloadditions of (1a) with (2a–h) were correlated with Okamoto–Brown's σ_p^+ constants and the ρ value was -0.941 . This result suggests that the cycloaddition is classified as a Diels–Alder reaction with inverse electron demand. By contrast, in the correlation for the cycloaddition of (1b) with (2a–h), two lines with markedly different slopes were observed, which can be ascribed to a Diels–Alder reaction with neutral electron demand. The initial cycloadditions of (1a) and (1b) with tropone (29) gave the [4 + 6] π adducts (32a, b). Subsequently the adduct (32b) underwent oxy-Cope rearrangement to (35). The cycloadditions of (1a) and (1b) with 2-chlorotropone also gave oxy-Cope-type rearrangement products (34a, b).

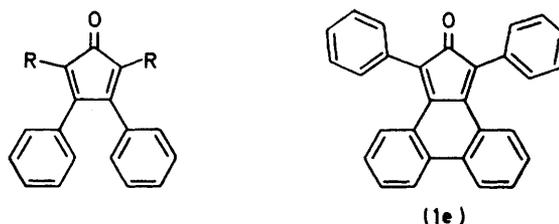
ALTHOUGH the Diels–Alder reaction is one of the best-known reactions and has been the subject of numerous studies,¹ a fundamental understanding of the reactivity, regioselectivity, and periselectivity has only recently been developed.² According to a first approximation of the perturbation theory proposed by Sustmann,³ the dominant role in determining reactivity,⁴ regioselectivity, and periselectivity is believed to be played by the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). It is known that the energy levels of frontier orbitals obey the function of the electronic characters of the substituents,⁵ namely, electron-attracting substituents will lower and electron-donating substituents will raise the energy of HOMOs and LUMOs.³ In this connection, cyclopentadienone derivatives are good diene components for studying the Diels–Alder reaction because of their high reactivity.^{6,7,8,9} To the best of our knowledge, few kinetic studies on cycloadditions of cyclopentadienones having electron-attracting substituents have been reported.[†]

In this paper, we discuss the kinetic data for the cycloaddition reactions of 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone¹¹ (CPC) (1a), having electron-attracting substituents, and 2,5-diethyl-3,4-diphenylcyclopentadienone⁷ (EPC) (1b), as a diene having the opposite electronic character, with some dienophiles.

Theoretical Expectations.—Semi-empirical Pariser, Parr, and Pople SCF molecular-orbital calculations¹² as shown in Table I predict that the energy separations between the LUMO of CPC (1a) and the HOMO of a series of *para*-substituted styrenes (2a–h) are considerably smaller than the energy separations between the HOMO of CPC (1a) and the LUMO of the dienophiles

† Another cyclopentadienone reported having electron-attracting substituents is 2,3,4,5-tetra(trifluoromethyl)cyclopentadienone,¹⁰ which reacts with various dienophiles in an inverse-type Diels–Alder reaction.

(2a–h), and that both energy levels[‡] of the HOMO and the LUMO of EPC (1b) are considerably higher than



- (1) a, R = CO₂Me (CPC)
 b, R = Et (EPC)
 c, R = Me (MPC)
 d, R = Ph

that of CPC (1a). Consequently, it is expected that CPC (1a) acts probably as an electron-deficient diene and reacts preferentially with more electron-rich dienophiles

TABLE I

Frontier orbital energies (eV) for CPC (1a), MPC (1c), and a series of *para*-substituted styrenes (2a–h) calculated by the semi-empirical P.P.P. SCF MO method

Compound	E_{HOMO}	E_{LUMO}
(1a)	-11.215	-3.368
(1c)	-10.301	-2.709
(2a)	-9.213	-0.489
(2b)	-9.879	-0.461
(2c)	-10.360	-0.823
(2d)	-10.530	-0.660
(2e)	-10.058	-0.451
(2f)	-9.680	-0.310
(2g)	-10.682	-1.317
(2h)	-11.581	-2.303

in inverse Diels–Alder reactions. Though the cycloadditions of EPC (1b) with several electron-rich dienophiles (*p*-dimethylaminostyrene, *etc.*) are expected to

‡ The frontier-orbital energy levels for EPC (1b) were tentatively assigned by use of the calculated values for 2,5-dimethyl-3,4-diphenylcyclopentadienone (MPC) (1c).

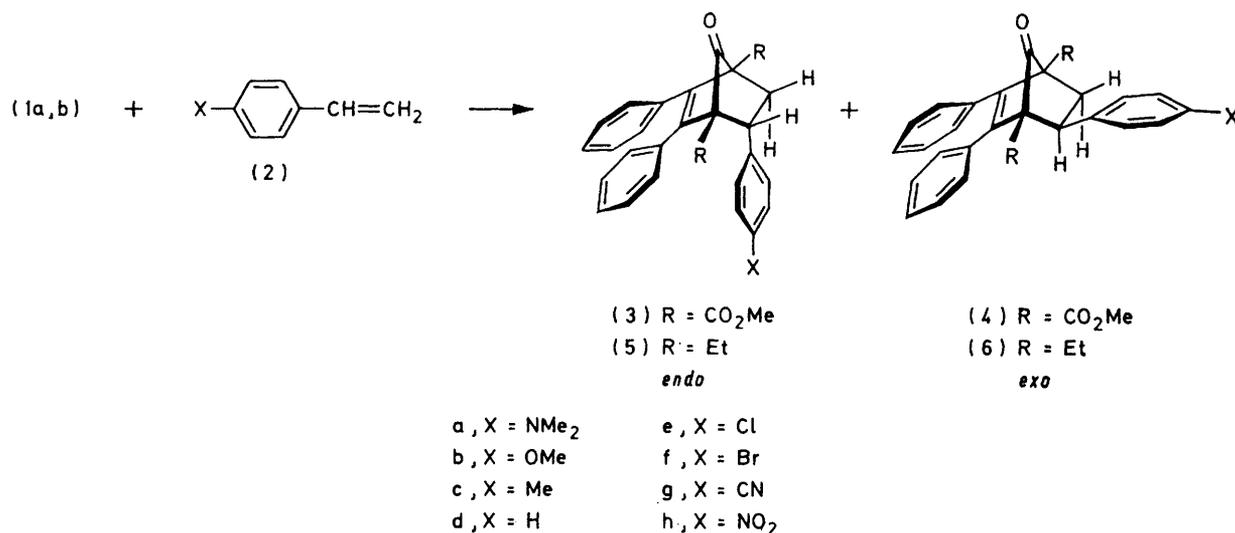
react in the inverse type, the cycloadditions of EPC (1b) with most of the dienophiles are expected to react in the neutral type because of the relative frontier-energy levels of EPC (1b) and the *para*-substituted styrenes (2a—h).

RESULTS AND DISCUSSION

Ratios of endo : exo in the Cycloadditions of CPC (1a) with a Series of para-Substituted Styrenes (2a—h).—Cycloadditions of CPC (1a) with (2a—h) in benzene gave a mixture of *endo*- (3a—h) and *exo*-adducts (4a—h) in high yields. The n.m.r. spectra of the crude products showed signals arising from both the *endo*- and the *exo*-adducts. As a typical example, the methyl ester resonances of the adduct of CPC (1a) with *p*-bromostyrene

of *endo*- (3f) and *exo*-adducts (4f) in a ratio of *ca.* 84 : 16. The adducts were separated by fractional recrystallization. The i.r. spectrum of (3f) exhibited, in addition to an ester carbonyl absorption at 1740 cm⁻¹, an absorption at 1800 cm⁻¹ characteristic of a strained carbonyl group. Furthermore, as shown in Table 3, the n.m.r. resonances of the five protons of the CPC phenyl group experienced an upfield shift: δ 6.18—6.40 (2 H, m), 6.78—7.04 (3 H, m). Molecular models indicate that the five aromatic protons of the phenyl group on the CPC moiety will lie in the shielding zone of an *endo-p*-bromophenyl group. From these data, the major [4 + 2] π adduct (3f) was assigned the *endo*-configuration.

On the other hand, the mass spectrum of the minor adduct (4f) showed a characteristic molecular ion at



SCHEME 1

(2f), which appear at δ 3.41 and 3.71 for the *endo*-adduct (3f) and at δ 3.30 and 3.60 for the *exo*-adduct (4f), are especially noteworthy, since integration of the methyl ester resonances for a series of adducts was used to determine the ratios of *endo*- to *exo*-adducts^{13,14,15} (Table 2).

TABLE 2

Ratios of *endo*- to *exo*-adducts and total yields for cycloadditions of CPC (1a) with *para*-substituted styrenes (2a—h)

X	Adducts	Total yield (%) of adducts	Ratio (<i>endo</i> / <i>exo</i>)
NMe ₂	(3a) and (4a)	84	6.69
OMe	(3b) and (4b)	82	7.33
Me	(3c) and (4c)	84	8.09
H	(3d) and (4d)	94	7.33
Cl	(3e) and (4e)	87	5.25
Br	(3f) and (4f)	94	5.25
CN	(3g) and (4g)	88	5.25
NO ₂	(3h) and (4h)	85	2.57

Cycloaddition of CPC (1a) with p-Bromostyrene (2f).—The cycloaddition of CPC (1a) with (2f) gave a mixture

m/e 531, suggesting also a 1 : 1 adduct. In the n.m.r. spectrum of (4f), the resonances of the aromatic protons appeared as multiplets between δ 6.9 and 7.5, and an upfield shift due to an anisotropic effect was not observed. Accordingly, the adduct (4f) was assigned the *exo*-configuration. The similarity of the n.m.r. spectral patterns of the series of adducts (3a—h) indicates that they all have the *endo*-configuration of (3a—h). The n.m.r. spectral data and the physical, analytical, and i.r. spectral data for these adducts are summarized in Tables 3 and 4, respectively.

Cycloaddition of EPC (1b) with p-Bromostyrene (2f).—Although cycloaddition of EPC with (2f) gave a mixture of *endo*- (5f) and *exo*-adducts (6f), only one isomer (5f) was isolated by recrystallization from the crude adduct. The i.r. spectrum of (5f) showed a carbonyl stretching absorption at 1757 cm⁻¹, and a [4 + 2] π adduct was anticipated because the carbonyl stretching absorption was in accord with that of the [4 + 2] π adduct of 2,5-dimethyl-3,4-diphenylcyclopentadienone (1c) with fulvene.¹⁶ The pattern of the aromatic region in the n.m.r. spectrum of (5f) was very similar to that of (3f). This fact may be explained by considering the adduct to

TABLE 3
I.r. ^a and ¹H n.m.r. spectra ^b of *endo*-adducts (3a—h)

Adduct	Substituent (X)	$\nu_{\max.}/\text{cm}^{-1}$	Chemical shift (δ)
(3a)	NMe ₂	1 800, 1 745	2.34 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 2.94 (6 H, s), 3.00 (1 H, dd, <i>J</i> 10.1, 13.5 Hz), 3.46 (3 H, s), 3.70 (3 H, s), 4.26 (1 H, dd, <i>J</i> 10.1, 6.4 Hz), 6.25—6.42 (2 H, m), 6.62—6.96 (3 H, m), 7.20—7.52 (9 H, m)
(3b)	OMe	1 795, 1 745	2.34 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.00 (1 H, dd, <i>J</i> 10.1, 13.5 Hz), 3.46 (3 H, s), 3.70 (3 H, s), 3.78 (3 H, s), 4.27 (1 H, dd, <i>J</i> 10.1, 6.4 Hz), 6.20—6.40 (2 H, m), 6.80—6.96 (3 H, m), 7.16—7.50 (9 H, m)
(3c)	Me	1 790, 1 740	2.34 (3 H, s), 2.41 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.01 (1 H, dd, <i>J</i> 10.1, 13.1 Hz), 3.47 (3 H, s), 3.72 (3 H, s), 4.32 (1 H, dd, <i>J</i> 10.1, 6.4 Hz), 6.18—6.36 (2 H, m), 6.72—7.00 (3 H, m), 7.03—7.60 (9 H, m)
(3d)	H	1 800, 1 735	2.43 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.03 (1 H, dd, <i>J</i> 10.1, 13.5 Hz), 3.48 (3 H, s), 3.72 (3 H, s), 4.36 (1 H, dd, <i>J</i> 10.1, 6.4 Hz), 6.16—6.34 (2 H, m), 6.72—7.02 (3 H, m), 7.18—7.62 (10 H, m)
(3e)	Cl	1 820, 1 740	2.36 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.05 (1 H, dd, <i>J</i> 10.5, 13.5 Hz), 3.50 (3 H, s), 3.74 (3 H, s), 4.32 (1 H, dd, <i>J</i> 10.5, 6.4 Hz), 6.21—6.41 (2 H, m), 6.80—7.08 (3 H, m), 7.20—7.60 (9 H, m)
(3f)	Br	1 800, 1 740	2.32 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.02 (1 H, dd, <i>J</i> 10.5, 13.5 Hz), 3.47 (3 H, s), 3.71 (3 H, s), 4.29 (1 H, dd, <i>J</i> 10.5, 6.4 Hz), 6.18—6.40 (2 H, m), 6.78—7.04 (3 H, m), 7.18—7.56 (9 H, m)
(3g)	CN	1 795, 1 735	2.36 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.10 (1 H, dd, <i>J</i> 10.5, 13.5 Hz), 3.50 (3 H, s), 3.72 (3 H, s), 4.37 (1 H, dd, <i>J</i> 10.5, 6.4 Hz), 6.20—6.30 (2 H, m), 6.78—7.16 (3 H, m), 7.48—7.84 (4 H, m)
(4h)	NO ₂	1 800, 1 740	2.40 (1 H, dd, <i>J</i> 6.4, 13.5 Hz), 3.10 (1 H, dd, <i>J</i> 10.5, 13.5 Hz), 3.50 (3 H, s), 3.72 (3 H, s), 4.40 (1 H, dd, <i>J</i> 6.4, 10.5 Hz), 6.18—6.38 (2 H, m), 6.76—7.10 (3 H, m), 7.20—7.50 (5 H, m), 7.70 (2 H, d, <i>J</i> 9.0 Hz), 8.16 (2 H, d, <i>J</i> 9.0 Hz)

^a In CCl₄. ^b In CDCl₃.

TABLE 4
Endo-adducts (3a—h)

Adduct	Substituent (X)	M.p. (°C)	Yield (%)	Found (%)			Formula	Requires (%)		
				C	H	N		C	H	N
(3a)	Me ₂ N	153.5—155.5	73	74.85	5.85	2.8	C ₂₁ H ₂₉ NO ₅	75.13	5.90	2.83
(3b)	MeO	167.0—168.5	72	74.3	5.4		C ₃₀ H ₂₆ O ₆	74.67	5.43	
(3c)	Me	172.0—173.0	75	77.0	5.45		C ₃₀ H ₂₆ O ₅	77.23	5.62	
(3d)	H	161.0—163.0	83	76.85	5.35		C ₂₉ H ₂₉ O ₅	76.97	5.35	
(3e)	Cl	185.5—186.0	73	71.55	4.7		C ₂₉ H ₂₃ ClO ₅	71.53	4.76	
(3f)	Br	183.5—185.0	79	65.4	4.25		C ₂₉ H ₂₃ BrO ₅	65.54	4.37	
(3g)	CN	202.5—204.0	74	76.75	5.15	2.8	C ₃₀ H ₂₃ NO ₅ ·½C ₆ H ₆	76.73	5.07	2.71
(3h)	NO ₂	206.5—207.0	61	69.81	4.59	3.05	C ₂₉ H ₂₃ NO ₇	70.01	4.66	2.82

be of the *endo*-configuration. The similarity of the n.m.r. spectral patterns of the series of adducts (5a—h) indicates them all to have the *endo*-configuration. The n.m.r. spectral data and the physical, analytical, and

i.r. spectral data for these adducts are summarized in Tables 5 and 6, respectively.

As described above, the major adducts formed in the cycloadditions of CPC (1a) and EPC (1b) are *endo*,

TABLE 5
I.r. ^a and ¹H n.m.r. spectra ^b of *endo*-adducts (5a—h)

Adduct	Substituent (X)	$\nu_{\max.}/\text{cm}^{-1}$	Chemical shift (δ)
(5a)	NMe ₂	1 750	0.72 (3 H, t, <i>J</i> 7.2 Hz), 0.84 (3 H, t, <i>J</i> 7.2 Hz), 1.77 (4 H, q, <i>J</i> 7.2 Hz), 1.99 (1 H, dd, <i>J</i> 6.6, 12.4 Hz), 2.42 (1 H, dd, <i>J</i> 9.6, 12.4 Hz), 2.94 (6 H, s), 3.46 (1 H, dd, <i>J</i> 9.6, 6.6 Hz), 6.16—6.26 (2 H, m), 6.71—6.90 (3 H, m), 7.14—7.26 (9 H, m)
(5b)	OMe	1 760	0.72 (3 H, t, <i>J</i> 7.3 Hz), 0.84 (3 H, t, <i>J</i> 7.3 Hz), 1.78 (2 H, q, <i>J</i> 7.3 Hz), 1.81 (2 H, q, <i>J</i> 7.3 Hz), 2.00 (1 H, dd, <i>J</i> 6.5, 12.4 Hz), 2.46 (1 H, dd, <i>J</i> 9.8, 12.4 Hz), 3.42 (1 H, dd, <i>J</i> 9.8, 6.5 Hz), 3.82 (3 H, s), 6.12—6.24 (2 H, m), 6.74—6.96 (3 H, m), 7.12—7.28 (9 H, m)
(5c)	Me	1 760	0.72 (3 H, t, <i>J</i> 7.4 Hz), 0.84 (3 H, t, <i>J</i> 7.4 Hz), 1.78 (2 H, q, <i>J</i> 7.4 Hz), 1.80 (2 H, q, <i>J</i> 7.4 Hz), 2.03 (1 H, dd, <i>J</i> 6.5, 12.8 Hz), 2.38 (3 H, s), 2.44 (1 H, dd, <i>J</i> 9.9, 12.8 Hz), 3.43 (1 H, dd, <i>J</i> 9.9, 6.5 Hz), 6.08—6.20 (2 H, m), 6.72—6.96 (3 H, m), 7.12—7.32 (9 H, m)
(5d)	H	1 760	0.72 (3 H, t, <i>J</i> 7.4 Hz), 0.84 (3 H, t, <i>J</i> 7.4 Hz), 1.79 (2 H, q, <i>J</i> 7.4 Hz), 1.81 (2 H, q, <i>J</i> 7.4 Hz), 2.05 (1 H, dd, <i>J</i> 12.7, 6.5 Hz), 2.46 (1 H, dd, <i>J</i> 9.8, 12.7 Hz), 3.74 (1 H, dd, <i>J</i> 9.8, 6.5 Hz), 6.06—6.14 (2 H, m), 6.70—6.92 (3 H, m), 7.14—7.36 (10 H, m)
(5e)	Cl	1 755	0.72 (3 H, t, <i>J</i> 7.4 Hz), 0.83 (3 H, t, <i>J</i> 7.4 Hz), 1.56—1.96 (4 H, m), 1.97 (1 H, dd, <i>J</i> 11.5, 5.5 Hz), 1.56—1.96 (4 H, m), 2.47 (1 H, dd, <i>J</i> 8.5, 11.5 Hz), 3.43 (1 H, dd, <i>J</i> 5.5, 8.5 Hz), 6.12—6.23 (2 H, m), 6.76—6.96 (3 H, m), 7.10—7.40 (9 H, m)
(5f)	Br	1 755	0.72 (3 H, t, <i>J</i> 7.3 Hz), 0.84 (3 H, t, <i>J</i> 7.3 Hz), 1.76 (2 H, q, <i>J</i> 7.3 Hz), 1.80 (2 H, q, <i>J</i> 7.3 Hz), 1.96 (1 H, dd, <i>J</i> 6.8, 12.8 Hz), 2.46 (1 H, dd, <i>J</i> 9.8, 12.8 Hz), 6.11—6.22 (2 H, m), 6.76—6.96 (3 H, m), 7.10—7.32 (7 H, m), 7.44—7.54 (2 H, m)
(5g)	CN	1 760	0.76 (3 H, t, <i>J</i> 7.5 Hz), 0.86 (3 H, t, <i>J</i> 7.5 Hz), 1.72 (2 H, q, <i>J</i> 7.5 Hz), 1.76 (2 H, q, <i>J</i> 7.5 Hz), 2.08 (1 H, dd, <i>J</i> 6.7, 12.8 Hz), 2.53 (1 H, dd, <i>J</i> 9.8, 12.8 Hz), 3.55 (1 H, dd, <i>J</i> 9.8, 6.7 Hz), 6.08—6.20 (2 H, m), 6.84—6.96 (3 H, m), 7.04—7.36 (5 H, m), 7.40—7.75 (4 H, m)
(5h)	NO ₂	1 760	0.76 (3 H, t, <i>J</i> 7.3 Hz), 0.88 (3 H, t, <i>J</i> 7.3 Hz), 1.82 (2 H, q, <i>J</i> 7.3 Hz), 1.84 (2 H, q, <i>J</i> 7.3 Hz), 2.08 (1 H, dd, <i>J</i> 6.3, 12.8 Hz), 2.56 (1 H, dd, <i>J</i> 9.5, 12.8 Hz), 3.62 (1 H, dd, <i>J</i> 9.5, 6.3 Hz), 6.02—6.24 (2 H, m), 6.75—6.96 (3 H, m), 7.08—7.32 (5 H, m), 7.50 (2 H, d, <i>J</i> 9.0 Hz), 8.21 (2 H, d, <i>J</i> 9.0 Hz)

^a In CCl₄. ^b In CDCl₃.

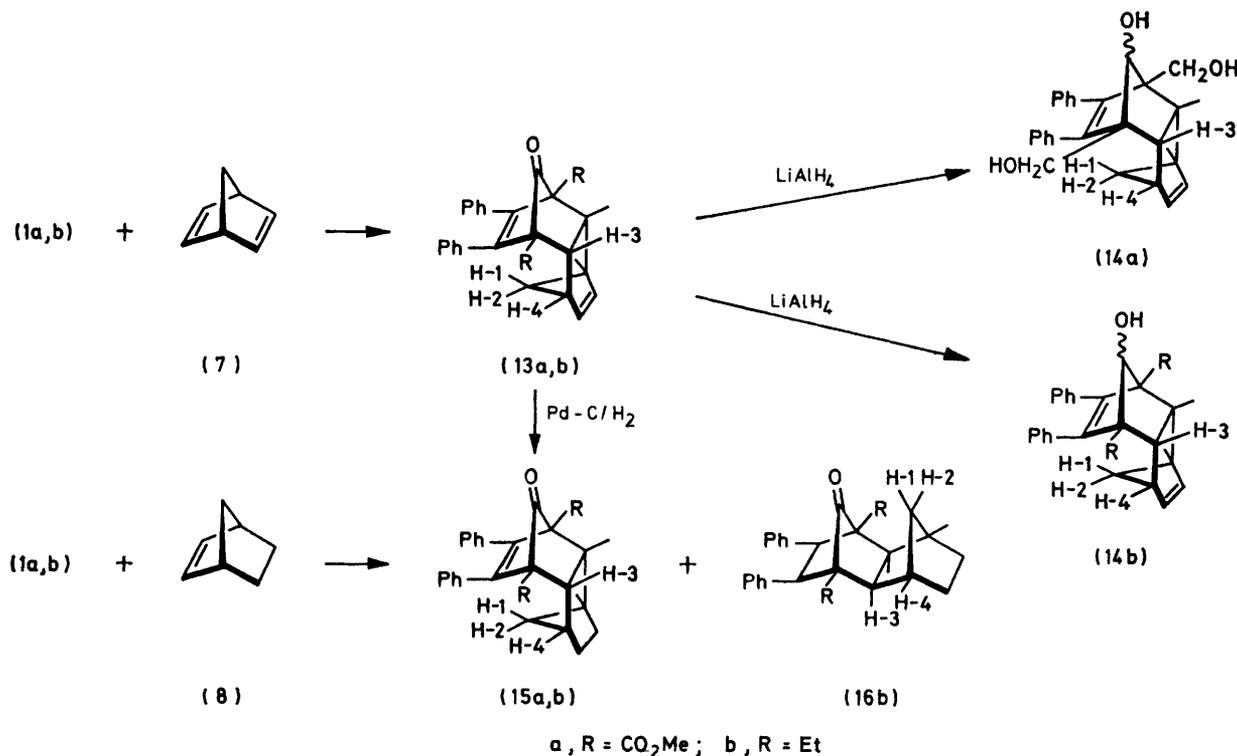
TABLE 6
Endo-adducts (5a—h)

Adduct	Substituent (X)	M.p. (°C)	Yield (%)	Found (%)			Formula	Requires (%)		
				C	H	N		C	H	N
(5a)	NMe ₂	136—137	74	85.35	7.6	3.2	C ₃₁ H ₃₃ NO	85.48	7.64	3.22
(5b)	OMe	104—105	40	85.3	7.05		C ₃₀ H ₃₀ O ₂	85.27	7.16	
(5c)	Me	124—126	73	88.6	7.4		C ₃₀ H ₃₀ O	88.63	7.44	
(5d)	H	133—134	84	88.6	7.15		C ₂₉ H ₂₈ O	88.73	7.19	
(5e)	Cl	158.5—159	96	81.6	6.3		C ₂₉ H ₂₇ ClO	81.58	6.37	
(5f)	Br	170—172	90	73.8	5.7		C ₂₉ H ₂₇ BrO	73.88	5.77	
(5g)	CN	177—182	87	86.05	6.6	3.4	C ₃₀ H ₂₇ NO	86.29	6.52	3.35
(5h)	NO ₂	132—136	94	79.5	6.2	3.25	C ₂₉ H ₂₇ NO ₂	79.61	6.22	3.20

compatible with the importance of secondary orbital interactions, and the existence of small amounts of *exo*-adduct suggests steric repulsion* between the phenyl group on the CPC or EPC moiety and the phenyl group on the *para*-substituted styrene moiety because of non-coplanarity between the five-membered ring cyclopentadienone system and its phenyl group.

Cycloadditions of CPC (1a), EPC (1b), and MPC (1c) with Electron-rich Dienophiles (7), (8), and (9).—Each of the cycloadditions of CPC, EPC, and MPC with norbornadiene (7), norbornene (8), and 1,4-dihydro-1,4-

[4 + 2] π adducts. The n.m.r. spectrum of (13b) exhibited signals for a methylene bridge at δ 1.29 (1 H, d, J 9.4 Hz, H-1) and 2.54 (1 H, d, J 9.4 Hz, H-2), for two centre-bridge protons at δ 2.12 (2 H, s, H-3), and for two allylic bridgehead protons at δ 3.04—3.16 (2 H, m, H-4). A singlet due to the centre-bridge proton at δ 2.12 indicates that the dihedral angles between the bridgehead and the centre-bridge protons is *ca.* 90° on the basis of the Karplus correlation.¹⁸ Moreover, the resonance of the methylene bridge protons (H-1 and H-2) was shifted both upfield (δ 1.29) and downfield (δ 2.54),



SCHEME 2

epoxynaphthalene (9) in benzene gave exclusively the single 1 : 1 adducts (13a,b), (15a), and (17a,b,c). The n.m.r. spectra of these adducts were simple and compatible with symmetrical structures, indicating the

* It has been reported that the cycloaddition of phencyclone¹⁷ gave only an *endo*-adduct because of greater secondary orbital interaction and less steric repulsion due to coplanarity of the structure of the fused ring.

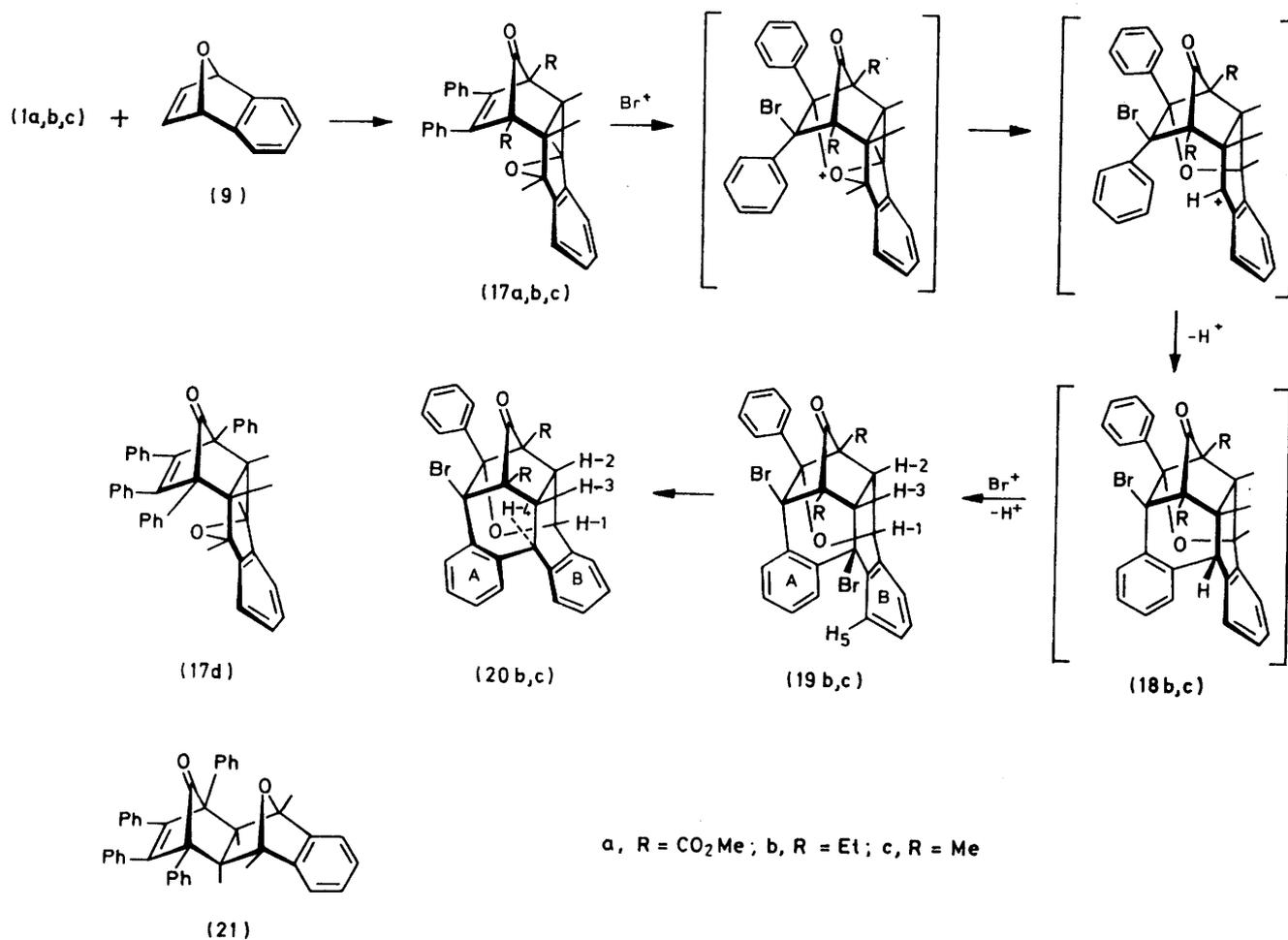
indicating that the methylene bridge proton (H-1) exists in the shielding zone of the carbonyl group^{14a} or olefin^{14a} on the stilbene moiety. The n.m.r. spectrum of the alcohol (14b), obtained by reduction of (13b) with lithium aluminium hydride, showed very similar chemical shifts for the methylene bridge protons, these resonating at δ 1.30, and 2.48. From these data, the structure was determined as an *endo-exo* configuration, and thus the

exo-endo, *exo-exo*, and *endo-endo* configurations could be ruled out.

In the case of (13a), a similar effect was seen on comparison of the n.m.r. spectrum with that of (14a), and the configuration was determined as *endo-exo*. Cycloaddition of EPC (1b) with norbornene (8) in benzene gave a mixture of the *endo-exo*- (15b) and *exo-exo*-adducts (16b) in a ratio of ca. 4 : 1. The adducts (15b) and (16b) were isolated by fractional recrystallization from the reaction mixture. The major adduct (15b) was identical with the product obtained from chemical conversion by catalytic hydrogenation of (13b) over 5% palladium-charcoal in ethanol. The n.m.r. spectrum of (16b) exhibited a doublet for the centre-bridge proton at δ 2.07 (J 1.0 Hz). However, on account of fewer spin-spin coupling constants than those expected for *endo-endo* and *exo-endo* configurations, the adduct (16b) would be *exo-exo*. On the other hand, cycloaddition of CPC (1a) with (8) gave exclusively the *endo-exo*-adduct (15a), the configuration of (15a) being based upon comparison of its n.m.r. spectrum with that of (13a). The centre-bridge proton of (15a) appeared as a singlet at δ 2.78, comparable with that of (13b) (δ 2.76). Although we have no explanation for formation of the *exo-exo*-adduct

(16b) because of a lack of the same stereoisomer in the case of cycloaddition of CPC with (8), it is interesting that this *exo-exo*-adduct could be detected in the cycloaddition. The adduct (17b) has the same fundamental structure as (13b), as shown by its similar spectral pattern; the resonance assignable to the centre-bridge proton appeared as a singlet (see Experimental section). However, the configuration of (17b) could not be determined by the method described above because of the lack of methylene bridge protons. Thus, the stereochemistry of (17b) was determined by chemical transformation. The bromination of (17b) was completed on standing overnight, and the dibromide (19b) was isolated, but was extremely sensitive to heat: on reflux in benzene it was converted into the monobromide (20b). The mass spectrum of (19b) exhibited signals at m/e 588 (M^+), 590 ($M^+ + 2$), and 592 ($M^+ + 4$), respectively.

Since the ratio of these intensities is 1 : 2 : 1, the compound was established to have the molecular formula $C_{31}H_{26}Br_2O_2$. The n.m.r. spectrum of (19b) showed an interesting downfield shift of an aromatic signal at δ 8.6 (1 H, br d, J 7.5 Hz, $^{19}H-5$), and signals for three methine protons at δ 3.02 (1 H, dd, $J_{1,2}$ 2.8 Hz, $J_{2,3}$ 11.6 Hz, H-2), 3.99 (1 H, d, $J_{2,3}$ 11.6 Hz, H-3), and



SCHEME 3

4.94 (1 H, d, $J_{1,2}$ 2.8 Hz, H-1). The H-2 proton of (19b) was found to be coupled with H-1 and H-3 by spin-decoupling methods. Decoupling of the aromatic protons at δ 7.6 reduced the broad doublet at δ 8.6 to a singlet. The downfield shift of H-5 would be due to the anisotropy of the aromatic ring A (the aromatic ring B is perpendicular to the plane of ring A).

Moreover, the structure of the dibromide (19b) is supported by the ^{13}C n.m.r. chemical shifts (Figure 1). The occurrence of an intramolecular Friedel-Craft reaction might be explained as the result of a proximity effect between a phenyl group and a carbonium cation formed by bromination of (17b).

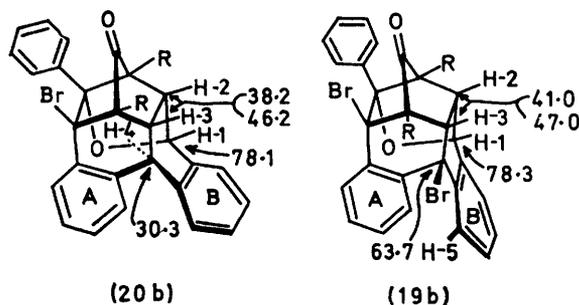


FIGURE 1 ^{13}C N.m.r. chemical shifts (p.p.m.) for compounds (19b) and (20b)

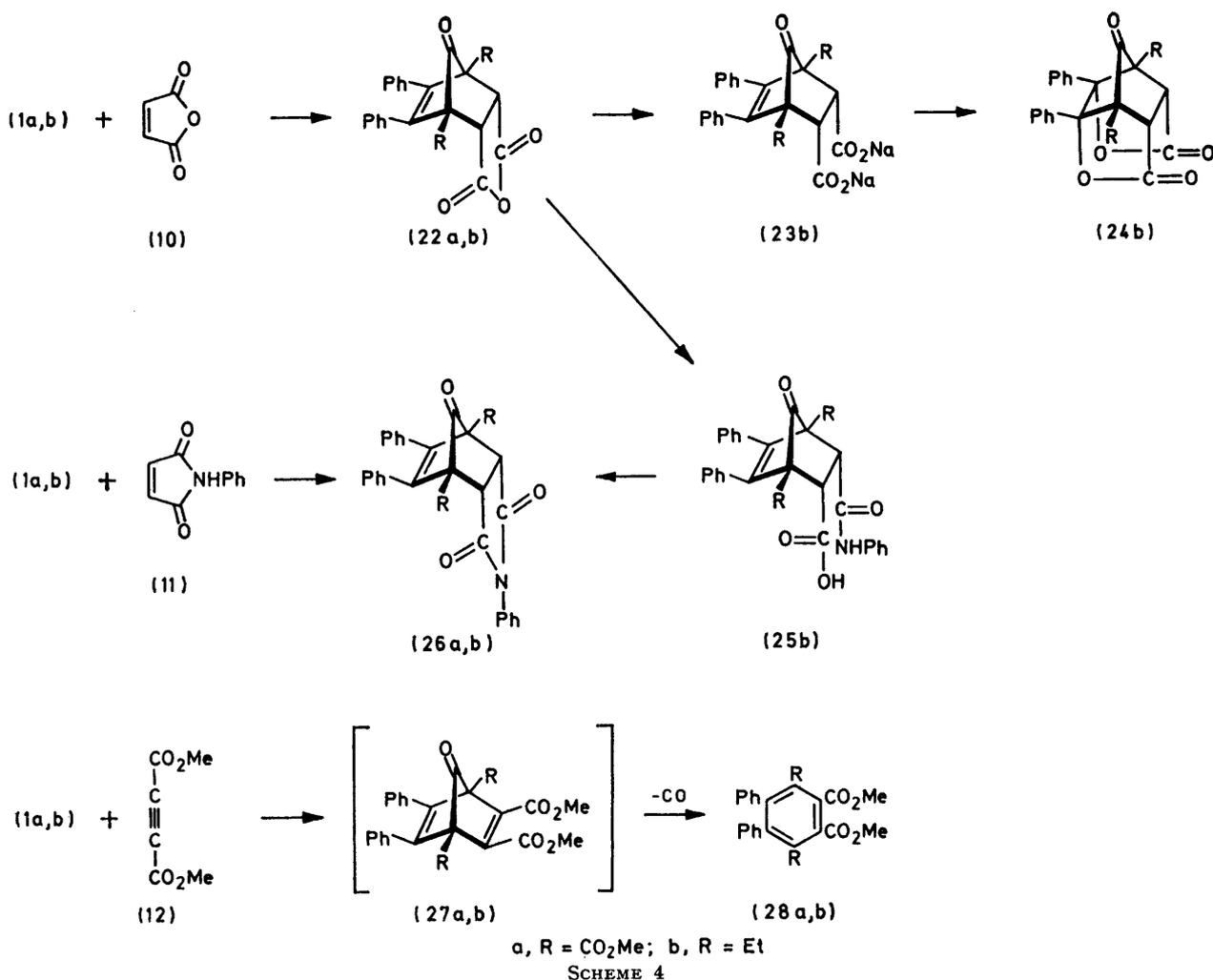
Compound (20b) was established to have the molecular formula $\text{C}_{31}\text{H}_{27}\text{BrO}_2$ because of the equal intensities of the peaks at m/e 510 (M^+) and 512 ($M^+ + 2$). The n.m.r. spectrum of (20b) exhibited signals for four methine protons at δ 2.82 (1 H, dd, $J_{1,2}$ 2.6, $J_{2,3}$ 11.3 Hz, H-2), 3.12 (1 H, dd, $J_{2,3}$ 11.3, $J_{3,4}$ 8.3 Hz, H-3), 4.44 (1 H, d, $J_{3,4}$ 8.4 Hz, H-4), and 4.96 (1 H, d, $J_{1,2}$ 2.6 Hz, H-1), and a downfield shift of the aromatic proton was not observed. This suggests that the arrangement of the four methine protons is H-1-H-2-H-3-H-4, and that rings A and B lie substantially in the plane. This configuration is compatible with the difference in coupling constants of $J_{1,2}$ and $J_{3,4}$. Moreover, the structure of the monobromide (20b) was supported by the ^{13}C n.m.r. chemical shifts (Figure 1). This compound (20b) is not identical with an intermediate (18b) in the formation of the dibromide (19b) since no dibromide is obtained from bromination of (20b). Furthermore, reductive debromination by catalytic hydrogenation of (19b) over 5% palladium-charcoal and reaction of (19b) with sodium methanethiolate¹⁹ gave only the same compound (20b). In view of these data, adduct (17b) was assigned the *endo-exo*-configuration. Recently, it was reported by Tan, Russell, and Warrener¹⁵ that the stereochemistry of adducts derived from tetrasubstituted cyclopentadienones can be readily assigned by long-range coupling (^{13}C -H) between the carbonyl carbon and the *endo*-bridge-junction proton in the ^{13}C n.m.r. spectrum. This application led to the conclusion that the *exo-exo*-structure¹⁴ of (21) should be revised to the *endo-exo*-adduct (17d) (see Scheme 3). In the case of (17b), no such coupling was observed, and consequently,

this stereochemistry was identical with that deduced on the basis of chemical evidence. The stereochemistry of adduct (17c) was decided to be *endo-exo* on the basis of similar chemical evidence. The similarity of the spectral data of both (17a) and (17b), namely, the resonances assigned to the centre-bridge proton and the bridgehead proton appearing as singlets at δ 2.96 and 5.61, respectively, indicates that both compounds have the same fundamental structure. Unfortunately, the bromination of (17a) resulted in the formation of complex products, and purification was difficult at the present stage. However, (17a) was also assigned the *endo-exo*-configuration, since coupling between the carbonyl carbon and the centre-bridge proton in the ^{13}C n.m.r. spectrum was not observed.

Cycloadditions of CPC (1a) and EPC (1b) with Electron-deficient Dienophiles (10), (11), and (12).—Each of the cycloadditions of (1a and b) with maleic anhydride (10) and *N*-phenylmaleimide (11) in benzene gave exclusively the single 1 : 1 adducts (22a,b) and (26b) in good yield. On the other hand, the cycloadditions of (1a,b) with dimethyl acetylenedicarboxylate (12) gave the decarbonylated products (28a,b) in high yield (see Scheme 4). The configuration of the adducts could not be determined from the n.m.r. spectral data because of the absence of any anisotropic effect of the kind observed for the adducts of phencyclone (1d).¹⁷ Therefore, the configurations for these adducts were also assigned on the basis of chemical transformations. The adduct (22b) was hydrolysed with 10% aqueous sodium hydroxide followed by bromination to give a dilactone (24b). Thus, (22b) was assigned the *endo*-configuration. The reaction of the adduct (22b) with aniline in ether afforded a carboxylic acid (25b), which was converted with acetic anhydride and sodium acetate²⁰ into the ring-closed compound (26b). This compound was identical on the basis of spectroscopic evidence with the adduct (26b) obtained from *N*-phenylmaleimide. The lactonization of (22a) by bromination resulted in the formation of complex products and chemical evidence for stereochemistry could not be obtained because of difficulties encountered during purification. However, the adduct (22a) could be assigned the *endo*-configuration because no coupling was observed between the carbonyl carbon atom and the methine proton in the ^{13}C n.m.r. spectrum.

Each of the cycloadditions of (1a,b) with dimethyl acetylenedicarboxylate (12) in benzene afforded exclusively the decarbonylated products (28a,b).

Kinetics of the Cycloadditions of CPC (1a) and EPC (1b) with a Series of para-Substituted Styrenes (2a-h) and Other Dienophiles (7)-(12).—The kinetic runs were studied by monitoring the disappearance of the cyclopentadienones [CPC (1a) and EPC (1b)] in the u.v.-visible regions, as described in the Experimental section when excellent second-order kinetics were always obtained. In this paper, we discuss the overall rate constants of the cycloadditions, because the exact partial rate constants could not be determined by n.m.r. measurements, and the mixed adducts could not be



separated by t.l.c. The kinetic data of the cycloadditions of CPC (1a) with (2a—h) showed that electron-attracting substituents decrease the rate, whereas electron-donating substituents lead to an increase. We applied the Hammett equation by using the σ_p constants. A plot of $\log k/k_H$ against the σ_p constants for the cycloadditions of CPC (1a) with (2a—h) gave a curved line with a slope of -1.388 ($r = -0.948$). An improved correlation was obtained for Okamoto-Brown's σ_p^+ constants²¹⁻²⁴ which gave a slope calculated by the method of least squares of -0.930 ($r = -0.985$) (see Figure 2, and Table 7).

We next examined the cycloadditions of CPC (1a) and EPC (1b) with dienophiles in the presence of *t*-butylcatechol as a radical scavenger: variations in the rate constants were seen to be due to random deviations rather than to kinetically significant results. The results rule out a free-radical mechanism for the cycloaddition. Contrary to the previous data of the cycloadditions of CPC (1a), the plots of $\log k/k_H$ against the σ_p^+ constants for the cycloadditions of EPC with a series of *para*-substituted styrenes (2a—h) do not lead to a simple linear relationship. Interestingly, the data

appear to define two lines with markedly different slopes (see Figure 2 and Table 7). The reactivities of the electron-donating substituents (*p*-dimethylamino, *p*-

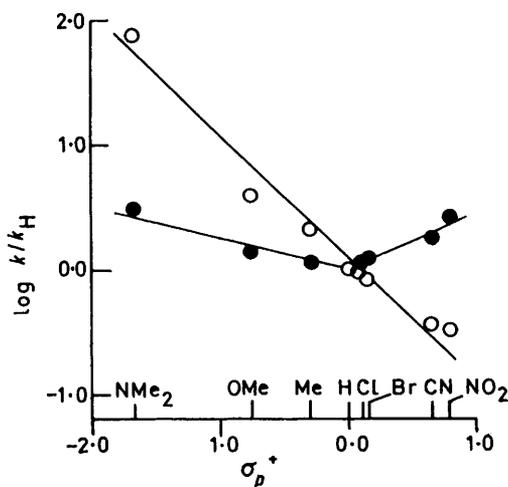


FIGURE 2 Correlation of $\log k/k_H$ vs. σ_p^+ for the cycloadditions of CPC (1a) (O) and EPC (1b) (●) with a series of *para*-substituted styrenes (2a—h)

TABLE 7

Second-order rate constants (k) and Okamoto-Brown parameters (σ_p^+) for cycloadditions of CPC (1a) and EPC (1b) with a series of *para*-substituted styrenes (2a—h) in chlorobenzene

Dienophile [X]	$k \times 10^4 /$ $1 \text{ mol}^{-1} \text{ s}^{-1}$ CPC (1a) at 34.1 °C (log k/k_H)	$k \times 10^4 /$ $1 \text{ mol}^{-1} \text{ s}^{-1}$ EPC (1b) at 65.4 °C (log k/k_H)	σ_p^+
(2a) [NMe ₂]	1 980.0 (1.86)	10.70 (0.501)	-1.7
(2b) [OMe]	108.0 (0.59)	4.85 (0.157)	-0.778
(2c) [Me]	57.8 (0.32)	4.04 (0.078)	-0.311
(2d) [H]	27.6 (0.0)	3.38 (0.0)	0.0
(2e) [Cl]	25.8 (-0.029)	4.07 (0.081)	0.114
(2f) [Br]	22.5 (-0.089)	4.30 (0.105)	0.150
(2g) [CN]	9.16 (-0.479)	6.21 (0.264)	0.659
(2h) [NO ₂]	8.76 (-0.498)	9.03 (0.427)	0.790

methoxy, and *p*-methyl) towards cycloaddition fall on a negative slope, while those of the electron-deficient substituents (*p*-nitro, *p*-cyano, *p*-bromo, and *p*-chloro) fall on a positive slope. A dual linear relationship has previously been reported in the cycloadditions of *para*-substituted styrenes with tetracyclone (1d)⁸ and phenacyclone (1e),⁹ and this type of reaction has been rationalized as a neutral Diels-Alder reaction. Sustmann³ classified these cycloadditions according to three types (Figure 3) from the relative relationship of both HOMO-LUMO interactions of diene and dienophile, and used this to explain the reactivity in the Diels-Alder reaction.

Reaction constants (ρ) for the cycloadditions of CPC (1a) with (2a—h) have a negative value, so that an indication of the controlling interaction between the LUMO of the diene and the HOMO of the dienophile is obtained, classified as inverse electron demand [Figure

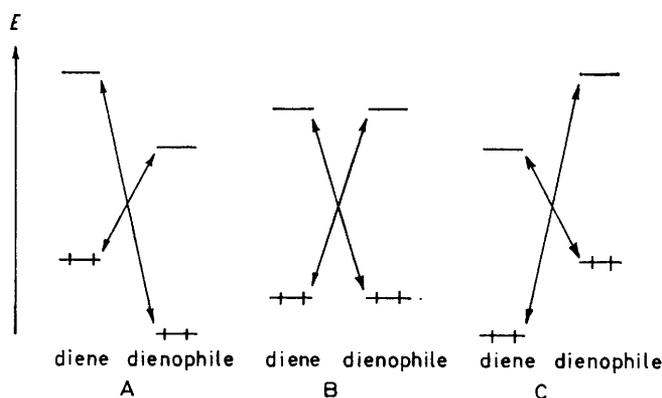


FIGURE 3 Relative positions of frontier orbitals in direct (A), neutral (B), and inverse (C) Diels-Alder reactions

3(C)]. On the other hand, although the cycloadditions of EPC (1b) with *para*-substituted styrenes having electron-donating substituents (2a) and (2b) may be

considered as inverse-type, the cycloadditions of EPC (1b) are generally classified as neutral-type from the character of the HOMO-LUMO-controlled reaction described above and the data shown in Table 1.

The stabilization energy of interaction, ΔE_{FMO} , is calculated by equation (1).³

$$\Delta E_{\text{FMO}} = 2\gamma^2 \left[\frac{1}{E_{\text{HOMO(dienophile)}} - E_{\text{LUMO(diene)}}} + \frac{1}{E_{\text{HOMO(diene)}} - E_{\text{LUMO(dienophile)}}} \right] \quad (1)$$

The relation²⁵ between reaction rate constants and interaction energies is shown in equation (2), where

$$\ln k/k_H = \Delta E - \Delta E_H \quad (2)$$

k is the rate constant for the cycloaddition of *para*-substituted styrene, k_H is that of styrene, and ΔE is the interaction energy for the cycloaddition of the *para*-substituted styrene and ΔE_H is that of styrene.

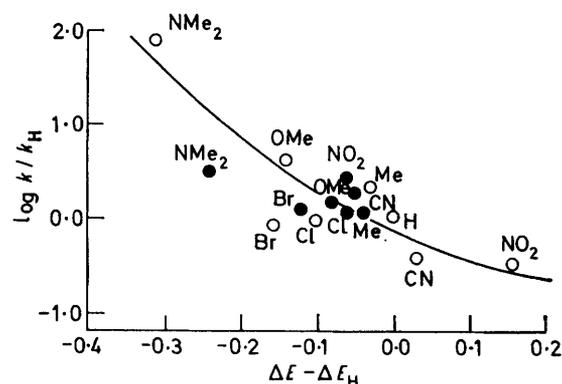


FIGURE 4 Correlation of $\log k/k_H$ vs. difference in interaction energy ($\Delta E - \Delta E_H$) for the cycloadditions of CPC (1a) (○) and EPC (1b) (●) with a series of *para*-substituted styrenes

The relation between the logarithm of the rate constants of the cycloadditions and the calculated interaction energies was then examined. In the case of the cycloaddition of CPC (1a), the hyperbolic curve shown in Figure 4 was obtained. The result implies that the reactivity of CPC (1a) is largely determined by the electronic factor of the dienophile, and that the HOMO-LUMO interaction is of the inverse type.

In contrast, the reactivity of EPC does not correlate as a hyperbolic curve, and the difference in reactivity in the electronic properties of dienophiles is much lower than in the case of CPC. If we exclude the cycloaddition of *p*-dimethylaminostyrene, which has an unusual deviation, the result is classified as a neutral type, because one of the HOMO-LUMO interactions will be strengthened as the second is weakened. Its deviation in reactivity in the cycloaddition of *p*-dimethylaminostyrene can probably be interpreted in terms of the different HOMO-LUMO interaction, which is of the inverse type because of the electron-donating property of the dimethylamino-group.

Tables 8 and 9 show the rate constants and activation

parameters for the cycloadditions of CPC (1a) and EPC (1b) with a variety of dienophiles in chlorobenzene.

In the case of the cycloadditions of CPC, the results showed the electron-rich dienophile (1,4-dihydro-1,4-epoxynaphthalene) to be extremely reactive, whereas the electron-deficient dienophile (maleic anhydride) had remarkably low reactivity, the ratio of both reaction rate constants being *ca.* 40 000 (Table 8). The tendency is similar to that found for the cycloadditions of CPC (1a)

for (7) and $-19.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ for (8)] of the activation entropy over other examples [-32.4 to $-36.5 \text{ cal K}^{-1} \text{ mol}^{-1}$] and a lack of secondary orbital interactions in the transition state, it may be that the cycloadditions of (7) and (8) are thermodynamically controlled, subject to steric control owing to non-coplanarity²⁷ of the phenyl group, whilst the others are kinetically controlled.

The solvent effect on the reaction rate constants was investigated for the cycloadditions of CPC (1a) with

TABLE 8

Second-order rate constants (*k*) and activation parameters for cycloadditions of CPC (1a) with dienophiles (7)–(12) in chlorobenzene

Dienophile	<i>k</i> /l mol ⁻¹ s ⁻¹				ΔH^\ddagger / kcal mol ⁻¹	ΔS^\ddagger / cal K ⁻¹ mol ⁻¹
	34.1 °C	99.1 °C	105.1 °C	119.8 °C		
(9)	5.03×10^{-1}	5.91×10^{-1} ^a	7.40×10^{-1} ^b	9.16×10^{-1} ^c	8.8	-34.1
(7)	1.96×10^{-3}					
(8)	3.65×10^{-4}					
(11)	1.30×10^{-4}					
(10)	1.38×10^{-5}	1.45×10^{-3}	2.14×10^{-3}	4.75×10^{-3}	15.5	-32.4
(12)	1.25×10^{-5}	9.61×10^{-4}	1.27×10^{-3}	2.72×10^{-3}	14.3	-36.5

^a At 38.2 °C. ^b At 42.7 °C. ^c At 47.4 °C.

TABLE 9

Second-order rate constants (*k*) and activation parameters for cycloadditions of EPC (1b) with dienophiles (7)–(12) in chlorobenzene

Dienophile	<i>k</i> /l mol ⁻¹ s ⁻¹					ΔH^\ddagger / kcal mol ⁻¹	ΔS^\ddagger / cal K ⁻¹ mol ⁻¹
	34.1 °C	60.0 °C	65.4 °C	98.8 °C	74.8 °C		
(9)	1.43×10^{-3}	7.81×10^{-3}	1.02×10^{-2}	1.36×10^{-2}	1.81×10^{-2}	12.7	-32.8
(7)	5.85×10^{-6}	1.31×10^{-4}	1.50×10^{-4}	2.94×10^{-4}	5.69×10^{-4}	22.7	-10.8
(8)	1.30×10^{-6}	1.91×10^{-5}	4.42×10^{-5}	5.19×10^{-5}	7.81×10^{-5}	21.0	-19.2
(11)	8.85×10^{-3}	3.88×10^{-2}	5.12×10^{-2}	6.34×10^{-2}	8.22×10^{-2}	10.9	-34.4
(10)	7.03×10^{-3}	2.99×10^{-2}	4.15×10^{-2}	4.83×10^{-2}	6.40×10^{-2}	10.8	-35.2
(12)	5.91×10^{-4}	3.10×10^{-3}	4.07×10^{-3}	5.46×10^{-3}	7.02×10^{-3}	12.3	-35.4

with the series of *para*-substituted styrenes (2a–h). However, in the case of the cycloadditions of CPC (1a) with (2a–h), the reactivity of *p*-dimethylaminostyrene was greater than that of *p*-nitrostyrene by a factor of only 226. The large difference in the reactivity is explained on the basis of the extent of the change of the HOMO energy levels from the electron-rich dienophile to the electron-deficient dienophile, namely, the extent of change of HOMO energy levels from 1,4-dihydro-1,4-epoxynaphthalene to maleic anhydride would be larger than that of *p*-dimethylaminostyrene to *p*-nitrostyrene. The similar tendency for the cycloadditions suggests that that of CPC (1a) is a Diels–Alder reaction with inverse electron demand. The values of the activation parameters are similar to those for the reported Diels–Alder reaction²⁶ (see Table 8). The large negative entropies of activation are as expected for a concerted transition state and the low value of the sensitivity to solvent effects (see later) supports this mechanism (Table 10). The data in Tables 8 and 9 show a higher reactivity for the addition of CPC (1a) and EPC (1b) to norbornadiene (7) than to norbornene (8). This must be due to a statistical factor [(7) contains two equivalent double bonds compared to (8)'s one] since the steric environment of (7) is almost identical with that of (8). In the light of the large values [$-10.8 \text{ cal K}^{-1} \text{ mol}^{-1}$

1,4-dihydro-1,4-epoxynaphthalene (9) (see Table 10). The E_T -values of Dimroth²⁸ were used as a scale of solvent-ionizing power. A plot of $\log k/k_H$ vs. E_T -values for each solvent showed a linear relationship with

TABLE 10

Solvent effects on cycloaddition of CPC (1a) with 1,4-dihydro-1,4-epoxynaphthalene (9) at 34.1 °C

Solvent	E_T -Value	<i>k</i> /l mol ⁻¹ s ⁻¹	log <i>k</i>
Toluene	33.9	0.635	-0.197
Benzene	34.5	0.503	-0.298
Chlorobenzene	37.5	0.485	-0.314
Bromobenzene	37.5	0.534	-0.273
Acetophenone	41.3	0.484	-0.315
DMF	43.8	0.406	-0.391

a least-squares slope of -1.37×10^{-2} (r 0.833). That the slope is negative shows that the rate of the cycloaddition is greater in non-polar solvents such as toluene than in polar solvents such as *NN*-dimethylformamide (DMF). The same effect has been reported for other diene–dienophile combinations.²⁹ It seems reasonable that the rate of reaction in the concerted mechanism should be lowest in the polar solvent (DMF), because the activation enthalpy is increased by solvation of the dienophile. Table 11 shows the effect of solvent on the cycloadditions of CPC (1a) and EPC (1b) with (2a), (2d),

and (2h), respectively. In the case of CPC (1a) little solvent effect on the overall rate constants was observed for styrene (2d) and *p*-nitrostyrene (2h). However, in the case of the electron-rich dienophile *p*-dimethylaminostyrene (2a), the rate was approximately doubled on changing the solvent from toluene to DMF. On the other hand, for the cycloadditions of EPC (1b) the increase in rate was about twice in the reactions of both electron-rich and electron-deficient dienophiles on changing the solvent from toluene to DMF. The magnitude of the solvent effects on changing the solvent from toluene to DMF in the cycloadditions of CPC (1a) and EPC (1b) with dienophiles are different. Although the magnitude falls over the range of the concerted mechanism, it may

non-conjugated carbonyl absorption due to the tropone moiety at 1725 cm⁻¹, an intense absorption at 1765 cm⁻¹ characteristic of a strained carbonyl group. The n.m.r. spectrum exhibited signals for two allylic bridgehead methine protons as a doublet at δ 3.55 (H-1), for four olefinic protons as multiplets at δ 5.16–5.40 (H-2) and 5.72–5.92 (H-3). The resonance of H-2 was found to be coupled with that of H-1 and H-3 by spin decoupling. This spectral pattern was simple and compatible with a symmetrical structure, indicating the [4 + 6] π adduct. This adduct (32b) was determined to have the *exo*-[4 + 6] π structure because the chemical shift of H-1 was similar to that of the *exo*-[4 + 6] π adduct³⁰ obtained by the cycloaddition of MPC (1c)

TABLE 11
Solvent effects on cycloadditions of CPC (1a) and EPC (1b) with *para*-substituted styrenes (2a, d, and h)

Solvent	E_T -value	k/l mol ⁻¹ s ⁻¹ ^a for CPC (1a)			k/l mol ⁻¹ s ⁻¹ ^b for EPC (1b)		
		(2a)	(2d)	(2h)	(2a)	(2d)	(2h)
Toluene	33.9	1 320.0	26.0	11.3	10.2	3.36	9.46
Anisole	37.2	2 580.0	31.1	10.2	14.8	4.58	11.0
Chlorobenzene	37.5	1 980.0	27.6	8.8	10.7	3.38	9.67
DMF	43.8	2 510.0	25.4	10.4	26.5	3.43	19.5

^a At 34.1 °C. ^b At 65.4 °C.

be due to the amount of polar character of the transition state.

Cycloadditions of CPC (1a) and EPC (1b) with Tropone (29) and 2-Chlorotropone (30).—To establish their capability for cycloaddition, we also examined the cycloadditions of CPC (1a) and EPC (1b) with the tropones (29) and (30). Treatment of CPC (1a) with tropone (29) in benzene afforded a single [4 + 6] π adduct (32a) in quantitative yield. The i.r. spectrum of (32a) showed characteristic carbonyl group absorptions at 1790 and 1745 cm⁻¹. The structure of (32a) was shown to be a [4 + 6] π adduct by the symmetrical pattern of the n.m.r. spectrum, which exhibited for the two methyl ester protons a singlet at δ 3.64, for the two allylic bridgehead protons a multiplet at δ 4.16–4.26, for the four olefinic protons a multiplet at δ 5.95–6.05, and for the ten aromatic protons a multiplet at δ 7.00–7.32. It is well known that phencyclone (1e) and MPC (1c) react with tropone to give [4 + 6] π adducts; tetracyclone (1d), acecyclone, indanocyclone, and phenalenocyclone, however, do not afford any such adducts. The non-reactivity of tetracyclone (1d) with tropone may be due to steric hindrance caused by the four non-coplanar phenyl groups. However, although the steric character of the four substituents on CPC (1a) is similar to that of tetracyclone, CPC (1a) does react with tropone. The difference in reactivity can be understood in terms of the size of the energy gap between the diene LUMO and dienophile HOMO: lowering of the frontier energy level by the electron-attracting substituent (methoxycarbonyl group) on CPC (1a) narrows the energy gap.

The cycloaddition of EPC with tropone (29) in acetone afforded a single [4 + 6] π adduct (32b) in high yield. The i.r. spectrum of (32b) showed, in addition to a

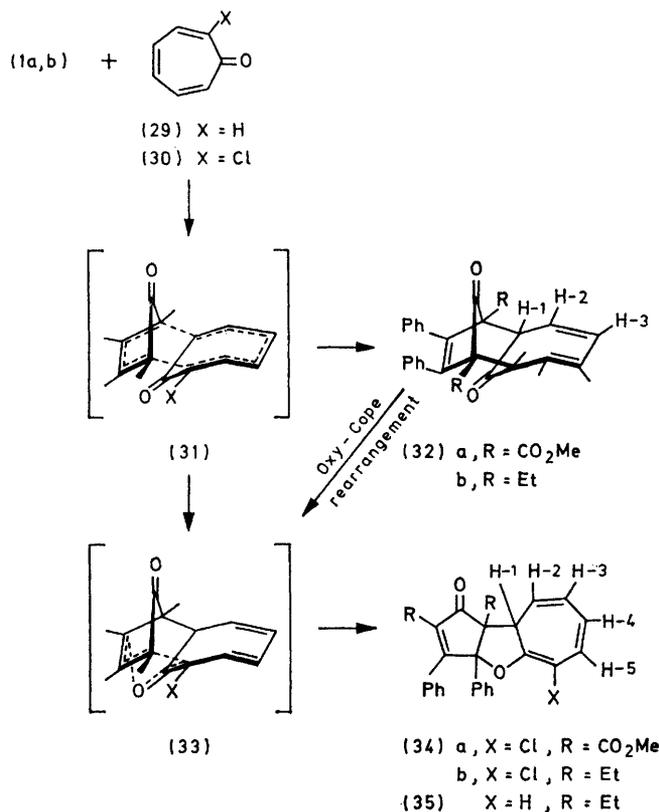
with tropone. Refluxing EPC (1b) with tropone (29) in benzene afforded a mixture of adducts (32b) and (35). The two substances were separated by preparative t.l.c. and the compound (35) was determined to be the [2 + 8] π adduct from comparison of its spectra with those of a previously reported [2 + 8] π adduct.³⁰ When a solution of the pure [4 + 2] π adduct (32b) in chloroform was heated at 70 °C in a sealed tube, formation of (35) was observed (n.m.r.), the reaction proceeding through an oxy-Cope rearrangement *via* the transition state (33) (Scheme 5). In case of (32a), the oxy-Cope rearrangement product was not detected.

On the other hand, the cycloaddition of CPC (1a) with 2-chlorotropone (30) in benzene afforded a single [2 + 8] π adduct (34a) in 56% yield. The n.m.r. spectrum of this product showed signals for two methyl ester protons as singlets at δ 3.08 and 3.89, for a methine proton (H-1) as a multiplet at δ 3.76–3.85, for an olefinic proton (H-2) as a double doublet at δ 5.26, for three olefinic protons (H-3, -4, and -5) as multiplets at δ 6.07–6.56, and for ten aromatic protons as multiplets at δ 7.14–7.60; this pattern suggested an unsymmetrical structure. The i.r. spectrum of (34a) exhibited absorptions at 1715 cm⁻¹, characteristic of a conjugated five-membered-ring carbonyl group, and at 1740 cm⁻¹ caused by an ester carbonyl group. The H-2 proton of this adduct was found to be coupled with H-1 and H-3 (centred at δ 6.16), and H-3 was observed to couple with H-2 and H-4. The compound (34a) was thus identified as the [2 + 8] π adduct.

The cycloaddition of EPC (1b) with 2-chlorotropone also afforded a [2 + 8] π adduct (34b) in 74% yield. The relative orientations of the addend moieties in the adducts were established as shown in structures (34a,b) because

the large difference in the chemical shifts of the methine proton (H-1) of (34a,b) would not occur if the inverse relationship existed.

It is considered that the [4 + 6] π -like approach by dipole-dipole interaction in the cycloadditions of CPC (1a) and EPC (1b) with 2-chlorotropone (30) would first



SCHEME 5

stabilize the transition state (31). However, formation of the [4 + 6] π adduct would be inhibited by steric hindrance owing to the chlorine atom at the 2-position of the tropone. As a result, the unsymmetrical transition state (31) would afford the [2 + 8] π adducts *via* the oxy-Cope rearrangement (31) \rightarrow (33) \rightarrow (34a,b) as shown in Scheme 5.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micromelting-point apparatus. ¹H N.m.r. spectra were recorded with a JEOL PS-100 spectrometer (100 MHz; tetramethylsilane as lock signal and dimethyl sulfoxide as reference). ¹³C N.m.r. spectra were obtained with a JEOL FX-100 Fourier-transform spectrometer. I.r. spectra were taken with a JASCO DS-701G spectrometer, u.v. spectra with a Hitachi EPS-3T, and mass spectra with a JEOL JMS-01SG double-focusing spectrometer operating at an ionization potential of 75 eV.

General Procedure for Cycloadditions of CPC (1a) and EPC (1b) with a Series of para-Substituted Styrenes (2a—h).—A mixture of compounds (1a,b) (10 mmol) and (2a—h) (10—40 mmol) was refluxed in benzene for 4 h. The solvent was removed under reduced pressure and the residue was recrystallized from ether to give the *endo*-adduct (3a—h)

or (5a—h); yields, m.p.s, characteristic i.r. and n.m.r. absorptions, and elemental analyses are given in Tables 3, 4, 5, and 6; the *exo*-adduct was not isolated. However, in the case of cycloaddition of compounds (1a) with (2f), both the *endo*- (3f) and *exo*-adducts (4f) were separated by fractional recrystallization. The adduct (4f) had m.p. 188—190 °C; *m/e* 531 (*M*⁺); δ (C₆D₆) 2.51 (1 H, dd, *J* 11.0 and 13.0 Hz), 2.85 (1 H, dd, *J* 5.7 and 13.0 Hz), 2.95 (3 H, s), 3.24 (1 H, dd, *J* 5.7 and 11.0 Hz), 3.27 (3 H, s), and 6.80—7.20 (14 H, m); and the resonances of aromatic protons in chloroform appeared as multiplets between δ 6.9 and 7.5.

Cycloadditions of CPC (1a) with Dienophiles.—(a) *With norborna-2,5-diene (7).* A solution of compounds (1a) (348 mg) and (7) (110 mg) in benzene (3 ml) was refluxed for 5 h. The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give the *adduct* (13a) (432 mg, 96%) m.p. 165.0—166.5 °C (Found: C, 76.55; H, 5.6. C₂₈H₂₄O₅ requires C, 76.35; H, 5.49%); δ (CDCl₃) 1.27 (1 H, d, *J* 9.3 Hz), 2.32 (1 H, d, *J* 9.3 Hz), 2.76 (2 H, s), 3.24—3.38 (2 H, m), 3.52 (6 H, s), 6.42—6.52 (2 H, m), and 7.05—7.50 (10 H, m), ν_{\max} (KBr) 1 800 and 1 735 cm⁻¹.

(b) *With norborn-2-ene (8).* A solution of compounds (1a) (348 mg) and (8) (220 mg) in benzene (3 ml) was refluxed for 7 h. The solvent was distilled off and the residue was recrystallized from methanol to give the *adduct* (15a) (420 mg, 95%), m.p. 147—150 °C (Found: C, 75.85; H, 5.85. C₂₈H₂₆O₅ requires C, 75.99; H, 5.92%); δ (CDCl₃) 1.08 (1 H, d, *J* 9.4 Hz), 1.30—1.70 (4 H, m), 2.10 (1 H, d, *J* 9.4 Hz), 2.66—2.80 (2 H, m), 2.78 (2 H, s), 3.54 (6 H, s), and 7.20 (10 H, s), ν_{\max} (KBr) 1 800 and 1 738 cm⁻¹.

(c) *With 1,4-dihydro-1,4-epoxynaphthalene (9).* A solution of compounds (1a) (697 mg) and (9) (288 mg) in benzene (3 ml) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was recrystallized from benzene to give the *adduct* (17a) (907 mg, 97%), m.p. 196.0—198.0 °C (Found: C, 77.5; H, 5.35. C₃₁H₂₄O₆·C₆H₆ requires C, 77.88; H, 5.30%); δ (CDCl₃) 2.96 (2 H, s), 3.67 (6 H, s), 5.61 (2 H, s), and 7.12—7.40 (14 H, m), δ_C (CDCl₃) 167.5 (s, CO₂⁻), and 185.4 (s, CO), ν_{\max} (KBr) 1 800 and 1 735 cm⁻¹.

(d) *With maleic anhydride (10).* A solution of compounds (1a) (679 mg) and (10) (196 mg) in benzene (5 ml) was heated in a sealed tube at 100 °C for 7 h. The precipitate was recrystallized with benzene to give the *adduct* (22a) (590 mg, 66%), m.p. 173.0—177.0 °C (Found: C, 69.4; H, 4.55. C₂₅H₁₈O₈·0.5C₆H₆ requires C, 69.14; H, 4.32%); δ (CDCl₃) 3.75 (6 H, s), 4.48 (2 H, s), and 7.10—7.33 (10 H, m), δ_C (CDCl₃) 164.1, 166.9 (s, CO₂⁻), and 202.1 (s, CO), ν_{\max} (KBr) 1 870, 1 800, 1 795, and 1 735 cm⁻¹.

(e) *With dimethyl acetylenedicarboxylate (12).* A solution of compounds (1a) (697 mg) and (12) (284 mg) in benzene (3 ml) was heated in a sealed tube at 100 °C for 10 h. The precipitate was recrystallized from methanol to give the *adduct* (28a) (820 mg, 84%), m.p. 226.0—230.0 °C (Found: C, 67.75; H, 4.95. C₂₆H₂₂O₈ requires C, 67.52; H, 4.80%); δ (CDCl₃) 3.44 (6 H, s), 3.86 (6 H, s), and 7.05 (10 H, s), ν_{\max} (KBr) 1 730 cm⁻¹.

(f) *With tropone (29).* A solution of compounds (1a) (697 mg) and (29) (316 mg) in benzene (3 ml) was refluxed for 10 h. The solvent was removed and the residue recrystallized from n-hexane to give the *adduct* (32a) (890 mg, 88%), m.p. 178.0—179.0 °C (Found: C, 73.6; H, 4.85. C₂₈H₂₂O₆ requires C, 74.00; H, 4.88%); δ (CDCl₃) 3.64 (6 H, s), 4.16—4.26 (2 H, m), 5.95—6.05 (4 H, m), and

6.80—7.40 (10 H, m), ν_{\max} (Nujol) 1 790, 1 745, and 1 735 cm^{-1} .

(g) *With 2-chlorotropone (30)*. A solution of compounds (1a) (662 mg) and (30) (320 mg) in benzene (3 ml) was refluxed for 7 h. The solvent was removed under reduced pressure and the residue was subjected to chromatography on silica gel using benzene as eluant to give the *adduct* (34a) (56%), m.p. 134.5—137.0 °C (Found: C, 68.65; H, 4.25. $\text{C}_{28}\text{H}_{21}\text{O}_6\text{Cl}$ requires C, 68.79; H, 4.33%); δ (CDCl_3) 3.08 (3 H, s), 3.76—3.85 (1 H, m), 3.89 (3 H, s), 5.13—5.34 (1 H, m), 6.06—6.56 (3 H, m), and 7.14—7.60 (10 H, m), ν_{\max} (CHCl_3) 1 740 and 1 715 cm^{-1} .

Cycloadditions of EPC (1b) with Dienophiles.—(a) *With norborna-2,5-diene (7)*. A solution of compounds (1b) (288 mg) and (7) (550 mg) in benzene (3 ml) was refluxed for 7 h. The solvent was removed under reduced pressure and the residue was recrystallized from benzene–n-hexane to give the *adduct* (13b) (285 mg, 75%), m.p. 133.5—134.5 °C (Found: C, 87.6; H, 7.3. $\text{C}_{28}\text{H}_{20}\text{O}\cdot 0.25\text{H}_2\text{O}$ requires C, 87.35; H, 7.46%); δ (CDCl_3) 0.76 (6 H, t, J 7.5 Hz), 1.29 (1 H, d, J 9.4 Hz), 1.86 (4 H, q, J 7.5 Hz), 2.12 (2 H, s), 2.54 (1 H, d, J 9.4 Hz), 3.04—3.16 (2 H, m), 6.32—6.42 (2 H, m), and 7.00—7.48 (10 H, m), ν_{\max} (Nujol) 1 765 cm^{-1} .

(b) *With norborn-2-ene (8)*. A solution of compounds (1b) (500 mg) and (8) (1.0 g) in benzene (5 ml) was refluxed for 5 h. The solvent was removed under reduced pressure and the residue was subjected to chromatography on silica gel using 5% benzene–n-hexane as eluant to give (15b) (199 mg, 30%) and (16b) (50 mg, 7%). The *adduct* (15b) had m.p. 120.0 °C (from ethanol) (Found: C, 87.65; H, 7.9. $\text{C}_{28}\text{H}_{30}\text{O}$ requires C, 87.91; H, 7.90%); δ (CDCl_3) 0.73 (6 H, t, J 7.5 Hz), 1.07br (1 H, d, J 10.5 Hz), 1.16—1.34 (4 H, m), 1.74 (2 H, q, J 7.5 Hz), 1.87 (2 H, q, J 7.5 Hz), 2.12 (2 H, s), 2.28br (1 H, d, J 10.5 Hz), 2.48 (2 H, m), and 6.96—7.26 (10 H, m), ν_{\max} (Nujol) 1 765 cm^{-1} .

The *adduct* (16b) had m.p. 153.0 °C (from ethanol) (Found: C, 87.8; H, 8.0. $\text{C}_{28}\text{H}_{30}\text{O}$ requires C, 87.91; H, 7.90%); δ (CDCl_3) 0.58 (6 H, t, J 7.5 Hz), 0.86 (1 H, d, J 11.0 Hz), 1.10—1.42 (4 H, m), 1.80 (2 H, q, J 7.5 Hz), 1.92 (2 H, q, J 7.5 Hz), 2.06 (1 H, d, J 11.0 Hz), 2.07 (1 H, d, J 1.5 Hz), 2.32 (1 H, m), and 6.90—7.28 (10 H, m), ν_{\max} (Nujol) 1 760 cm^{-1} .

(c) *With 1,4-dihydro-1,4-epoxynaphthalene (9)*. A solution of compounds (1b) (770 mg) and (9) (385 mg) in benzene (5 ml) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was recrystallized from benzene to give the *adduct* (17b) (1.14 g, 99%), m.p. 191.0—193.0 °C (Found: C, 85.85; H, 6.45. $\text{C}_{31}\text{H}_{28}\text{O}_2$ requires C, 86.28; H, 6.31%); δ (CDCl_3) 0.84 (6 H, t, J 7.5 Hz), 1.95 (2 H, q, J 7.5 Hz), 2.07 (2 H, q, J 7.5 Hz), 2.36 (2 H, s), 5.48 (2 H, s), and 7.08—7.34 (14 H, m), δ_{C} (CDCl_3) 200.5 (s, CO), ν_{\max} (Nujol) 1 774 cm^{-1} .

(d) *With maleic anhydride (10)*. A solution of compounds (1b) (500 mg) and (10) (170 mg) in benzene (5 ml) was refluxed for 7 h. The solution was concentrated under reduced pressure, and the precipitated *adduct* was recrystallized from benzene–n-hexane to give the *adduct* (22b) (665 mg, 99%), m.p. 153.0—155.5 °C (Found: C, 77.45; H, 5.95. $\text{C}_{25}\text{H}_{22}\text{O}_4$ requires C, 77.70; H, 5.74%); δ (CDCl_3) 1.01 (6 H, t, J 7.5 Hz), 2.02 (2 H, q, J 7.5 Hz), 2.26 (2 H, q, J 7.5 Hz), 3.78 (2 H, s), and 6.96—7.36 (10 H, m), ν_{\max} (Nujol) 1 860 and 1 778 cm^{-1} .

(e) *With N-phenylmaleimide (11)*. A solution of compounds (1b) (832 mg) and (11) (500 mg) in benzene (5 ml) was refluxed for 1 h. The solvent was removed under

reduced pressure and the residue was recrystallized from benzene to give the *adduct* (26b) (1.33 g, 99%), m.p. 179.0—182.0 °C (Found: C, 80.25; H, 5.83; N, 3.21. $\text{C}_{31}\text{H}_{27}\text{O}_3\text{N}$ requires C, 80.67; H, 5.90; N, 3.03%); δ (CDCl_3) 0.96 (6 H, t, J 7.5 Hz), 2.03 (2 H, q, J 7.5 Hz), 2.23 (2 H, q, J 7.5 Hz), 3.58 (2 H, s), and 6.88—7.50 (15 H, m), ν_{\max} (Nujol) 1 719 and 1 776 cm^{-1} .

(f) *With dimethyl acetylenedicarboxylate (12)*. A solution of compounds (1b) (817 mg) and (12) (284 mg) in benzene (5 ml) was refluxed for 17 h. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give the *adduct* (28b) (1.2 g, 99%), m.p. 217.0—219.0 °C (Found: C, 77.3; H, 6.45. $\text{C}_{26}\text{H}_{26}\text{O}_4$ requires C, 77.59; H, 6.51%); δ (CDCl_3) 0.95 (6 H, t, J 7.5 Hz), 2.52 (4 H, q, J 7.5 Hz), 3.90 (6 H, s), and 6.84—7.15 (10 H, m), ν_{\max} (Nujol) 1 734 cm^{-1} .

(g) *With tropone (29)*. A solution of compounds (1b) (816 mg) and (29) (316 mg) in acetone (4 ml) was refluxed for 7 h. The precipitate was recrystallized from acetone to give the *adduct* (32b) (981 mg, 88%), m.p. 144.0—146.0 °C (Found: C, 85.05; H, 6.6. $\text{C}_{28}\text{H}_{26}\text{O}_3$ requires C, 85.25; H, 6.64%); δ (CCl_4) 0.64 (6 H, t, J 7.5 Hz), 1.50 (2 H, q, J 7.5 Hz), 1.82 (2 H, q, J 7.5 Hz), 3.55 (2 H, d, J 6.8 Hz), 5.40—5.60 (2 H, m), 5.87—6.08 (2 H, m), and 6.96—7.30 (10 H, m), ν_{\max} (Nujol) 1 725 and 1 765 cm^{-1} . When (32b) in benzene was refluxed, the pattern of the ^1H n.m.r. spectrum changed as shown below; δ (CCl_4) 0.64 (3 H, t, J 7.5 Hz), 1.16 (3 H, t, J 7.5 Hz), 1.40—1.84 (2 H, m), 2.24 (2 H, q, J 7.5 Hz), 2.75 (1 H, d, J 4.8 Hz), 5.06 (1 H, dd, J 4.8 and 9.0 Hz), 5.80—6.60 (4 H, m), and 6.98—7.40 (10 H, m).

(h) *With 2-chlorotropone (30)*. A solution of compounds (1b) (576 mg) and (30) (300 mg) in benzene (3 ml) was refluxed for 12 h. The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give the *adduct* (34b) (74%), m.p. 117.0—118.0 °C (Found: C, 78.2; H, 5.95. $\text{C}_{28}\text{H}_{25}\text{O}_2\text{Cl}$ requires C, 78.40; H, 5.87%); δ (CDCl_3) 0.68 (3 H, t, J 7.5 Hz), 1.20 (3 H, t, J 7.5 Hz), 1.61 (2 H, q, J 7.5 Hz), 2.48 (2 H, q, J 7.5 Hz), 2.91 (1 H, d, J 4.5 Hz), 5.24 (1 H, dd, J 4.5 and 9.5 Hz), 6.04—6.56 (3 H, m), and 7.12—7.52 (10 H, m), ν_{\max} (Nujol) 1 700 cm^{-1} .

Cycloaddition of MPC (1c) with 1,4-Dihydro-1,4-epoxynaphthalene (9).—A solution of compounds (1c) (1.3 g) and (9) (720 mg) in benzene (3 ml) was refluxed for 3 h. The solvent was distilled off and the residue was recrystallized from chloroform to give the *adduct* (17c) (1.5 g, 78%), m.p. 224.0 °C (Found: C, 84.9; H, 5.9. $\text{C}_{29}\text{H}_{24}\text{O}_2\cdot 1/3\text{H}_2\text{O}$ requires C, 84.77; H, 6.00%); δ (CDCl_3) 1.43 (6 H, s), 2.21 (2 H, s), 5.44 (2 H, s), and 7.16 (14 H, s), ν_{\max} (Nujol) 1 770 cm^{-1} .

Hydrogenation of Adduct (13a) by Lithium Aluminium Hydride.—A solution of compound (13a) (900 mg) and LiAlH_4 (400 mg) in absolute tetrahydrofuran (THF) was refluxed and stirred for 4 h. After the solution had been treated with saturated aqueous ammonium chloride, the THF was distilled off and the residue was extracted with ether. The ether layer was washed with water and dried (MgSO_4). The ether was distilled off, giving a crystalline residue which was recrystallized from methanol to give the *adduct* (14a), m.p. 232.0—233.5 °C (Found: C, 78.55; H, 6.8. $\text{C}_{26}\text{H}_{26}\text{O}_3\cdot 0.5\text{H}_2\text{O}$ requires C, 78.96; H, 6.88%); δ [$(\text{CD}_3)_2\text{CO}$] 1.25 (1 H, d, J 9.3 Hz), 2.35 (2 H, s), 2.58 (1 H, d, J 9.3 Hz), 2.72—2.84 (2 H, m), 3.15 (2 H, t, J 5.0 Hz), 3.82 (4 H, q, J 5.0 Hz), 4.18 (1 H, d, J 3.0 Hz), 4.43 (1 H, d,

J 3.0 Hz), 6.22—6.32 (2 H, m), and 7.02—7.28 (10 H, m), ν_{\max} (Nujol) 3 300 cm^{-1} .

Hydrogenation of the Adduct (13b) by Lithium Aluminium Hydride.—A solution of compound (13b) (800 mg) and LiAlH_4 (600 mg) in absolute ether was refluxed and stirred for 1 h. After the solution had been treated with saturated aqueous ammonium chloride, the ethereal layer was washed with water and dried (MgSO_4). The ether was removed under reduced pressure, giving a crystalline residue which was recrystallized with methanol to give the adduct (14b), m.p. 151.0—153.0 °C, m/e 382 (M^+); δ (CDCl_3) 0.60 (6 H, t, J 7.5 Hz), 1.27br (1 H, s), 1.30 (1 H, d, J 9.4 Hz), 1.68 (4 H, q, J 7.5 Hz), 2.23 (2 H, s), 2.48 (1 H, d, J 9.4 Hz), 2.80—2.92 (2 H, m), 3.77br (1 H, s), 6.30—6.40 (2 H, m), and 7.04—7.40 (10 H, m), ν_{\max} (Nujol) 3 360 cm^{-1} .

Hydrogenation of the Adduct (13b) over 1% Pd-C.—A mixture of compound (13b) and 1% Pd-C in ethanol was hydrogenated on a shaker at room temperature for 24 h. The catalyst was filtered off, and the filtrate was concentrated to a small volume. The residue was recrystallized from ethanol to give the adduct (15b), m.p. 115.0 °C; ν_{\max} (Nujol) 1 765 cm^{-1} ; identical (^1H N.m.r.) with the sample prepared earlier.

Bromination of Adduct (17b).—To a solution of compound (17b) (100 mg) in chloroform was added an excess of bromine at room temperature and the mixture was stirred at the same temperature for 24 h. The chloroform solution was washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and water, and then dried (MgSO_4). The solvent was removed under reduced pressure and the residue was washed with a little *n*-hexane at room temperature, giving the crystalline dibromide (19b) (74 mg, 54%), m.p. 208.0—210.0 °C, the ratio of intensities for m/e 588 ($M^+ - 2$), 590 (M^+), and 592 ($M^+ + 2$) was 1 : 2 : 1, (Found: C, 62.95; H, 4.55. $\text{C}_{31}\text{H}_{28}\text{Br}_2\text{O}_2$ requires C, 62.90; H, 4.76%); δ (CDCl_3) 0.94 (3 H, t, J 7.5 Hz), 1.28 (3 H, t, J 7.5 Hz), 1.36 (1 H, m), 1.88 (1 H, q, J 7.5 Hz), 2.30 (1 H, q, J 7.5 Hz), 3.02 (1 H, dd, J 2.8 and 11.6 Hz), 3.99 (1 H, d, J 11.6 Hz), 4.94 (1 H, d, J 2.8 Hz), 6.88—7.66 (14 H, m), and 8.60 (1 H, d, J 7.5 Hz), ν_{\max} (Nujol) 1 770 cm^{-1} .

Solvolysis of the Dibromide (19b).—A solution of compound (19b) in benzene was refluxed for 1 h and the solvent was removed under reduced pressure and the residue was recrystallized from acetone to give the monobromide (20b), m.p. 257.0—258.0 °C; the values of intensity for m/e 510 (M^+) and 512 ($M^+ + 2$) were equivalent (Found: C, 72.95; H, 5.3. $\text{C}_{31}\text{H}_{27}\text{BrO}_2$ requires C, 72.80; H, 5.32%); δ (CDCl_3) 0.96 (3 H, t, J 7.5 Hz), 1.00 (3 H, t, J 7.5 Hz), 1.20—1.60 (2 H, m), 2.32 (1 H, q, J 7.5 Hz), 2.82 (1 H, dd, J 2.6 and 11.3 Hz), 2.88 (1 H, q, J 7.5 Hz), 3.12 (1 H, dd, J 11.3 and 8.3 Hz), 4.44 (1 H, d, J 8.3 Hz), 4.96 (1 H, d, J 2.6 Hz), and 6.88—7.46 (13 H, m), ν_{\max} (Nujol) 1 765 cm^{-1} .

Hydrogenation of the Adduct (19b) over 5% Pd-C.—A mixture of compound (19b) and 5% Pd-C in ethanol was hydrogenated on a shaker at room temperature for 10 h. The catalyst was filtered off, and the filtrate was concentrated to a small volume. The residue was recrystallized from acetone to give the monobromide (20b), identical (^1H n.m.r.) with the sample obtained from solvolysis of (19b).

Reaction of the Adduct (19b) with Sodium Methanethiolate.—A solution of compound (18b) and an excess of sodium methanethiolate in ethanol was refluxed for 24 h. The solvent was removed under reduced pressure and chloroform was added to the cooled reaction mixture. The chloroform

layer was washed with water and dried (MgSO_4), and the chloroform was removed. Recrystallization of the residual solid from acetone gave the monobromide (20b), identical (^1H n.m.r.) with the product from solvolysis of (19b).

Dilactonization of Compound (22b).—Compound (22b) (1.0 g) was dissolved in a solution of sodium hydroxide (0.35 g) in water (8 ml) containing methanol (1 ml), and the solution was allowed to stand overnight at room temperature. To the solution was added an excess of bromine (0.8 g) at room temperature and the mixture was allowed to stand for 2 h. A precipitate product was recrystallized from ethanol to give the bis-carbolactone (24b) (350 mg, 34%), m.p. 286.0—288.0 °C, m/e 402 (M^+) (Found: C, 74.25; H, 5.45. $\text{C}_{25}\text{H}_{23}\text{O}_5$ requires C, 74.43; H, 5.75%); δ [$(\text{CD}_3)_2\text{CO}$] 0.76 (6 H, t, J 7.5 Hz), 1.74 (2 H, q, J 7.5 Hz), 2.04 (2 H, q, J 7.5 Hz), 3.82 (2 H, s), and 7.04 (10 H, s), ν_{\max} (Nujol) 1 770 and 1 810 cm^{-1} .

Conversion of the Adduct (22b) into Compound (26b).—A solution of compound (22b) (455 mg) and aniline (111 mg) in ether (20 ml) was allowed to stand overnight at room temperature. After the solvent had been removed under reduced pressure, anhydrous sodium acetate (500 mg) and acetic anhydride (2 ml) were added to the residue, and the mixture was heated on a water bath at 95 °C for 3 h. The mixture was then poured into ice-water (100 ml), and the precipitate was recrystallized from benzene-*n*-hexane to give the aza-compound (26b) (226 mg, 42%), m.p. 184.0—186.0 °C (Found: C, 80.4; H, 5.9; N, 3.05. $\text{C}_{31}\text{H}_{27}\text{NO}_3$ requires C, 80.67; H, 5.90; N, 3.03%), identical (^1H n.m.r.) with the sample prepared previously.

Bromination of the Adduct (17c).—To a solution of compound (17c) (500 mg) in carbon tetrachloride was added an excess of bromine at room temperature and the mixture was stirred at the same temperature for 24 h. The solution was washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and water, and then dried (MgSO_4). The solvent was distilled off and the residue was recrystallized from chloroform to give the bromide (20c) (581 mg, 97%), m.p. 296—297 °C; the values of intensity for m/e 482 (M^+) and 484 ($M^+ + 2$) were equivalent (Found: C, 72.1; H, 4.65. $\text{C}_{29}\text{H}_{23}\text{BrO}_2 \cdot \text{HBr}$ requires C, 72.01; H, 4.80%); δ (CDCl_3) 1.38 (3 H, s), 1.39 (3 H, s), 2.43 (1 H, dd, J 2.7 and 11.3 Hz), 2.86 (1 H, dd, J 11.3 and 8.5 Hz), 4.52 (1 H, d, J 8.5 Hz), 5.00 (1 H, d, J 2.7 Hz), and 7.00—7.60 (13 H, m), ν_{\max} (Nujol) 1 770 cm^{-1} .

Kinetic Measurements.—The progress of each Diels-Alder reaction was followed quantitatively by observing the rate of disappearance of the $n \rightarrow \pi^*$ absorption maximum of the cyclopentadienones [(1a) and (1b)] in the visible region [430 and 420 nm for (1a) and (1b), respectively]. A Hitachi EPS-3T spectrometer equipped with an interval timer and with a constant-temperature cell-compartment maintained at appropriate temperature was used for all absorption measurements, and the thermostat temperature was maintained to ± 0.1 °C. Standard solutions of cyclopentadienones [1.0×10^{-3} and 2.0×10^{-3} mol l^{-1} for (1a) and (1b), respectively], and dienophiles were thermostatted for 1 h before the kinetic experiment. The rate constants were calculated from the slopes of plots of $\log(a - x/b - x)$ vs. time.

Molecular-orbital Calculations.—Molecular wave functions were calculated using the semi-empirical Pariser, Parr, and Pople SCF molecular-orbital method employing the original parameterization given by Pople *et al.*¹¹ In the present study, standard bond lengths and angles were used to

estimate geometries. The bond angles for cyclopentadienone were assumed as follows: C(5)-C(1)-C(2), 108.0°; C(1)-C(2)-C(3), 106.0°; C(2)-C(3)-C(4), 109.9°.

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