J. Org. Chem. **1980**, *45*, 659-664

High Peri- and Regiospecificity of Phencyclone: Kinetic Evidence of the Frontier-Controlled Cycloaddition Reaction and Molecular Structure of the Cycloadduct

Masami Yasuda, Kazunobu Harano, and Ken Kanematsu*

Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi, Higashi-ku, Fukuoka, 812, Japan

Received June 27, 1979

Phencyclone (2-oxo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthrene, **1a**) demonstrates a high reactivity for dienophiles of the styrene family, as well as a number of cyclic olefins, to give endo [4 + 2]π cycloadducts specifically. The configuration of the adducts was assigned after the spectra and properties of the adducts were found to be comparable to those of one determined crystallographically. In these reactions, the substituent effects on the reaction rate were examined by using para-substituted styrenes **3a–h** and 2-oxo-1,3-bis(para-substituted phenyl)-2*H*-cyclopenta[*l*]phenanthrenes **1b,c**. The pseudo-first-order rate constants of these reactions were obtained by following the decrease of the absorption band in the visible region by UV spectrometry. It is observed that the reaction was slowest for the unsubstituted styrene and faster when either electron-withdrawing or -donating substituents were present. We carried out LCAO MO calculations for the reactants and discuss the correlation between the kinetic data and the energies of the frontier orbitals of the reactants. Phencyclone is found to have a high reactivity toward dienophiles, and the specificity is discussed in terms of the following controlling factors: (1) HOMO–LUMO control, (2) secondary orbital interaction, (3) steric interaction, (4) dipole–dipole interaction, (5) coplanarity.

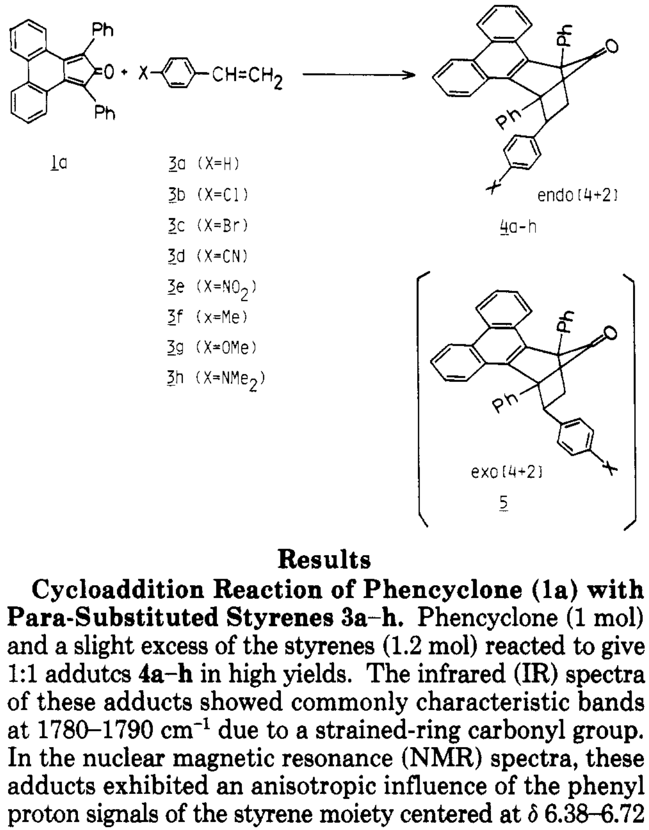
Sustmann[1] first applied a frontier molecular orbital (FMO) concept to reactivity in 1,3 dipolar cycloadditions and Diels–Alder reactions and classified these allowed reactions into three types of cycloadditions according to the relative positions of the frontier orbitals of the reagents (Figure 1). In the normal Diels–Alder reaction (type A), the interactions LUMO–dienophile and HOMO–diene are the dominant stabilizing factor. For the inverse type reaction (type C) the predominant interactions become HOMO–dienophile and LUMO–diene. A third type of orbital arrangement for a Diels–Alder reaction might be called neutral (type B). The HOMO–LUMO separations are similar; therefore, electron attraction and release should increase the reactivity. Typical examples of each type, mainly the A type, have been investigated from the kinetic point of view, and the results have been rationalized in terms of the frontier orbital interactions.[2] However, B- and C-type cycloadditions have been investigated far less.

In the previous paper,[3] we have investigated the cycloaddition reactions of phencyclone with various dienophiles by the qualitative frontier orbital analysis and indicated that phencyclone (**1a**) is a more reactive and stable compound than other cyclopentadienone derivatives (**2**, Figure 2) and that the reaction can be rationalized as a "neutral" Diels–Alder, i.e., B-type, reaction where both electron-releasing and -attracting substituents on the dienophile accelerate the reaction rate.

Quantitative studies seem to be necessary for a more precise discussion of the cycloaddition reactions of phencyclone (**1a**).

In this paper, we wish to discuss the kinetic and MO calculation data of the reaction between phencyclones **1a–c** and para-substituted styrenes **3a–h**, very suitable model compounds for examination of substituent effects of dienophilicity (Scheme I).

Scheme I



Results

Cycloaddition Reaction of Phencyclone (1a) with Para-Substituted Styrenes 3a–h. Phencyclone (1 mol) and a slight excess of the styrenes (1.2 mol) reacted to give 1:1 addutcs **4a–h** in high yields. The infrared (IR) spectra of these adducts showed commonly characteristic bands at 1780–1790 cm^{-1} due to a strained-ring carbonyl group. In the nuclear magnetic resonance (NMR) spectra, these adducts exhibited an anisotropic influence of the phenyl proton signals of the styrene moiety centered at δ 6.38–6.72 because of the phenanthrene ring-current effect, suggesting the endo [4 + 2]π structure for the adducts (Figure 3). This has been verified by X-ray crystallography as described below. The appearance of the triplet at δ 8.72 of H_F indicated the formation of the phenanthrene ring by cycloaddition of **1a** with **3c** and suggested the endo configuration of the adduct **4c**. The physical data were summarized in Tables I and II.

Kinetics of the Cycloaddition Reactions. Reactions of 1a–c with 3a–h. The pseudo-first-order rate constants of these reactions in chlorobenzene at 34.1 °C were obtained by following the disappearance of the absorption

---

(1) Sustmann, R. *Tetrahedron Lett.* **1971**, 2717, 2721.

(2) (a) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16. (b) Desimoni, G.; Gamba, A.; Monticelli, M.; Nicola, M.; Tacconi, G. *J. Am. Chem. Soc.* **1976**, *98*, 2947 and references cited therein.

(3) Sasaki, T.; Kanematsu, K.; Iizuka, K. *J. Org. Chem.* **1976**, *41*, 1105.

(4) Harano, K.; Ban, T.; Yasuda, M.; Kanematsu, K. *Tetrahedron Lett.* **1978**, 4037.

0022-3263/80/1945-0659$01.00/0

Table I. IR Spectra, Physical Constants, and Elemental Analyses of Cycloadducts 4a-h

compd	ν_{max},[c] cm^{-1} (C=O)	mp (dec), °C	anal.[d] C	H	N
4a (X = H)	1777	261-267	91.33 91.37	5.39 5.50	
4b (X = Cl)	1781	243-250.5	85.29 85.36	4.84 4.92	
4c (X = Br)	1783	253-257	78.58 78.65	4.46 4.57	
4d (X = CN)[a]	1782	239-246	87.67 87.69	5.03 5.15	2.69 2.60
4e (X = NO_2)[b]	1777	262-265.5	80.85 80.57	4.95 4.68	2.55 2.47
4f (X = Me)	1777	231.5-235	91.18 91.10	5.64 5.64	
4g (X = OMe)	1783	238-244	88.34 88.29	5.46 5.71	
4h (X = NMe_2)	1781	236-238	88.44 88.25	5.90 5.83	2.64 2.76

[a] $C_{38}H_{25}NO\cdot{}^1/_2H_2O$. [b] $C_{37}H_{25}NO_3\cdot H_2O$. [c] In Nujol. [d] The calculated value is given first and the found value underneath it.

band of phencyclone in the visible region by ultraviolet (UV) spectrometry. The second-order rate constants were calculated according to usual method.

The second-order rate constants (k_2) and the relative rates (log k_2/k_2(H)) are summarized in Tables III and IV.

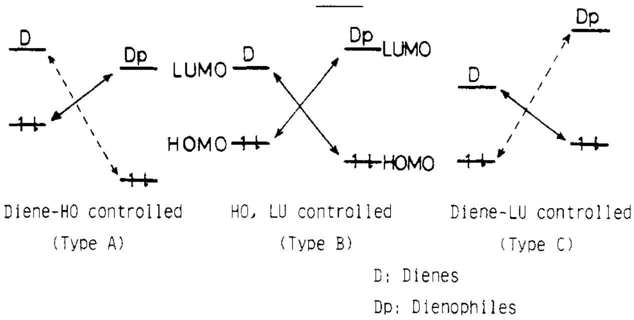
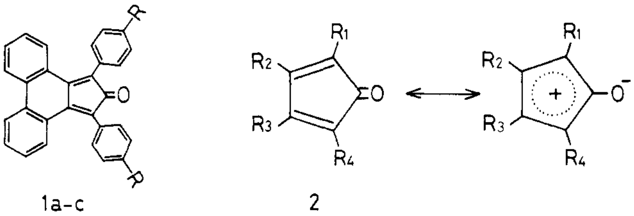


Figure 1. Frontier orbitals in direct (A), neutral (B), and inverse (C) cycloadditions.



1a-c
1a:R=H
1b:R=Cl
1c:R=OMe

2

Figure 2.

Streitwieser has reviewed the effect of substituent on the ionization potentials (or HOMO energies) of substituted aromatics;[5] good correlation is found for ionization

Table II. NMR Data[a] for Cycloadducts 4a-h[c]

compd	chemical shift, δ[b]
4a (X = H)	2.39 (dd, 1 H, J_{AB} = 12, H_A), 3.53 (dd, 1 H, J_{BC} = 10, H_B), 4.48 (dd, 1 H, J_{CA} = 6, H_C), 6.60-8.00 (m, 21 H, aromatic H), 8.72 (t, 2 H, J = 8, 2 H_F)
4b (X = Cl)	2.30 (dd, 1 H, J_{AB} = 12, H_A), 3.54 (dd, 1 H, J_{BC} = 10, H_B), 4.46 (dd, 1 H, J_{CA} = 6, H_C), 6.56, 6.82 (AB q, 4 H, J = 8.5, 2 H_D, 2 H_E), 6.68-7.88 (m, 16 H, aromatic H), 8.74 (t, 2 H, J = 8, 2 H_F)
4c (X = Br)	2.27 (dd, 1 H, J_{AB} = 12, H_A), 3.51 (dd, 1 H, J_{BC} = 10, H_B), 4.41 (dd, 1 H, J_{CA} = 6, H_C), 6.50, 6.94 (AB q, 4 H, J = 8.5, 2 H_D, 2 H_E), 6.68-7.88 (m, 16 H, aromatic H), 8.72 (t, 2 H, J = 8, 2 H_F)
4d (X = CN)	2.35 (dd, 1 H, J_{AB} = 12, H_A), 3.56 (dd, 1 H, J_{BC} = 10, H_B), 4.55 (dd, 1 H, J_{CA} = 6, H_C), 6.72, 7.12 (AB q, 4 H, J = 8, 2 H_D, 2 H_E), 6.88-7.84 (m, 16 H, aromatic H), 8.76 (t, 2 H, J = 8, 2 H_F)
4e (X = NO_2)	2.21 (dd, 1 H, J_{AB} = 12, H_A), 3.38 (dd, 1 H, J_{BC} = 10, H_B), 4.41 (dd, 1 H, J_{CA} = 6, H_C), 6.62, 6.76 (AB q, 4 H, J = 8, 2 H_D, 2 H_E), 6.64-7.72 (m, 16 H, aromatic H), 8.64 (t, 2 H, J = 8, 2 H_F)
4f (X = Me)	2.16 (dd, 1 H, J_{AB} = 12, H_A), 2.32 (dd, 1 H, J_{BC} = 10, H_B), 3.52 (dd, 1 H, J_{CA} = 6, H_C), 6.52, 6.68 (AB q, 4 H, J = 8, 2 H_D, 2 H_E), 6.80-7.94 (m, 16 H, aromatic H), 8.73 (t, 2 H, J = 7, 2 H_F)
4g (X = OMe)	2.17 (dd, 1 H, J_{AB} = 12, H_A), 3.02 (dd, 1 H, J_{BC} = 10, H_B), 4.16 (dd, 1 H, J_{CA} = 6, H_C), 6.24, 6.52 (AB q, 4 H, J = 9, 2 H_D, 2 H_E), 6.68-8.04 (m, 16 H, aromatic H), 8.52 (t, 2 H, J = 8, 2 H_F)
4h (X = NMe_2)	2.30 (dd, 1 H, J_{AB} = 12, H_A), 2.72 (dd, 1 H, J_{BC} = 10, H_B), 3.50 (dd, 1 H, J_{CA} = 6, H_C), 6.22, 6.50 (AB q, 4 H, J = 9, 2 H_D, 2 H_E), 6.72-8.00 (m, 16 H, aromatic H), 8.72 (t, 2 H, J = 8, 2 H_F)

[a] Solvent $CDCl_3$. [b] J values are given in Hz. [c] See Figure 3 for atom labels.

Table III. Rate Constants (10^3k_2[a]) for Cycloaddition Reactions of 1a-c with *p*-Substituted Styrenes 3a-h

	Y (σ_p^+)[b]							
	NMe_2 (−1.7)	OMe (−0.778)	Me (−0.311)	H (0.0)	Cl (0.114)	Br (0.150)	CN (0.659)	NO_2 (0.790)
1a (R = H)	69.5	8.95	5.22	3.12	4.30	4.61	4.78	9.91
1a (R = Cl)	118	12.5	6.94	4.10	4.84	5.07	4.91	6.97
1c (R = OMe)	47.9	8.24	5.06	3.25	4.90	5.25	7.83	12.6

[a] Mol^{-1} s^{-1}. [b] Brown-Okamoto value in parentheses.

Table IV. Relative Rates (log k_2/k_2(H)) for Cycloaddition Reactions of 1a-c with *p*-Substituted Styrenes 3a-h

	Y (σ_p^+)[a]							
	NMe_2 (−1.7)	OMe (−0.778)	Me (−0.311)	H (0.0)	Cl (0.114)	Br (0.150)	CN (0.659)	NO_2 (0.790)
1a (R = H)	1.35	0.47	0.22	0.0	0.14	0.17	0.34	0.50
1b (R = Cl)	1.47	0.49	0.24	0.0	0.07	0.10	0.08	0.24
1c (R = OMe)	1.17	0.40	0.19	0.0	0.18	0.21	0.38	0.59

[a] Brown-Okamoto value in parentheses.

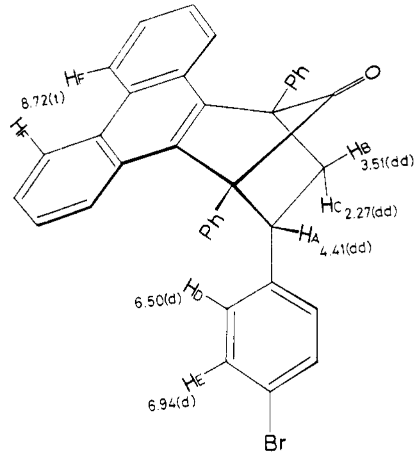


Figure 3. Endo [4 + 2]π cycloadduct **4c**.

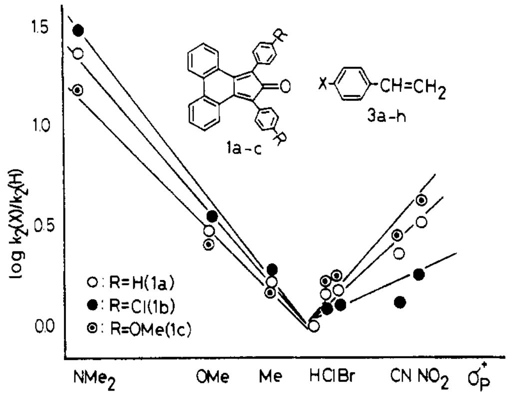


Figure 4. Plot of log k_2/k_2(H) Against σ_p^+ for cycloaddition reactions of **1a–c** with **3a–h**.

potentials as a function of the σ_p^+ parameter.[2b]

The substituent effects of **1** and **3** on the cycloaddition reaction rates were examined by plotting log k_2/k_2(H) against σ_p^+. As can be seen in Figure 4, linear correlations were obtained both in electron-rich styrenes [**3f–h**, negative slope ($\rho_{1a} = -0.79$, $\rho_{1b} = -0.86$, $\rho_{1c} = -0.69$)] and in electron-deficient styrenes [**3b–e**, positive slope ($\rho_{1a} = 0.59$, $\rho_{1b} = 0.27$, $\rho_{1c} = 0.68$)]. The reaction rate was a minimum for unsubstituted styrene (**3a**), and the correlation showed a V-shaped line.

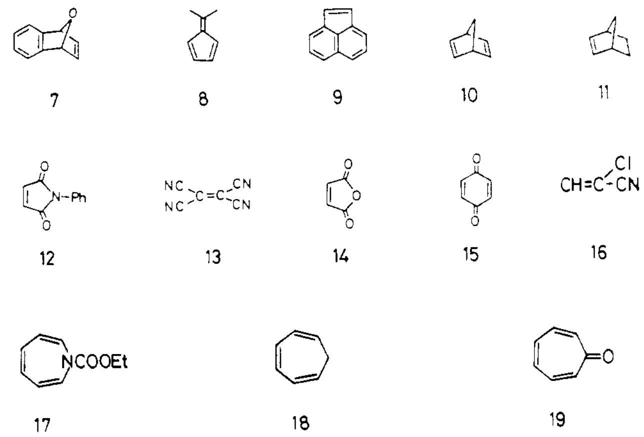
Chloro-substituted phencyclone (**1b**) reacts fastest in the $\sigma_p^+ < 0$ region but slowest in the $\sigma_p^+ > 0$ region, whereas the reverse is true for methoxy-substituted phencyclone (**1c**).

These facts may be attributed to the change of the frontier energy level on introduction of the substituent[1] (Cl, OMe) on **1a**.

Reactions of 1a with Various Dienophiles. In the cycloadditions of phencyclone (**1a**) with a variety of olefins involving seven-membered-ring unsaturated polyenes, phencyclone behaves as a 4π component, showing high peri- and regiospecificity.[3,4]

The rates of reaction of phencyclone (**1a**) with dienophiles **7–19** (Chart I) were obtained by essentially the same method as that described for the case of styrenes. The results were listed in Table V. A plot of the rate constants against the energy of the HOMO of a wide variety of olefins, which could be estimated by HMO calculations, also gave a U-shaped curve[1] (Figure 5). In conclusion, we can safely say that the behavior of phencyclone (**1a**) with various olefins is explained in terms of a "neutral" Diels–Alder, i.e., B-type, reaction.

Chart I



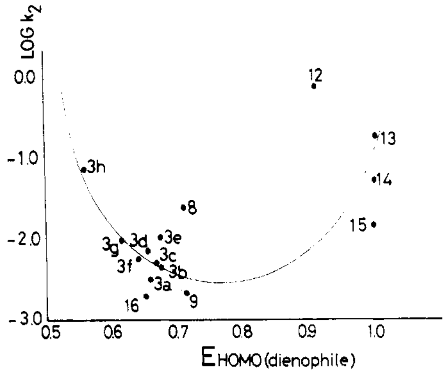


Figure 5. Plot of log k_2 for cycloaddition reactions against the E_{HOMO} of various olefins.

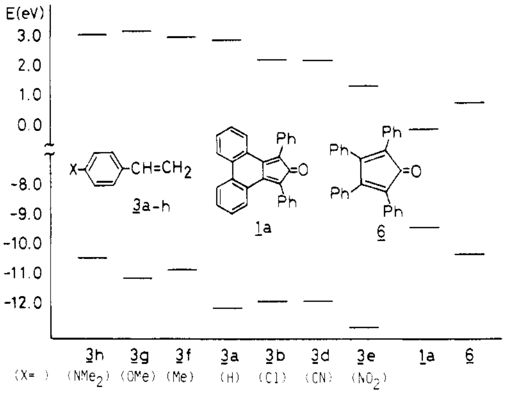


Figure 6. Frontier orbital energy levels calculated by the CNDO/2 MO Method.

With respect to the reactivity of seven-membered-ring unsaturated compounds toward phencyclone (**1a**), *N*-(ethoxycarbonyl)azepine (**17**) reacted much faster than the others (Table V). Thus phencyclone (**1a**) shows high reactivity toward the unsaturated ring compounds in comparison with other cyclopentadienones.

MO Calculations. The calculations reported here were carried out by HMO,[5] PPP MO,[6] and CNDO/2 MO[7] methods.

The orbital energies for the related compounds studied here are shown in Figure 6 and Table VI.

---

[5] Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961.

[6] (a) Parr, R. G. "The Quantum Theory of Molecular Electronic Structure"; W. A. Benjamin: New York, 1963. (b) Two-center repulsion integral (*rr*|*ss*): Nishimoto, K.; Mataga, N. *Z. Phys. Chem.* (*Frankfurt am Main*) **1957**, *13*, 140. (c) Core resonance integral (β_{rs}): Wolsberg, M.; Helmholtz, L. *J. Chem. Phys.* **1952**, *20*, 837.

[7] Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

Table V. Rate Constants for Cycloaddition Reactions of Phencyclone (1a) with Various Olefins and Calculated HOMO Energy Levels[a] by the HMO Method

compd	k_2[b] (log k_2)	HOMO[c]	compd	k_2[b] (log k_2)	HOMO[c]
7	2.14×10^{-2} (−1.55)		14	4.84×10^{-2} (−1.32)	0.649
8	2.32×10^{-2} (−1.63)	0.710	15	1.35×10^{-2} (−1.87)	1.015
9	2.05×10^{-3} (−2.69)	0.715	16	1.73×10^{-3} (−2.76)	1.000
10	8.15×10^{-4} (−3.09)		17	2.03×10^{-3} (−2.69)	
11	2.35×10^{-4} (−3.63)		18	3.27×10^{-4} (−3.49)	
12	1.41 (0.15)	0.912	19	1.80×10^{-4} (−3.47)	
13	1.73×10^{-1} (−0.76)	1.009			

[a] $E = \alpha + \lambda\beta$. [b] $\mathrm{Mol^{-1}\,s^{-1}}$. [c] In β. The heteroatomic parameters were taken from ref 19.

Table VI. FMO Energy Levels of *p*-Substituted Styrenes 3a–h, Phencyclone (1a), and Tetracyclone (6) Calculated by HMO,[5] PPP MO,[6] and CNDO/2 MO[7] Methods

		3a	3b	3c[a]	3d	3e	3f	3g	3h	1a[a]	6
HMO	LUMO[b]	−0.662	−0.640	−0.645	−0.596	−0.412	−0.659	−0.668	−0.683	−0.339	−0.415
	HOMO[b]	0.662	0.674	0.669	0.656	0.686	0.640	0.615	0.554	0.449	0.569
PPP	LUMO[c]	−1.59	−1.46	−0.86	−2.10	−3.39	−1.72	−1.46	−1.46	−3.89	−3.61
	HOMO[c]	−9.60	−9.32	−8.27	−9.67	−8.53	−9.47	−9.20	−8.76	−8.50	−8.90
CNDO/2	LUMO[c]	2.84	2.07		2.06	1.16	2.92	3.06	−3.02	−0.22,[d] −0.51[e]	0.59,[d] 0.21[e]
	HOMO[c]	−12.13	−11.93		−11.94	−12.81	−10.91	−11.13	−10.50	−9.50,[d] −8.51[e]	−10.40,[d] −9.96[e]

[a] For technical reasons, CNDO/2 MO calculations could not be performed on 1b, 1c, and 3c. [b] In β. [c] In eV. [d] Rotational conformer (80°). See also ref 8. [e] Rotational conformer (30°). See also ref 8.

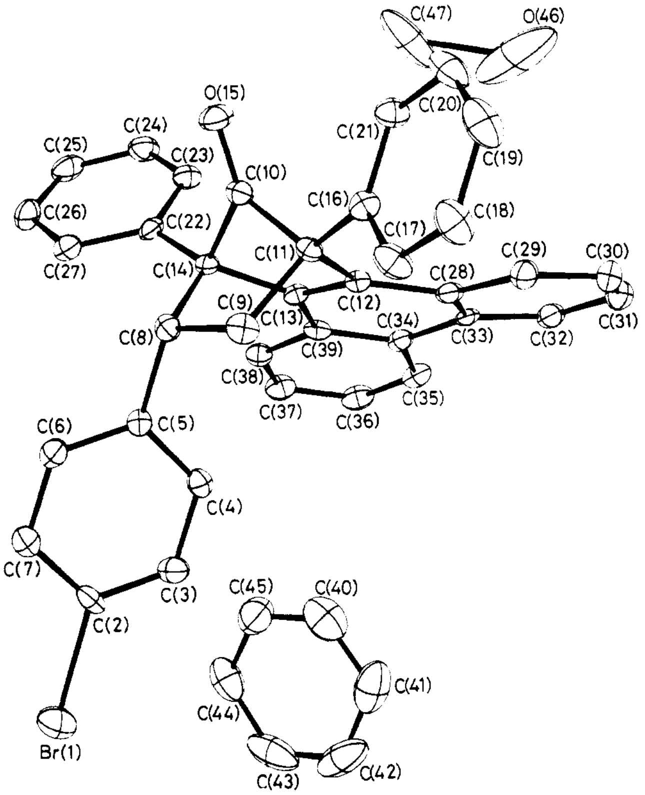


Figure 7. ORTEP drawing of endo [4 + 2]π cycloadduct **4c**.

In the CNDO/2 MO method, calculations on conformational changes were also considered in which phenyl groups were rotated by 30–80°[8] with respect to the planes of cyclopentadienones, wherein considerable energy separation was observed (Table VI).

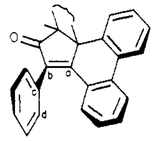
As can be seen in Figure 6, the frontier molecular orbital (FMO) energy difference (HOMO–LUMO) of phencyclone (**1a**) is very narrow and is situated among the FMO energy levels of the para-substituted styrenes **3a–h**. The prediction for the reactivities based on the MO calculations is compatible with the kinetic data supporting the proposal that phencyclone (**1a**) participates in a neutral-type cycloaddition (type B in Figure 1).

Crystallographic Study. As described above, the NMR spectra of the cycloadducts of phencyclone (**1a**) with various olefins showed some characteristic spectral patterns.

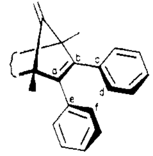
The magnetic anisotropy alone cannot characterize the relative proximity and orientations of the plane of the

---

[8] (a) On the basis of X-ray results and total energies calculated by the CNDO/2 MO approximation, it seems reasonable to expect that the ground-state conformation of **6** is one in which the phenyl groups are rotated by 60° out of the plane of cyclopentadienone; X-ray results of the [2 + 4]π^4 (A) and [4 + 6]π^4 (B) cycloadducts from *N*-(ethoxycarbonyl)-



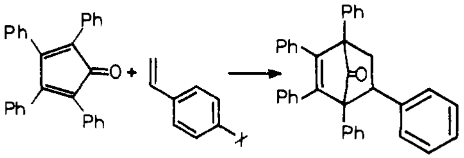
A, $\phi_f(C_aC_bC_cC_d) = 80°$



B, $\phi_r(C_aC_bC_cC_c) = \phi_r(C_bC_aC_eC_f) = 60°$

azepine and phenyl-substituted cyclopentadienones similar to **6** indicate the dihedral angles (ϕ_r) shown. The calculations of total energy for conformational isomers of **1a** in which phenyl groups were rotated by 30° (**1a**-1) to 80° (**1a**-2) out of the plane of cyclopentadienone indicate that **1a**-1 is less stable by 3 eV than **1a-2**, which can be understood from the degree of van der Waals repulsion between the hydrogen atoms on the phenyl groups and the phenanthrene ring. (b) Alston P. V. *J. Org. Chem.* 1978, *43*, 1864.

Scheme II



6 3

X :	NMe_2	OMe	H	Cl	NO_2
k_2 (x 10^6 $mol^{-1}sec^{-1}$):	338	102	73	78	88

aromatic rings in the endo and exo isomers[2b] (Scheme I).

Therefore, in order to elucidate the complete stereostructure of a cycloadduct and to account for the spectroscopic data, a crystallographic analysis was carried out for the cycloadduct of phencyclone (**1a**) and *p*-bromostyrene (**3c**).

The structural analysis showed that the crystals contained three kinds of molecules: the adduct, benzene, and methanol. The configuration of the adduct with the numbering sequence used in this paper is illustrated in Figure 7 where each atom is represented as an ellipsoid with 20% probability. The molecular structure was confirmed as the endo [4 + 2]π cycloadduct.

The bond lengths of cycloadduct **4c** have the normal values. The bicyclo[2.2.1]hepta-7-one moiety is strained considerably. In the absence of strain, the bond angle of C–CO–C would be ca. 120°, but this angle is reduced to 99.2 ± 0.7°. This agrees with the IR band for the carbonyl at 1777 cm^{-1}.

The dihedral angle between the plane through atoms C(28), C(29), C(30), C(31), C(32), and C(33) and the plane through atoms C(34), C(35), C(36), C(37), C(38), and C(39) is 12.5°, causing the boat deformation of the central phenyl ring of the phenanthrene ring. As a result, the carbon atoms C(12) and C(28) lie about 0.2 Å above the best plane through carbon atoms C(13), C(39), C(34), and C(33). These facts suggest that the low-field resonance of two aromatic methine protons is magnetically nonequivalent and is ascribable to the H(32) and H(35) methine protons. The observed anisotropic effect on H(4) [H(6)] in the NMR spectra described above could arise from its position just below the aromatic carbon, C(13), and about 2.5 Å from the plane of the phenanthrene ring (Table IX, see supplementary material).

Discussion

As described above, the reaction was the slowest for unsubstituted styrene (**3a**) and was faster when either electron-donating or -withdrawing substituents were present. These facts may be attributed to the change of the frontier energy level on introduction of the substituents on **1a** and **3a**. Moreover, with respect to various olefins, phencyclone (**1a**) reacts rapidly with electron-poor and electron-rich olefins but slowly with a cyclic olefin. These facts suggest that the cycloaddition reactions of phencyclone (**1a**) with olefins were controlled by neutral electron demand.

Recently, Konovalov[9] has observed a similar trend for the reactions of tetracyclone (2,3,4,5-tetraphenylcyclopentadienone, **6**) with para-substituted styrenes at 60 °C (Scheme II).

The expected relative reactivities of tetracyclone (**6**) and phencyclone (**1a**) based on frontier orbital arguments are of interest.

The PPP MO calculations show that the frontier orbitals of **6** have approximately the same energy as those of **1a** (Table VI). Therefore, qualitative similarities in reactivity between the two compounds are expected, but the rates of reaction do not support this assumption.

Phencyclone (**1a**) reacts 50–200 times faster than tetracyclone (**6**) with a series of para-substituted styrenes even at a temperature of 25 °C or lower.

In order to account for the reactivity and specificity in the cycloadditions of phencyclone (**1a**), we have considered several controlling factors such as frontier orbital[1,10] (HOMO–LUMO), secondary orbital,[11] dipole–dipole,[12] and steric[12] interactions between reactants.

Of these controlling factors, dipole–dipole interactions may be negligible since there is little difference in both the direction and the magnitude[13] of the dipole moments.

The marked difference in reactivity between phencyclone (**1a**) and tetracyclone (**6**) may be accounted for by consideration of the actual geometries of the reactants. According to the CNDO/2 MO calculations on the nonplanar geometries of **1a** and **6**, considerable energy separation is observed; the calculations indicate a 0.9-eV lowering of the HOMO and a 0.8-eV raising of the LUMO for tetracyclone (**6**) as compared to phencyclone (**1a**) (see Table VI). Thus, the nonplanar conformation of tetracyclone (**6**) affects not only the FMO energy separation but also the steric interaction closely related to secondary orbital interaction, resulting in low additivity to dienophiles. In fact, **6** shows little reactivity toward nonplanar seven-membered-ring unsaturated compounds such as cycloheptatriene, tropone, azepine, and cyclooctatetraene in their pericyclic reactions.

In cycloaddition reactions of phencyclone (**1a**) with various olefins, only endo isomers were observed, owing to the greatly enhanced secondary orbital interactions.

From the facts stated above, we can draw the following conclusion: the source of the high reactivity and specificity of phencyclone (**1a**) in the cycloadditions will be not only due to the narrow frontier orbital separation but also due to the effectiveness of secondary orbital interactions assisted by a coplanarity effect.

In addition to these, energetic preference of formation of the fused phenanthrene ring resonance in the cycloadduct might also promote the reactivity.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. The UV spectra were determined with a Hitachi EPS-3T spectrophotometer. The NMR spectra were taken with a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard, and the chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO DS-701G infrared spectrophotometer. Mass spectra were obtained with a JEOL JMS-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C.

Preparation of Styrenes (3a–h). *p*-Chlorostyrene (Nakarai Kagaku Co.), *p*-methylstyrene (Tokyo Kasei Co.), and styrene (Kanto Kagaku Co.) were used after distillation.

p-Bromo-,[14] *p*-cyano-,[15] *p*-nitro-,[16] and *p*-methoxystyrene[16] were

---

[9] Konovalov, A. I.; Solomonov, B. N. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1973**, *211*, 1115.

[10] (a) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301. (b) Houk, K. N.; Luskus, L. J. *J. Org. Chem.* **1973**, *38*, 3836.

[11] Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797.

[12] Watson, P. L.; Warrener, R. N. *Aust. J. Chem.* **1973**, *26*, 1725.

[13] Calculated dipole moment by PPP MO method: **1a**, –2.63 D; **6**, –2.78 D.

[14] Overberger, C. G.; Saunders, J. H. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 204.

prepared according to the established methods.

p-(Dimethylamino)styrene was prepared by a Wittig reaction.[17] Sodium methylsulfinyl carbanion was prepared under nitrogen from 0.05 mol of sodium hydride and 25 mL of dimethyl sulfoxide. The solution was cooled in an ice bath and stirred during the addition of 20.2 g (0.05 mol) of methyltriphenylphosphonium iodide in 50 mL of dimethyl sulfoxide, whereupon the deep yellow color of the methylenetriphenylphosphorane was produced. After stirring at room temperature for 70 min, 7.46 g (0.05 mol) of *p*-(dimethylamino)benzaldehyde was added, and stirring was continued for 3.5 h at room temperature. About 100 mL of cold water was poured into the reaction mixture, and the precipitated solid was filtered off. The liquid was extracted with 100-mL portions of ether, and the extract was washed once with water, dried over anhydrous magnesium sulfate, evaporated, and filtered through 20 g of neutral alumina by using 50 mL of petroleum ether to elute the product. Evaporation of the petroleum ether gave about 5.20 g (71%) of the product (**3h**) as a light yellow liquid. This compound was identified by comparing its IR spectrum with that of an authentic sample.[18]

Cycloaddition Reactions of Phencyclone (1a) with Various Olefins. General Procedure for Cycloaddition. A solution of phencyclone[3] (**1a**) and a slight excess amount of dienophiles was stirred at room temperature until the deep green color had faded away. The mixture was diluted with methanol, and the precipitated solid was filtered off and purified by recrystallization.[3]

Phencyclone–Styrene Adducts 4a–h. The adducts of **4a–h** were prepared according to the general procedure by use of a slight excess amount of styrenes **3a–h**. The results were summarized in Tables I and II.

Kinetics. A chlorobenzene solution (4 mL) containing phencyclone (**1a**; 1×10^{-3} M) and styrene (1×10^{-2} M) was prepared. Pseudo-first-order conditions were maintained by using a 100:1 ratio of alkene to phencyclone derivatives in chlorobenzene solvent. The rate was followed at a given temperature by the loss of the long-wavelength absorbance of phencyclone chromophore in the visible spectrum (630 nm) by using a 10 × 10 mm quartz cell which was thermostated with flowing water at constant temperature. All spectra were calculated by means of a nonweighted least-squares program (see Table III).

Method of MO Calculations. In the HMO calculations, Streitwieser's empirical parameters[5] were used with the exception of heteroatomic parameters.[19] In the case of PPP MO calculations, values for the one-center coulomb repulsion integral, the valance-state ionization potential, and the effective nuclear charge used in the calculation were those reported by Kwiatkowski.[20] The methyl group was treated as a hyperconjugation model.[21] Values for atomic distances and bond angles in the cyclopentadienone ring were taken from the X-ray results of the anti–endo $[2 + 4]\pi$ cycloadduct[4] of phencyclone (**1a**) and azepine (**17**) and those of the phenanthrene ring from the endo $[4 + 2]\pi$ cycloadduct **4c**.

The optimum geometry of tetracyclone (**6**) was determined from X-ray results,[22] in which the 3- and 4-phenyl substituents were rotated by 60°[8] out of the plane of cyclopentadienone.

The geometries of *p*-substituted styrenes were assumed to be planar, and distances and angles were taken from the standard values reported,[7] with the exception of *p*-nitro-,[23] *p*-cyano-,[24] and *p*-methoxystyrene.[25]

X-ray Crystallography. Single crystals of the compound **4c** were prepared by slow evaporation of a benzene–methanol solution at room temperature. Crystals of the compound **4c** are colorless parallelepipeds. The density was measured by flotation in an aqueous potassium iodide solution.

The cell constants were found by a least-squares procedure using the values of the Bragg angles of 15 reflections. The space group $P\bar{1}$ was selected from the number of molecules per unit cell ($Z = 2$) and was later confirmed in the course of the structure refinement. Crystals of the adduct **4c** are triclinic with the following unit-cell parameters: $a = 13.227$ (4) Å, $b = 13.777$ (4) Å, $c = 12.876$ (4) Å, $\alpha = 97.56$ (3)°, $\beta = 128.26$ (2)°, $\gamma = 101.34$ (2)°, $d_{\text{exptl}} = 1.303$ g cm^{-1} (KI), $d_{\text{calcd}} = 1.315$ g cm^{-3}, $V = 1706$ (1) Å^3. Intensity data were collected on a Syntex P$\bar{1}$ automated diffractometer with Mo Kα radiation monochromatized with a graphite crystal and by using θ–2θ scans to a limit of $2\theta = 55°$. A variable scan rate from 24.0 to 4.0 °/min was used. Three reflections were monitored after every measurement of 97 reflections. Of 3836 independent reflections, 2546 were treated as observed ($I > 2.5\sigma(I)$). 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 amplitudes, $|E|$ values, by use of the scale factor and the overall temperature factor obtained from Wilson's statistics.[26] The structure was solved by the direct method using the MULTAN series of programs.[14] An E map calculated with 455 signed E's ($|E| \geq 1.6$), which gave the absolute figure of merit (ABS FOM) 1.072, revealed the positions of 29 of the nonhydrogen atoms. At this stage, the positions of the remaining 18 atoms, including a benzene molecule and a methanol molecule, were located on a subsequent difference Fourier map. Three cycles of block-diagonal least-squares minimizing $\sum(|F_o| - k|F_c|)^2$ by varying the positions and isotropic vibrational amplitudes of the C and O atoms led to $R = 0.14$. Six further cycles of least-squares refinement of atomic parameters with anisotropic vibrational amplitudes for the C and O atoms and isotropic amplitudes for the H atoms converged to $R = 0.085$. All but the four hydrogens derived from the methanol molecule were located from difference electron density maps. After adding the hydrogens, keeping their vibrational amplitudes fixed ($B = 2.92$ Å^2), and refining with anisotropic U's for all the C and O atoms, we obtained a final R of 0.061. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1974). All the calculations were performed on the FACOM M-190 computer in the computer center of Kyushu University with the Universal Crystallographic Computation Program System UNICS II.[27]

Acknowledgment. The authors are grateful to Professor I. Ueda and Assistant Professor S. Kawano (College of General Education, Kyushu University) for providing their X-ray crystallography programs and to Dr. Y. Ono for helpful discussions and suggestions on the MO calculations.

Registry No. 1a, 5660-91-3; **1b**, 62336-65-6; **1c**, 62336-67-8; **3a**, 100-42-5; **3b**, 1073-67-2; **3c**, 2039-82-9; **3d**, 3435-51-6; **3e**, 100-13-0; **3f**, 622-97-9; **3g**, 637-69-4; **3h**, 2039-80-7; **4a**, 72496-20-9; **4b**, 72444-21-4; **4c**, 72496-21-0; **4d**, 72444-22-5; **4e**, 72496-22-1; **4f**, 72444-23-6; **4g**, 72496-23-2; **4h**, 72496-24-3; **6**, 479-33-4; **7**, 573-57-9; **8**, 2175-91-9; **9**, 208-96-8; **10**, 121-46-0; **11**, 498-66-8; **12**, 941-69-5; **13**, 670-54-2; **14**, 108-31-6; **15**, 106-51-4; **16**, 920-37-6; **17**, 2955-79-5; **18**, 544-25-2; **19**, 539-80-0; *p*-(dimethylamino)benzaldehyde, 100-10-7.

Supplementary Material Available: Figure 8 (packing diagram), Table VII (bond lengths), Table VIII (bond angles), Table IX (least-squares best planes), Table X (dihedral angles), Table XI (final atomic parameters), and Table XII (final anisotropic thermal parameters) (7 pages). Ordering information is given on any current masthead page.

---

(15) Overberger, C. G.; Allen, R. E. *J. Am. Chem. Soc.* **1946**, *68*, 722 and references cited therein.

(16) Wiley, R. H.; Smith, N. R. *Org. Synth.* **1953**, *33*, 62.

(17) Monson, R. S. "Advanced Organic Syntheses; Method and Technique"; Academic Press: New York and London, 1971; p 106.

(18) Strassburg, R. W.; Gregg, R. A.; Walling, C. *J. Am. Chem. Soc.* **1947**, *69*, 2141.

(19) Ono, Y.; Ueda, Y. *Chem. Pharm. Bull.* **1974**, *22*, 390.

(20) (a) Kwiatkowski, J. S. *Theor. Chim. Acta* **1968**, *10*, 47. (b) *Ibid.* **1968**, *11*, 167. (c) Berndt, M.; Kwiatkowski, J. S. *Ibid.* **1970**, *17*, 35.

(21) Morita, T. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1486.

(22) Harano, K.; Ban, T.; Yasuda, M.; Kanematsu, K. *Tetrahedron Lett.* **1979**, 1599.

(23) Trotter, J. *Tetrahedron* **1960**, *8*, 13.

(24) Hende, J. H.; Kende, A. S. *Chem. Commun.* **1965**, 384.

(25) Walling, C.; Wolfstirn, K. B. *J. Am. Chem. Soc.* **1947**, *69*, 852.

(26) Ashida, T. "SIGMA. The Universal Crystallographic Computing System (I)"; The Crystallographic Society of Japan: Tokyo, 1967; p 43.

(27) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *24*, 368.