

# Frontier-Controlled Cycloaddition Reactions of Phencyclone with Electron-Rich Dienophiles via Charge-Transfer Complexes: Kinetic Study and Its Mechanistic Aspects

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Received May 4, 1981

Quantitative spectroscopic evidence indicates that phencyclone (2-oxo-1,3-diphenyl-2*H*-cyclopenta[1]phenanthrene, **1a**) forms a charge-transfer complex with dienophiles involving medium-membered-ring unsaturated compounds. Analysis of the second-order rate constants for the cycloaddition in **1a** with the dienophiles shows that there is a decrease in the apparent rate constants with increased concentration of the dienophiles. These data can be interpreted as evidence for the presence of a charge-transfer complex in the reaction mixture. It appears likely that the cycloaddition of **1a** with good donor molecules proceeds via charge-transfer complexes, and the charge-transfer complexation plays an important role in determining both the regiochemistry and the stereochemistry of the adducts.

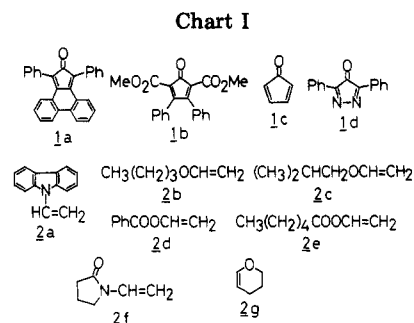
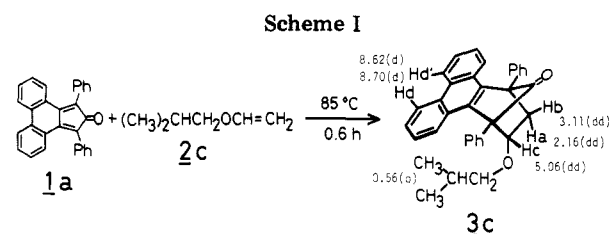
Recently, the development of the inter- and intramolecular Diels-Alder reactions as a basic synthetic strategy has seen rapid growth. Previously, we have investigated basic studies of factors influencing stereo-, regio-, and pericontrals. Especially, phencyclone (2-oxo-1,3-diphenyl-2*H*-cyclopenta[1]phenanthrene, **1a**) has shown high reactivity and peri- and regiospecificity toward various dienophiles involving medium-membered-ring unsaturated compounds,<sup>1</sup> and serves as an excellent trapping agent for unstable compounds.<sup>2</sup> The reactivity and specificity of phencyclone (**1a**) in the cycloadditions are mainly derived from the narrow energy gap of the frontier molecular orbital (FMO) and the effective secondary orbital interaction assisted by the planarity of the gross structure of **1a** in addition to energetic preference of formation of the fused phenanthrene ring resonance in the cycloadducts.<sup>3</sup>

In past years, the Diels-Alder reactions have been studied on the basis of the kinetic point of view, and rationalization of the kinetic results in terms of FMO interactions<sup>4a</sup> was given. In the cycloaddition, the presence of charge-transfer complex has been suggested, and it has been proposed that charge transfer is of importance in stabilizing the transition states.<sup>4b</sup>

This paper deals with the role of charge-transfer complexes in cycloaddition reactions of phencyclone **1a** with a series of electron-rich olefins such as alkyl vinyl ether and tropone.

## Results and Discussion

Phencyclone (**1a**) and an excess amount of the olefins reacted to give 1:1 adducts in high yields. The infrared (IR) spectra of these adducts showed commonly characteristic bands at 1780-1790 cm<sup>-1</sup> due to a strained-ring carbonyl group (Table I). In the nuclear magnetic resonance (<sup>1</sup>H NMR) spectra, these adducts exhibited an an-



isotropic influence of the signals of the O or N substituents of ethylene because of the phenanthrene ring-current effect, suggesting the endo [4 + 2]  $\pi$  structure of the adducts. For example, in the adduct of phencyclone (**1a**) and isobutyl vinyl ether (**2c**), the terminal methyl signal of the isobutyl moiety appeared as a quartet at 0.56 ppm, which has undergone an upfield shift relative to that of isobutyl vinyl ether (**2c**, 0.99 ppm), suggesting the endo [4 + 2]  $\pi$  structure for **3c** (Scheme I, Chart I). The typical NMR signals used for the determination of the configurations are summarized in Table II.

When the reactions were followed by UV spectrometry, a slightly increased absorbance in the visible region (400-500 nm) was observed. The visible absorption spectrum of the mixture was not that which results from the addition of the spectra of pure samples of the two solutes. The increase of the absorbance arises from a lowering of the energy of the  $\pi^*$  orbital<sup>5</sup> (lowest unoccupied molecular orbital) in **1a**, indicating the presence of a charge-transfer complex between **1a** and electron-rich dienophiles. On the basis of this assumption, the kinetic study of reaction of phencyclone (**1a**) with electron-rich species was undertaken. In all rate runs the concentration

(1) (a) Sasaki, T.; Kanematsu, K.; Iizuka, K. *J. Org. Chem.* **1976**, *41*, 1105-1112. (b) Yasuda, M.; Harano, K.; Kanematsu, K. *Ibid.* **1980**, *45*, 2368-2372.

(2) Phencyclone (**1a**) readily reacted with unstable 2,5-diphenyl-3,4-diazacyclopentadienone (**1d**) which is only provided on thermolysis of 1,3-bisdiazo-1,3-diphenyl-2-propanone to give endo [4 + 2]  $\pi$  cycloadduct in a high yield (see Experimental Section).

(3) Yasuda, M.; Harano, K.; Kanematsu, K. *J. Org. Chem.* **1980**, *45*, 659-664.

(4) (a) Desimoni, G.; Gamba, A.; Monticelli, M.; Nicola, M.; Tacconi, G. *J. Am. Chem. Soc.* **1976**, *98*, 2947-2952. Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 657-660. (b) Houk, K. N.; Sims, J.; Watts, C. R.; Lusku, L. *J. Am. Chem. Soc.* **1973**, *95*, 7301-7315. (c) Epiotis, N. D. *Ibid.* **1972**, *94*, 1924-1934.

(5) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1967; p 253.

Table I. Reactions Conditions, IR Spectral Data, and Physical Constants of the Cycloadducts 3a-g

olefin	mole ratio (1a:olefin)	reaction conditions		product (% yield)	IR $\nu_{\max}^a$ , cm <sup>-1</sup> (C=O)	mp (dec), °C
		temp, °C	time, h			
2a	1:1	70	9	3a (74)	1790	229-230
2b	1:2	80	2	3b (60)	1787	166-169
2c	1:10	85	0.5	3c (76)	1789	231-234
2d	1:10	60	1.5	3d (70)	1790	240.5-241
2e	1:10	60	3.5	3e (89)	1781	184.5-186
2f	1:10	60	1.2	3f (91)	1786	252-253
2g	1:30	80	7.5	3g (59)	1792	273.5-274.5

<sup>a</sup> In Nujol.Table II. NMR Data<sup>a</sup> for Cycloadducts 3a-g<sup>b</sup>

compd	chemical shift, <sup>c</sup> $\delta$
3a	3.01 (1 H, dd, H <sub>a</sub> , $J_{ab} = 12$ , $J_{ac} = 7$ ), 3.50 (1 H, dd, H <sub>b</sub> , $J_{bc} = 10$ ), 6.26 (1 H, dd, H <sub>c</sub> ), 6.72 (3 H, m, aromatic H), 7.08-8.08 (21 H, m, aromatic H), 8.68, 8.82 (2 H, d, H <sub>d</sub> , H <sub>d'</sub> , $J = 8$ )
3b	0.62 (3 H, m, CH <sub>3</sub> ), 0.84-1.48 (4 H, m, 2CH <sub>2</sub> ), 2.16 (1 H, dd, H <sub>a</sub> , $J_{ab} = 13$ , $J_{ac} = 3$ ), 3.12 (1 H, H <sub>b</sub> , $J_{bc} = 8$ ), 3.44 (2 H, t, CH <sub>2</sub> ), 5.09 (1 H, dd, H <sub>c</sub> ), 7.00-7.90 (16 H, m, aromatic H), 8.58, 8.68 (2 H, d, H <sub>d</sub> , H <sub>d'</sub> , $J = 4$ )
3c	0.56 (6 H, q, 2CH <sub>3</sub> ), 1.47 (1 H, m, methine H), 2.16 (1 H, dd, H <sub>a</sub> , $J_{ab} = 12$ , $J_{ac} = 4$ ), 3.11 (1 H, dd, H <sub>b</sub> , $J_{bc} = 8$ ), 3.24 (2 H, dd, CH <sub>2</sub> , $J = 5, 6$ ), 5.06 (1 H, dd, H <sub>c</sub> ), 6.96-7.82 (16 H, m, aromatic H), 8.62, 8.70 (2 H, d, H <sub>d</sub> , H <sub>d'</sub> , $J = 5$ )
3d	2.04 (1 H, dd, H <sub>a</sub> , $J_{ab} = 14$ , $J_{ac} = 3$ ), 3.58 (1 H, dd, H <sub>b</sub> , $J_{bc} = 8$ ), 6.57 (1 H, dd, H <sub>c</sub> ), 6.75-7.96 (21 H, m, aromatic H), 8.74 (2 H, d, H <sub>d</sub> , H <sub>d'</sub> , $J = 8$ )
3e	0.48-0.74 (3 H, m, CH <sub>3</sub> ), 0.74-1.36 (6 H, m, 3CH <sub>2</sub> ), 1.96 (2 H, t, CH <sub>2</sub> , $J = 6, 5$ ), 2.11 (1 H, dd, H <sub>a</sub> , $J_{ab} = 13.5$ , $J_{ac} = 3$ ), 3.51 (1 H, dd, H <sub>b</sub> , $J_{bc} = 8.5$ ), 6.40 (1 H, dd, H <sub>c</sub> ), 6.96-7.82 (16 H, m, aromatic H), 8.65, 8.74 (2 H, d, H <sub>d</sub> , H <sub>d'</sub> , $J = 4$ )
2f	1.16-1.60 (2 H, m, CH <sub>2</sub> ), 1.94-2.94 (4 H, m, 2CH <sub>2</sub> ), 2.19 (1 H, dd, H <sub>a</sub> , $J_{ab} = 13$ , $J_{ac} = 5$ ), 3.31 (1 H, dd, H <sub>b</sub> , $J_{bc} = 10$ ), 7.03-8.02 (16 H, m, aromatic H), 8.71 (2 H, H <sub>d</sub> , H <sub>d'</sub> , $J = 8$ )
3g	1.02, 1.60 (4 H, m, 2CH <sub>2</sub> ), 3.08-3.80 (3 H, m, CH <sub>2</sub> , H <sub>c</sub> ), 5.01 (1 H, d, H <sub>b</sub> , $J_{bc} = 8$ ), 6.98-7.90 (16 H, m, aromatic H), 8.71 (2 H, d, H <sub>d</sub> , H <sub>d'</sub> , $J = 8$ )

<sup>a</sup> Solvent CDCl<sub>3</sub>. <sup>b</sup> See Scheme I for atom labels. <sup>c</sup>  $J$  values are given in hertz.Table III. Second-Order Rate Constants<sup>a</sup> for Cycloaddition Reaction of 1a<sup>b</sup> with 2a at 34.1 °C in Various Solvents

solvent	$E_T$ , kcal/mol	[dienophile], M					
		0.029	0.050	0.074	0.100	0.149	0.200
chlorobenzene	37.5	7.47	5.78	4.15	3.33	2.96	2.67
benzene	34.5						2.39
chloroform	39.1						2.57
benzotrile	42.0						3.71
dimethylformamide	43.8						5.95

<sup>a</sup> M<sup>-1</sup> s<sup>-1</sup> × 10<sup>4</sup>. <sup>b</sup> 1 × 10<sup>-3</sup> M.Table IV. Second-Order Rate Constants<sup>a</sup> for Cycloaddition Reaction of 1a<sup>b</sup> with 2b at 34.1 °C in Chlorobenzene

[dienophile], M	0.021	0.050	0.097	0.146	0.198
rate constant	9.38	6.15	3.59	3.12	2.69

<sup>a</sup> M<sup>-1</sup> s<sup>-1</sup> × 10<sup>4</sup>. <sup>b</sup> 1 × 10<sup>-3</sup> M.

of the dienophile was in large excess over that of the cyclopentadienone. The pseudo-first-order rate constants of these reactions in chlorobenzene at various temperatures were obtained by following the disappearance of the absorption of phencyclone (1a) in the visible region by UV spectrometry. The second-order rate constants ( $k_2$ ) for various concentrations of the dienophile are summarized in Tables III-V. The rates of the reaction of 1a and *N*-vinylcarbazole (2a) in several solvents of varying polarity are also recorded in Table III. Phencyclone (1a) reacts readily with electron-rich olefins, e.g., 2g, but slowly with

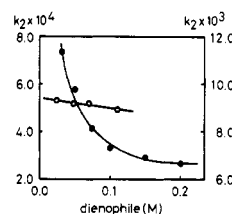


Figure 1. Variation in  $k_2$  for phencyclone 1a with dienophile concentration (chlorobenzene, 34.1 °C). The curve (left-hand ordinates) gives data for 2a. The straight line (right-hand ordinates) gives data for *p*-methoxystyrene.

electron-poor ones, e.g., 2d (Table V). This may be attributed to the changes of the frontier energy level on introduction of the substituent on ethylene. From the data, the activation parameters were calculated for the reactions of 1a with *N*-vinylcarbazole (2a) and *n*-butyl vinyl ether (2b, Table VI). The activation energies for

Table V. Second-Order Rate Constants<sup>a</sup> for Cycloaddition Reactions of 1a<sup>b</sup> with 2a-g at 34.1 °C in Chlorobenzene

[dienophile], M	dienophile						
	2a	2b	2c	2d	2e	2f	2g
0.020	7.47 <sup>c</sup>	9.38	8.81	7.28	7.35	8.73	9.70
0.100	3.33	3.59	3.29	1.78	1.48	3.20	2.17

<sup>a</sup> M<sup>-1</sup> s<sup>-1</sup> × 10<sup>4</sup>. <sup>b</sup> 1 × 10<sup>-3</sup>. <sup>c</sup> 0.029 M.

Table VI. Second-Order Rate Constants<sup>a</sup> and Activation Parameters for Cycloaddition Reactions of 1a<sup>b</sup> with 2a,b<sup>c</sup>

dienophile	temp, °C				$E_a$ , kcal/mol	$\Delta S^\ddagger$ , eu
	34.1	40.0	47.8	58.9		
2a	3.33	5.45	8.73	17.7	13.5	-34.1
2b	3.59	5.64	8.89	18.0	13.0	-36.1

<sup>a</sup>  $M^{-1} s^{-1} \times 10^4$ . <sup>b</sup>  $1 \times 10^{-3} M$ . <sup>c</sup> 0.10 M.

Table VII. Second-Order Rate Constants<sup>a</sup> for Cycloaddition Reaction of 1a<sup>b</sup> with *p*-Methoxystyrene at 34.1 °C in Chlorobenzene

[dienophile], M	0.024	0.048	0.071	0.110
rate constant	9.35	9.20	9.20	8.94

<sup>a</sup>  $M^{-1} s^{-1} \times 10^3$ . <sup>b</sup>  $1 \times 10^{-3} M$ .

#### Scheme II

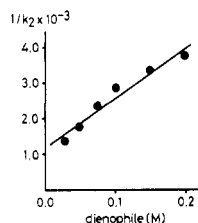
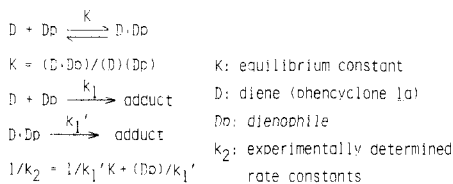


Figure 2. Plots of  $1/k_2$  vs. dienophile concentration for the cycloaddition reaction of 1a with 2a.

the reactions were found to be 13.4 kcal/mol for the former case and 13.0 kcal/mol for the latter one, slightly higher than that for the average Diels–Alder reaction, while the entropies of activation,  $\Delta S^\ddagger = -32.8$  eu for the former and  $\Delta S^\ddagger = -36.1$  eu for the latter, lie within the range reported for the typical Diels–Alder reaction<sup>6</sup> and suggest a highly ordered transition state.

As exemplified in Figure 1, the second-order rate constants for these reactions decrease as the dienophile concentration increases, suggesting that the adduct may be formed not only from the diene–dienophile complex but also from the direct cycloaddition of the free diene with dienophile (Scheme II). By use of the treatment of Andrews and Keefer,<sup>7</sup> plots of  $1/k_2$  vs. dienophile concentration should give a straight line of slope  $1/k_1'$  and an intercept of  $1/k_1'K$ . Figure 2 presents such a graphical interpretation of the data for the reactions of 1a with *N*-vinylcarbazole (2a) at 34.1 °C. From this linear plot, values of  $k_1' = 7.04 \times 10^{-5} s^{-1}$ ,  $k_1 = 7.29 \times 10^{-4} M^{-1} s^{-1}$ , and  $K = 12.0 M^{-1}$  have been calculated.<sup>8</sup> The equilibrium constant for the interaction of *p*-methoxystyrene and phencyclone (1a) ( $0.509 M^{-1}$ ) is considerably less than those for *N*-vinylcarbazole ( $12.0 M^{-1}$ ) and *n*-butyl vinyl ether ( $16.1 M^{-1}$ ) (Table VII and XI).

(6) Kwart, H.; King, K. *Chem. Rev.* 1968, 68, 415–447.

(7) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* 1955, 77, 6284–6289.

(8) Unfortunately, the equilibrium constant  $K$  could not be evaluated directly because Diels–Alder reaction occurred too rapidly to permit direct measurement<sup>7</sup> of the optical densities under the reaction conditions.

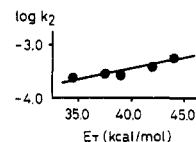


Figure 3. Plots of  $\log k_2$  vs.  $E_T$  for the cycloaddition of 1a with 2a.

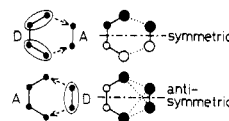


Figure 4. The modes of the electron shift associated with the orbital interactions to create intermolecular chemical bindings.

Bradsher et al.<sup>9</sup> have observed a similar change in rate constants for cationic polar cycloaddition and pointed out that the change is not due to the change in the polarity of the solvent when the concentration of the dienophile is changed, although polar cycloadditions are considered to be highly susceptible to slight changes in the polarity of the solvent.

The  $E_T$  values of Dimroth were used as a scale of solvent ionizing power in studying the effect of solvent on the rate of reaction.<sup>1b</sup> As illustrated in Figure 3, plots of  $\log k_2$  vs.  $E_T$  show a linear relationship. The magnitude of the slope has been used as a measure of the sensitivity of a reaction to the ionizing power of the medium. The value is only  $3.94 \times 10^{-2}$ , sensitivity to ionizing power being very low as compared with those of typical concerted reactions.<sup>1b</sup> The small response to variation of the polarity of the solvent rules out an intermediate involving any significant degree of charge separation.

From a theoretical standpoint, it is generally true that the [4 + 2]  $\pi$  cycloaddition is preceded via charge-transfer complex formation.<sup>4c</sup> Hence, the contribution of the charge-transfer structure to the transition state should be important.

Andrews and Keefer<sup>7</sup> demonstrated the existence of a charge-transfer complex in normal-type cycloaddition reactions of substituted anthracenes with maleic anhydride by analysis of the second-order rate constants.

In a recent rationalization of cycloaddition behavior,<sup>10</sup> the FMO theory has been used successfully in explaining the formation of charge-transfer complexes by considering the interactions of the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.

Interestingly, Fukui et al.<sup>11</sup> pointed out that the inverse-type cycloaddition is energetically unfavorable because of the electron density in the central part of the intermolecular region (Figure 4) owing to the symmetric FMO coefficients. In such a case, it is suggested that the cycloaddition will presumably be less concerted or experience complex formation before giving the final product.

Desimoni et al.<sup>4a</sup> studied inverse-type cycloaddition of a heterodiene (4-arylidene-5-pyrazolone) with alkyl vinyl ethers by quantitative spectroscopic analysis. However, the presence of charge-transfer complex was not detectable.

On the other hand, Bradsher et al.<sup>9</sup> have shown that cationic polar cycloaddition of acridizinium salt with ethyl vinyl ethers proceeds via charge-transfer complexes on the basis of kinetic and spectroscopic evidence.

(9) Bradsher, C. K.; Carlson, G. L. B.; Porter, N. A.; Westerman, I. J.; Wallis, T. G. *J. Org. Chem.* 1978, 43, 822–827.

(10) Salem, L. *J. Am. Chem. Soc.* 1968, 90, 543–553.

(11) Fujimoto, H.; Inagaki, S.; Fukui, K. *J. Am. Chem. Soc.* 1976, 98, 2670–2671. Fujimoto, H.; Sugiyama, T. *Ibid.* 1977, 99, 15–22.

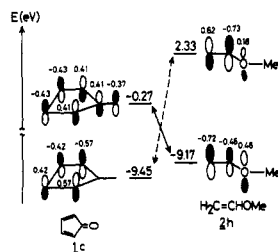


Figure 5. Calculated FMO energies and coefficients by the MINDO/3 MO method.

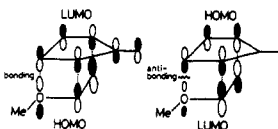


Figure 6. Transition states of 1 and 2h in endo addition.

Table VIII. Calculated FMO Energies<sup>a</sup> of 1a-c

compd	CNDO/2 MO		MINDO/3 MO	
	HOMO	LUMO	HOMO	LUMO
1a	-9.50	-0.22		
1b	-11.5	0.06		
1c	-13.0	0.67	-9.45	-0.27

<sup>a</sup> In eV.

More recently, one of us reported that 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (1b) shows an inverse electron demand toward various dienophiles in the cycloaddition reactions,<sup>12</sup> but the charge-transfer complex formation was not observed.

Thus, the cycloaddition reaction in relation to inverse electron demand has been investigated far less, and there are few reports concerned with charge-transfer complex formation between *uncharged* reactants as described here.

Schematic representation for the reagents with the eigenvalues and eigenvectors calculated by MINDO/3 MO approximation<sup>13a</sup> is shown in Figure 5. The calculated ionization potential (IP) for methyl vinyl ether is 9.17 eV which satisfactorily agreed with the experimental one (8.93 eV). It is clear that an inverse Diels-Alder reaction is dominated by the interaction of the LUMO of cyclopentadienone (1c, -0.27 eV) and the HOMO of the methyl vinyl ether (2h, -9.17 eV). The energy difference is 8.90 eV, whereas that of the HOMO of 1c (-9.45 eV) and the LUMO of 2h (2.33 eV) is 11.8 eV. From the deduction based on the discrepancy in energy levels calculated by the CNDO/2<sup>13b</sup> and MINDO/3 MO approximations, phencyclone (1a) might have its HOMO at ca. -6.0 eV and its LUMO at ca. -1.0 eV (Table VIII). The FMO energy difference of 1a is very narrow and is situated among the FMO energy levels of 2h, indicating that 1a participates in a neutral-type cycloaddition.<sup>3</sup> From this, both interactions play an important role in determining the reactivity for the cycloaddition. However, in a normal-type interaction (HOMO of 1a-LUMO of 2h), the secondary interaction of the FMOs is antibonding, whereas the reverse is true for the interaction between the LUMO of 1a and the HOMO of 2h. Thus, the predominant formation of endo [4 + 2]  $\pi$  cycloadduct was attributed to the stabili-

Table IX. Second-Order Rate Constants<sup>a</sup> for Cycloaddition Reaction of 1b<sup>b</sup> with 2a at 47.8 °C in Chlorobenzene

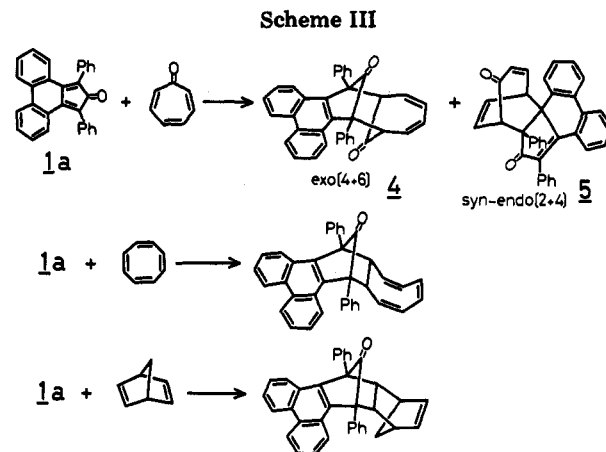
[dienophile], rate constant	0.010	0.051	0.099	0.150	0.191
	1.06	1.18	1.19	1.13	1.15

<sup>a</sup> M<sup>-1</sup> s<sup>-1</sup> × 10<sup>3</sup>. <sup>b</sup> 1 × 10<sup>-3</sup> M.

Table X. Second-Order Rate Constants<sup>a</sup> for Cycloaddition Reactions of 1a<sup>b</sup> with Tropone, Cyclooctatetraene, and Norbornadiene at 34.1 °C in Chlorobenzene

dienophile	[dienophile], M				
	0.020	0.040	0.050	0.100	0.200
tropone	8.90		3.19	2.04	1.36
cyclooctatetraene	8.23		4.19	2.10	1.33
norbornadiene	11.7	9.85		9.25	8.83

<sup>a</sup> M<sup>-1</sup> s<sup>-1</sup> × 10<sup>4</sup>. <sup>b</sup> 1 × 10<sup>-3</sup> M.



zation of the transition state by a secondary orbital effect<sup>14</sup> as depicted in Figure 6.

The LUMO of 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (1b) is approximately the same as that of phencyclone (1a, Table VIII), and qualitative similarities in reactivity between the two compounds are expected. However, the rate constants for the reaction of 1b with vinyl alkyl ethers or enamines do not show the decrease with increasing dienophile concentration which was observed for the corresponding reaction of 1a (Table IX). This implies the ability to form a plane seems to be important. Phencyclone (1a) can obtain coplanarity (phenanthrene ring moiety) in a cycloaddition reaction.<sup>3</sup> On the other hand, 1b, in which the two phenyl rings cannot be coplanar,<sup>15</sup> is likely not to form a complex with a dienophile. In pericyclic reactions of 1b with various unsaturated compounds such as para-substituted styrenes,<sup>12</sup> cycloheptatriene,<sup>24</sup> and *N*-(ethoxycarbonyl)azepine<sup>15</sup> the resulting cycloadducts are mixture of the stereoisomers, whereas the analogous reactions of 1a give single cycloadducts.<sup>1b,3,24</sup> This difference might be due to the planarity of the reactants. Since the transition state of cycloaddition seems to have a similar orientation to that of the charge-transfer complex,<sup>16</sup> the planarity of the reactants becomes

(12) Mori, M.; Hayamizu, A.; Kanematsu, K. *J. Chem. Soc., Perkin Trans. 1* 1981, 1259-1272.

(13) (a) The calculations were performed by using the following program with optimization: Dewar, M. J. S. *QCPE* 1975, 11, 279. (b) The QCPE version of the CNINDO/2 program was expanded to accommodate 60 atoms and modified for damped SCF calculation: Dobo, P. A. *Ibid.* 1969, 11, 141.

(14) The total energies for the reaction of 1c with methyl vinyl ether (2h) calculated by the previous method<sup>15</sup> suggest that the endo adduct formation (total energy -1781.93 eV) is energetically more favorable than the exo adduct one (total energy -1781.91 eV).

(15) Harano, K.; Yasuda, M.; Ban, T.; Kanematsu, K. *J. Org. Chem.* 1980, 45, 4455-4462.

(16) It is well-known that the crystal structures determined for a number of charge-transfer complexes have shown that the molecules are stacked in a parallel fashion.<sup>7</sup>

Table XI. Equilibrium Constants ( $K$ ) for Various Cycloaddition Reactions and Ionization Potentials for the Donor

reactants (donor-acceptor)	$K, M^{-1}$	ionization potential, eV	ref
anthracene-maleic anhydride	0.296		6
dimethylantracene-maleic anhydride	0.294		6
dimethylantracene-chloromaleic anhydride	0.398		6
<i>N</i> -vinylcarbazole-acridizinium salt <sup>b</sup>	0.650		7
<i>p</i> -methoxystyrene-phencyclone	0.509		c
norbornadiene-phencyclone	1.39	8.62 <sup>a</sup>	c
<i>N</i> -vinylcarbazole-phencyclone	12.0		c
<i>n</i> -butyl vinyl ether-phencyclone	16.1	9.08 <sup>b</sup>	c
tropone-phencyclone	30.5	8.90 <sup>a</sup>	c
cyclooctatetraene-phencyclone	48.1	8.21 <sup>a</sup>	c

<sup>a</sup> See ref 20. <sup>b</sup> See ref 18. <sup>c</sup> This work.

important in determining the regio-, peri-, and stereoselectivities of the cycloaddition.

To get additional evidence for the existence of charge-transfer complexes in the cycloaddition reaction, we have reinvestigated the cycloaddition reaction of phencyclone (1a) with several dienophiles. Tropone has a planar structure with an ionization potential at 8.90 eV<sup>17</sup> which is comparable to those of alkyl vinyl ethers<sup>18</sup> (9.08 eV for 2b and 8.93 eV for 2h). Phencyclone (1a) and a twofold excess of tropone reacted at room temperature for 1 month to afford exo [4 + 6]  $\pi$  and syn-endo [2 + 4]  $\pi$  cycloadducts 4 and 5 (Scheme III and Experimental Section). Both compounds were not formed from sigmatropic rearrangements<sup>1b,15,19</sup> of the primary adducts but from direct cycloadditions<sup>19</sup> of 1a with tropone. As expected, the second-order rate constants decrease significantly as the concentration of tropone increases (Table X). The value of the equilibrium constant ( $K$ ) is very large (30.5 M<sup>-1</sup>) as compared with those of reported reactions,<sup>7,9</sup> indicating that charge transfer may contribute to stabilization of the transition state (Table XI).

Furthermore, we have investigated cycloaddition of 1a with the powerful donor cyclooctatetraene which possesses a tub conformation in the ground state with a very high ionization potential (8.21 eV,<sup>20</sup> Table XI). The second-order rate constants also decrease significantly (Table X), and the  $K$  value is very large (48.1 M<sup>-1</sup>), indicating that the cycloaddition via charge-transfer complexation<sup>21</sup> is

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(21) It is well-known that *N,N*-dimethylaniline<sup>22</sup> form charge-transfer complexes with electron-deficient compounds. Thus, we have investigated the interactions of 1a with *N,N*-dimethylaniline, with an ionization potential (8.23 eV)<sup>23</sup> comparable to that of cyclooctatetraene, and evaluated the equilibrium constant  $K$  for the complex formation by graphical analysis<sup>7</sup> of the UV spectral data. The calculated value of  $K$  is 70.5 M<sup>-1</sup>, suggesting that those of this work seem to be reasonable.

(22) Mason, S. F. "Physical Methods in Heterocyclic Chemistry"; Katritzky, A. R. Ed.; Academic Press: New York, 1980; Vol. II, p 80.

(23) Crable, G. F.; Kearns, G. L. *J. Phys. Chem.* 1962, 66, 436-439.

predominant and cyclooctatetraene may adopt a nearly planar structure in the transition state<sup>24</sup> (Table XI).

Other evidence of interest is that the rate of cycloaddition of 1a with norbornadiene<sup>13</sup> (Scheme III), though it has a higher ionization potential (8.62 eV)<sup>20</sup> than tropone (8.90 eV), does not show an appreciable rate retardation with an increase of the concentration of norbornadiene (Table X). This fact suggests that charge-transfer complexation occurs only to a small extent, and this must be a consequence of the steric disadvantage of nonplanar norbornadiene.

On the other hand, in normal-type cycloaddition of phencyclone (1a) with *p*-benzoquinone (ionization potential 11.0 eV<sup>26</sup>), wherein the predominant interaction is between the HOMO of 1a and the LUMO of *p*-benzoquinone, the rate decrease due to the charge-transfer complexation was not observed, entirely.<sup>25</sup>

The facts support the idea that the charge-transfer complexation is a general phenomenon in the cycloaddition reactions of phencyclone (1a) with electron-rich species involving medium-membered-ring unsaturated compounds.

## Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. UV spectra were determined with a Hitachi EPS-3T spectrophotometer. <sup>1</sup>H NMR spectra were taken with a JEOL PS-100 spectrometer with Me<sub>4</sub>Si as an internal standard; chemical shifts are expressed in  $\delta$  values. IR spectra were taken with a JASCO DS-701G infrared spectrophotometer.

**Cycloaddition Reaction of Phencyclone (1a) with 2,5-Diphenyl-3,4-diazacyclopentadienone (1d).** A solution of 1a (0.19 g) and 1,3-diazo-1,3-diphenyl-2-propanone (0.17 g) in benzene (8 mL) was allowed to stand at room temperature for 1.5 h. The solution was diluted with methanol, and the precipitated solids were filtered off and recrystallized from benzene-methanol to give the endo [4 + 2]  $\pi$  adduct (0.29 g, 95%) as yellow cubes: mp 221-223.5 °C dec; IR (Nujol) 1792 (bridged C=O), 1714 (conjugated C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.08 (m, 2 H, phenyl H), 7.20-7.80 (m, 19 H, aromatic H), 8.52 (d, 2 H, aromatic H,  $J$  = 8 Hz).

**Cycloaddition Reactions of Phencyclone (1a) with Various Dienophiles 3a-g.** A solution of 1a and an excess amount of vinyl ethers 3a-g was heated until the deep green color had faded away. The cooled mixture was diluted with methanol, and the precipitated solid was filtered off and purified by recrystallization. The results are summarized in Tables I and II.

**Cycloaddition Reaction of Phencyclone (1a) with Tropone.** A solution of 1a (0.30 g) and tropone (0.17 g) in chloroform (1 mL) was allowed to stand at room temperature until the deep green color had disappeared. The solution was then evaporated under reduced pressure, and the residue was chromatographed on silica gel with *n*-hexane-benzene (4:1). The first fraction gave exo [4 + 6]  $\pi$  cycloadduct 4 (0.17 g, 44%) as colorless cubes: mp 215-217 °C dec; IR (Nujol) 1770 (bridged C=O), 1728 (ester C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.60 (d, 2 H, methine H,  $J$  = 5.5 Hz), 6.17 (m, 4 H, olefin H), 7.20-8.00 (m, 16 H, aromatic H), 8.70 (d, 2 H, aromatic H,  $J$  = 8.5 Hz).

The second fraction gave syn-endo [2 + 4]  $\pi$  cycloadduct 5 (0.15 g, 40%) as colorless prisms: mp 161-163 °C dec; IR (Nujol) 1710 (enone C=O), 1658 (tropone C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.50 (dd, 1 H, methine H,  $J$  = 8, 8 Hz), 4.94 (d, 1 H, methine H,  $J$  = 9 Hz), 5.87 (d, 1 H, olefin H,  $J$  = 10 Hz), 6.17-7.90 (m, 21 H, olefin H, aromatic H). The configuration of the adduct 5 was determined

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(25) The second-order rate constants for the cycloaddition reaction of phencyclone 1a (1  $\times$  10<sup>-3</sup> M) with *p*-benzoquinone (ionization potential 11.0 eV)<sup>26</sup> at 34.1 °C in chlorobenzene are as follows:  $k_2$  = 1.25  $\times$  10<sup>-2</sup> M<sup>-1</sup> s<sup>-1</sup> (8  $\times$  10<sup>-3</sup> M in *p*-benzoquinone);  $k_2$  = 1.35  $\times$  10<sup>-2</sup> M<sup>-1</sup> s<sup>-1</sup> (4  $\times$  10<sup>-2</sup> M in *p*-benzoquinone).

(26) MNDO calculation data: Osawa E. Hokkaido University, private communication.

by comparing the spectral data with those of the analogous compounds.<sup>1a,15,19</sup>

On the other hand, the reaction of 1a with tropone in benzene at 80 °C for 20 h gave exo [4 + 6]  $\pi$  adduct 4 in 70% yield.<sup>1a</sup>

**Kinetics.** The reaction rate was followed at a given temperature by measuring the loss of the long-wavelength absorbance of the 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. The pseudo-first-order rate constants were calculated from a plot of  $\ln(A_t - A_\infty)/(A_0 - A_\infty)$  vs. time by a least-squares method, where  $A_t$  is the absorbance at time  $t$  and  $A_\infty$  is the absorbance after about 10 half-lives. The second-order rate constants were obtained in the usual manner.

The treatment of Andrews and Keefer<sup>7</sup> was followed in the calculation of the equilibrium constants. The kinetic data are listed in Tables III-VII and IX-XI.

**Acknowledgment.** We thank Miss K. Konishi and Miss R. Kutsunai for experimental assistance.

**Registry No.** 1a, 5660-91-3; 1b, 16691-79-5; 1c, 13177-38-3; 1d, 32683-51-5; 2a, 1484-13-5; 2b, 111-34-2; 2c, 109-53-5; 2d, 769-78-8; 2e, 3050-69-9; 2f, 88-12-0; 2g, 110-87-2; 3a, 78456-56-1; 3b, 78456-57-2; 3c, 78456-58-3; 3d, 78456-59-4; 3e, 78456-60-7; 3f, 78456-61-8; 3g, 78479-40-0; 4, 57969-45-6; 5, 78456-62-9; 1,3-diazo-1,3-diphenyl-2-propanone, 26536-34-5; tropone, 539-80-0; *p*-methoxystyrene, 637-69-4; norbornadiene, 121-46-0; cyclooctatetraene, 629-20-9.

## Reagent Design and Study of *p*-Benzoquinone Derivatives. The Site-Selective Cycloaddition Reaction of Diquinones and Photochemical Cage Formation of the Adducts

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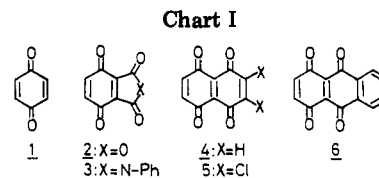
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Received June 12, 1981

Cycloaddition reactions of naphthodiquinone derivatives and the photochemical behavior of their adducts have been investigated. Naphthodiquinone (4) and dichloronaphthodiquinone (5) reacted exclusively at the internal double bond with both cyclopentadiene and quadricyclane to give the corresponding 1:1 adducts in high yields. While anthradiquinone (6) reacted also only at the internal double bond with quadricyclane, the reaction with cyclopentadiene took place at both the internal and terminal double bonds of 6. The stereochemistry of the adducts was determined by spectral inspections and chemical transformations. The cyclopentadiene adducts were photochemically converted into the cage compounds in high yields, although the quadricyclane adducts were photoinert. In the photochemical reactions, high site selectivity was observed; the intramolecular [2 + 2]  $\pi$  photoaddition occurred only between enedione (electron poor) and cyclopentene (electron rich) double bonds.

*p*-Benzoquinone (1, Chart I) is a versatile synthon for the preparation of cage compounds of current interest,<sup>1</sup> although 1 is not a powerful dienophile in the Diels-Alder reactions, and is rather inert to homodienes and conjugated medium-ring polyenes even under drastic conditions. Recently, on the basis of the concept of donor (HOMO)-acceptor (LUMO) relationships of the pericyclic reaction,<sup>2</sup> we were able to remarkably enhance the reactivity of *p*-benzoquinone by introducing strong electron-attracting substituents, which cause a lowering of the LUMO energy level.<sup>3</sup> Thus, *p*-benzoquinone-2,3-dicarboxylic anhydride (PBA, 2) and *N*-phenylimidine (PBI, 3) showed high reactivities toward the electron-rich dienes, homodienes, and trienes.<sup>3</sup> As a reasonable extension of our studies on the reagent design by FMO control, a series of diquinones such as 1,4,5,8-naphthodiquinone (NDQ, 4),<sup>4</sup> 2,3-dichloronaphthodiquinone (DNDQ, 5), and 1,4,9,10-anthradiquinone (ADQ, 6)<sup>5</sup> were prepared, and their cycloaddition reactions with electron-rich dienes were investigated.

Due to their direct applicability to a total synthesis of biologically important anthracycline antibiotics, there is



great current interest in the Diels-Alder reactions of naphthoquinone derivatives.<sup>6-11</sup> However, there still remains the ambiguity concerning the site selectivity in the cycloaddition reactions of bifunctional dienophiles such as ADQ (6) which can undergo initial Diels-Alder addition at the internal or terminal double bond.<sup>6,11,12</sup> Apparently, more experimental results are needed in order to clarify

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