procedure should be stressed. (a) The polymeric reagent was regenerated by electrochemical reaction in situ. No chemical oxidants were required for the regeneration of the reagent. (b) Since the polymeric reagent was recycled in situ, only a catalytic amount of it was sufficient for the reaction. (c) Clean and valuable hydrogen was formed quantitatively as a second product.

Indirect electrochemical oxidation of organic compounds has received increasing attention.[8] Direct electrochemical oxidation of alcohols is usually difficult due to the relatively high oxidation potential of alcohols. Recently an elegant electrochemical oxidation of alcohols using iodonium ions[8d] and thioanisole[8e] as a catalytic electron carrier has been reported. From this point of view, the present methodology has a high potential, since it may remove defects of the conventional electroorganic process such as difficulty in separation and recovery of the electrolyte.

Apparently the oxidation of alcohols is a well-established process in organic synthesis, but reconsideration from the environmental point of view seems to be necessary at present. The conventional procedures involve the use of stoichiometric amounts of organic or inorganic oxidants, causing a disposal problem of toxic wastes. The development of the present methodology may shed light on the solution of the problem and further study must be continued in the direction of "pollution-free" organic synthesis.

Registry No. 1, 65993-03-5; 2-octanol, 123-96-6; α-methylbenzenemethanol, 98-85-1; 5-nonanol, 623-93-8; cyclohexanol, 108-93-0; cyclododecanol, 1724-39-6; 2-(1-methylethyl)-5-methylcyclohexanol, 1490-04-6; 1-octanol, 111-87-5; 1,3-butanediol, 107-88-0; 2-octanone, 111-13-7; 1-phenylethanone, 98-86-2; 5-nonanone, 502-56-7; cyclohexanone, 108-94-1; cyclododecanone, 830-13-7; 2-(1-methylethyl)-5-methylcyclohexanone, 10458-14-7; octanoic acid, 124-07-2; octyl octanoate, 2306-88-9; 4-hydroxy-2-butanone, 590-90-9; PVP·HCl, 54907-32-3; HBr-pyridine, 18820-82-1; HBr, 10035-10-6.

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(8) For example: (a) Clarke, R.; Kuhn, A.; Okoh, E. *Chem. Br.* **1975**, *11*, 59–64; (b) Osa, T. *Yuki Gosei Kagaku Kyokaishi* **1979**, *37*, 361–371; (c) Dvonch, W.; Mehltretter, C. L. *J. Am. Chem. Soc.* **1952**, *74*, 5522–5523; (d) Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Tetrahedron Lett.* **1979**, 165–168; (e) Shono, T.; Matsumura, Y.; Mizoguchi, M.; Hayashi, J. *Ibid.* **1979**, 3861–3864; (f) Torii, S.; Uneyama, K.; Ono, M.; Tazawa, H.; Matsunami, S. *Ibid.* **1979**, 4661–4662; (g) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310–2312.

Observation in the Periselective Photoadditions of Electron-Donating or Electron-Accepting Anthracenes to Cyclohepta-1,3,5-triene by Orbital and Steric Interaction Controls

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Irradiations (I_2–CCl_4 filter solution, 340–420 nm) of substituted anthracenes with a large excess of cyclohepta-1,3,5-triene in various solvents afforded a variety of photoaddition products in moderate yields. These periselective formations are explained in terms of the following controlling factors: (1) orbital interactions, (2) steric interactions.

Since pericyclic syntheses are very valuable for stereo-, regio-, and periselective controls, they could provide for a logical assembling of molecules. Especially in the past decade, the thermal pericyclic reactions of conjugated medium-ring polyenes have aroused considerable interest, and much effort has been made to establish their capability for cycloadditions, and the donor–acceptor relationships of the cycloaddends in the reactions were pointed out to be important.[1-3] The recognition of the donor–acceptor relationships of the cycloaddends also leads to a description of the entire spectrum of photochemical cycloadditions.[4]

As a continuation of our previous reports,[5] we have examined the photoadditions of substituted anthracenes to cyclohepta-1,3,5-triene. These results are discussed here in detail in comparison with the previous work.

Theoretical Background.

A number of pericyclic reactions take place photochemically, usually with consequences different from those of analogous thermal reactions.[1,2] Epiotis[6] has reported that the effect of configuration interaction can reverse the stereoselectivity of the cycloadditions when the two cycloaddends have widely different polarities. On the other hand, Inagaki et al.[7] have pointed out the possible importance of an abnormal orbital interaction in excited-state reactions between electron donors and acceptors: the photochemical reactions between powerful electron donors and acceptors are likely controlled by the $(HOMO)_D$–$(LUMO)_A$ interaction involved in the D^*A–$D^{+*}A^-$ or DA^*–D^+A^{-*} interaction, the frontier orbital interaction being the same as one in the usual thermal reaction by the stereoselection rules. For example, *trans,trans*-2,4-hexa-

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(1) Woodward, R. B.; Hoffmann, R. "Conservation of Orbital Symmetry"; Academic Press: New York, 1971.

(2) Fuki, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: Heidelberg, 1970.

(3) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693–4701.

(4) Epiotis, N. D. "Theory of Organic Reactions"; Springer-Verlag: West Berlin, Heidelberg, and New York, 1978.

(5) Sasaki, T.; Kanematsu, K.; Hayakawa, K. *J. Am. Chem. Soc.* **1973**, *95*, 5632–5637.

(6) Epiotis, N. D. *J. Am. Chem. Soc.* **1972**, *94*, 1941–1950.

(7) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1978**, 135–138 and references cited therein.

Table I. Frontier Orbital Energy Levels Calculated by the PPP-SCF-MO Method for Substituted Anthracenes[a]

	1a	1b	1c	1d	1e	1f	1g	1h
LUMO[b]	−2.05	−2.22	−2.14	−2.45	−1.95	−2.39	−2.81	−1.37
HOMO[b]	−9.14	−8.92	−9.04	−8.74	−9.24	−9.43	−9.59	−8.08

[a] UV max: 369 nm (1a), 367 (1b), 380 (1c), 374 (1d), 359 (1e), 383 (1f), 402 (1g), 384 (1h). [b] In electron volts.

Table II. Yields of the Photoinduced Adducts

	yields (rel yields),[a] %					
compd	ene type (7)	[$_\pi 4 + {}_\pi 6$] (4)	[$_\pi 4 + {}_\pi 4$] (5)	[$_\pi 4 + {}_\pi 2$] (6)	dimer 3	ditropyl (8)
1a	7 (17)	9 (22)			26 (61)	
1b	22 (36)	38 (64)				
1c	69 (100)					
1d	73 (100)					
1e[b]		29 (43)	14 (20)		25 (37)	
1f	4 (23)		28 (42)	32 (35)		
1g				63 (100)		
1h				58		81

[a] Relative yields were measured with an Iatron TH-10 TLC analyzer. [b] See ref 5.

Table III. NMR Spectral Data for Cycloadducts[a]

compd	chemical shift, δ (*J*, Hz)
4a	1.43 (m, 1 H, syn H-13), 1.64 (m, 1 H, anti H-13), 1.98 (s, 3 H, CH_3), 2.60–2.84 (m, 2 H, H-2, H-7), 4.26 (d, 1 H, *J* = 7.0, H-8), 5.41–5.96 (m, 4 H, H-3, H-4, H-5, H-6), 6.95–7.32 (m, 8 H, aromatic H)
4b	1.42 (m, 1 H, syn H-13), 1.68 (m, 1 H, anti H-13), 2.82–3.64 (m, 2 H, H-2, H-7), 4.36 (d, 1 H, *J* = 7.0, H-8), 5.54–6.19 (m, 4 H, H-3, H-4, H-5, H-6), 6.82–7.50 (m, 13 H, aromatic H)
6g	1.66 (m, 1 H, H-3), 2.58 (m, 1 H, H-3), 3.04 (m, 2 H, *J* = 10.3, 2.5, H-2, H-8), 5.78–6.09 (m, 4 H, H-4, H-5, H-6, H-7), 7.25–7.79 (m, 8 H, aromatic H)
6h	1.68 (m, 1 H, H-3), 2.84 (m, 1 H, H-3), 3.18 (m, 2 H, *J* = 10.2, 2.2, H-2, H-8), 5.72–6.10 (m, 4 H, H-4, H-5, H-6, H-7), 7.20–7.92 (m, 8 H, aromatic H)
7a	1.95 (d, 3 H, *J* = 6.9, CH_3), 2.12 (m, 1 H, H-1), 4.04 (m, 2 H, H-8, H-10), 5.34 (dd, 2 H, *J* = 9.0, 5.6, H-2, H-7), 6.00 (dd, 2 H, *J* = 9.0, 3.3, H-3, H-6), 6.46 (t, 2 H, *J* = 3.3, H-4, H-5), 6.93–7.83 (m, 8 H, aromatic H)
7b	2.38 (m, 1 H, H-1), 3.80 (m, 1 H, H-10), 4.96 (s, 1 H, H-8), 5.40 (dd, 2 H, *J* = 8.4, 4.5, H-2, H-7), 6.24 (dd, 2 H, *J* = 8.4, 3.0, H-3, H-6), 6.68 (t, 2 H, *J* = 3.0, H-4, H-5), 6.84–7.38 (m, 8 H, aromatic H)
7c	1.74 (d, 3 H, *J* = 7.0, CH_3), 1.98 (s, 3 H, CH_3), 2.18 (t, 1 H, *J* = 5.5, H-1), 3.93 (d, 1 H, *J* = 7.0, H-8), 5.35 (dd, 2 H, *J* = 9.0, 5.5, H-2, H-7), 5.98 (dd, 2 H, *J* = 9.0, 3.3, H-3, H-6), 6.47 (t, 2 H, *J* = 3.3, H-4, H-5), 7.20–7.74 (m, 8 H, aromatic H)
7d	2.32 (t, 1 H, *J* = 6.0, H-1), 5.30 (s, 1 H, H-8), 5.43 (dd, 2 H, *J* = 9.0, 6.0, H-2, H-7), 6.08 (dd, 2 H, *J* = 9.0, 3.0, H-3, H-6), 6.62 (t, 2 H, *J* = 3.0, H-4, H-5), 6.84–7.38 (m, 18 H, aromatic H)
7f	1.72 (t, 1 H, *J* = 6.0, H-1), 3.87 (s, 2 H, H-8, H-9), 5.48 (dd, 2 H, *J* = 9.0, 6.0, H-2, H-7), 6.08 (dd, 2 H, *J* = 9.0, 3.0, H-3, H-6), 6.50 (t, 2 H, *J* = 3.0, H-4, H-5), 7.24–8.0 (m, 8 H, aromatic H)

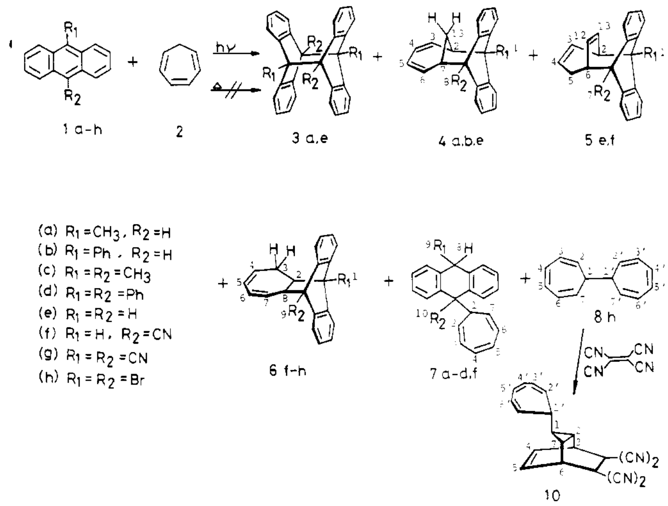
[a] Solvent was $CDCl_3$.

diene gives the photochemical "symmetry-allowed" [$_\pi 4 + {}_\pi 4$] cycloadduct with anthracene but the photochemical "symmetry-forbidden" [$_\pi 4 + {}_\pi 2$] cycloadduct with 9-cyanoanthracene.[8,9] Due to a low ionization potential and relatively low electron affinity, anthracene is predisposed to undergo highly polar nonionic cycloadditions with cyclic dienes and cyclic trienes. Accordingly, the photocycloadditions of excited anthracene and its derivatives may be suitable model compounds to establish their capability for the periselective photoadditions with cyclic trienes as 2π, 4π, and 6π components.

For the exact prediction, semiempirical Pariser–Parr–Pople SCF molecular orbital (PPP-SCF-MO) calculations were performed. As shown in Table I, the powerful electron-donating anthracenes are characterized by a high-lying filled molecular orbital (HOMO). By contrast, the strong electron-accepting anthracenes are characterized by a low-lying vacant orbital (LUMO).

Thus, it could be expected that the photochemical "symmetry-forbidden" reactions possibly occur between powerful electron-donating anthracene and the triene or strong electron-accepting anthracene and the triene as pointed out by Epiotis and Inagaki et al.[7]

Scheme I



Results

Photochemical Cycloaddition Reactions. Solutions of substituted anthracenes **1a–h** and a large excess of cyclohepta-1,3,5-triene (**2**) in various solvents were irradiated

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(8) Yang, N. C.; Srinivasachar, K.; Kin B.; Libman, J. *J. Am. Chem. Soc.* **1975**, *97*, 5006–5007.

(9) Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1972**, *94*, 1405–1406.

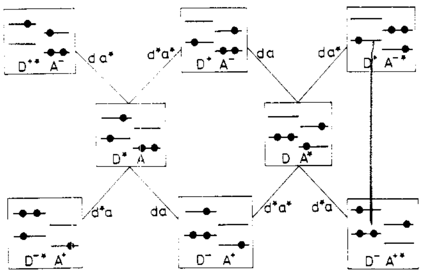

Figure 1. The important configuration (orbital) interactions which contribute to the intermolecular electron density (see ref 7).

with a high-pressure 100-W mercury lamp in an I_2–CCl_4 filter solution (340–420 nm) under nitrogen at room temperature. The photoproducts were separated by absorption chromatography on silica gel, and the yields were estimated by NMR inspection of appropriate chromatographic fractions. The product distributions were also determined with an Iatron TH-10 TLC analyzer. These results are summarized in Scheme I and Table II.

Structure Assignments of Adducts. Structure assignments for the photoproducts were determined on the basis of the NMR spectroscopic data. These spectral data are summarized in Table III.

The spectral patterns of the $[{}_\pi4 + {}_\pi6]$, $[{}_\pi4 + {}_\pi4]$, and $[{}_\pi4 + {}_\pi2]$ cycloadducts are grossly similar to those of the corresponding adducts as described in the previous reports.[5]

On the other hand, compounds **7a–d** and **7f** were identified as the corresponding ene-type products. Clearly, the NMR spectra for these compounds exhibited the characteristic signals of the cycloheptatriene moiety.

Interestingly, in the case of the photoaddition reaction of 9,10-dibromoanthracene (**1h**) with cyclohepta-1,3,5-triene, the $[{}_\pi4 + {}_\pi2]$ adduct (**6h**) was obtained together with ditropyl (**8**).[10] The structure of **8** was determined by chemical transformation: it was converted to a 1:1 adduct (**10**) by cycloaddition with tetracyanoethylene as depicted in Scheme I.

Discussion

The photocycloadditions of anthracene and substituted anthracenes to conjugated polyenes gave a variety of interesting products.

Yang et al. have investigated the photocycloadditions of anthracene to cyclopenta-1,3-diene and cyclohexa-1,3-diene and suggested a common biradical precursor to both the $[{}_\pi4 + {}_\pi2]$ and $[{}_\pi4 + {}_\pi4]$ adducts.[8,9] We have also studied the photocycloaddition of anthracene to cyclohepta-1,3,5-triene which afforded the $[{}_\pi4 + {}_\pi4]$ and $[{}_\pi4 + {}_\pi6]$ adducts.[5]

Subsequently Yang et al.[11] reported that these photocycloadditions may proceed via exciplex intermediates and that the reaction pathways may be influenced by the nature of the exciplex intermediates involved. Hammond et al.[12] have suggested that fluorescence from aromatic hydrocarbons such as naphthalene and its derivatives is quenched by conjugated dienes with variable efficiency, and a number of electronic configurations in the exciplex can contribute to binding as $(AQ)^* = A^*Q \leftrightarrow AQ^* \leftrightarrow A^+Q^- \leftrightarrow A^-Q^+$.

Table IV. Quantum Yields of Consumption of Substituted Anthracenes in the Presence of Cyclohepta-1,3,5-triene

compd	Φ_{-1}	λ_{max}, nm	compd	Φ_{-1}	λ_{max}, nm
1a	0.037	389	1d	0.004	395
1b	0.015	387	1g	0.145	402
1c	0.114	401	1h	0.040	406

Inagaki et al.[7] reported the important configuration (orbital) interactions in the excited-state reaction which contribute to the intermolecular electron density. Figure 1 schematically illustrates the change in the configuration energies as a function of the donor–acceptor properties of reactants.[7]

Enhancement of the donor–acceptor properties lowers $E_{D^+A^-}$ and $E_{D^{+*}A^-}$ and elevates $E_{D^-A^+}$ and $E_{D^{-*}A^+}$, presumably resulting in the reversal of $E_{D^-A^+}$ and $E_{D^{+*}A^-}$. The D^*A–$D^{+*}A^-$ interaction then contributes most significantly to the bonding since $D^{+*}A^-$ lies above D^*A and close to it. The configuration interaction involves the d–a* interaction. The frontier orbital interaction is the same as the one in most of the thermal interactions. Finally, they concluded that photochemical "symmetry-forbidden" reactions possibly occur between powerful donors and acceptors if the $D^{+*}A^-$ or D^+A^{-*} configuration is significantly lowered.

From these theoretical predictions it is noted that dominant interaction by intermolecular charge-transfer excitation from an excited anthracene (A*) to the triene (C) ($A^*C \leftrightarrow A^{+*}C^-$; in the photoaddition of a good electron-donor anthracene to the triene) leads to the stabilization of the transition state between the interactions of the diene SOMO and the triene LUMO and/or the diene SOMO′ and the triene HOMO. In the case of the disubstituted anthracenes, the largest increase in the electron-donating ability, the three-system interactions among the diene SOMO, the triene LUMO, and the C–H LUMO are formally possible. By contrast, in the photoaddition of a good electron-acceptor anthracene to the triene, dominant interactions by intermolecular charge-transfer excitation from C to A* ($A^*C \leftrightarrow A^-C^*$) lead to the stabilization of the transition state between the interactions of the diene SOMO′ and the triene HOMO and/or the diene SOMO and the triene LUMO.

Actually, the distribution of the $[{}_\pi4 + {}_\pi2]$, $[{}_\pi4 + {}_\pi4]$, and $[{}_\pi4 + {}_\pi6]$ cycloadducts between anthracene and cyclohepta-1,3,5-triene was observed to change significantly with the substitution at the 9- and 10-positions on anthracene as shown in Table II.

The photoaddition reaction of 9-methylanthracene, characterized by a electron-donating ability by the MO prediction, to cyclohepta-1,3,5-triene afforded the $[{}_\pi4 + {}_\pi6]$ adduct together with the ene-type addition compound in low yield. The same photoaddition of 9-phenylanthracene to cyclohepta-1,3,5-triene gave also the $[{}_\pi4 + {}_\pi6]$ adduct and the ene-type product but both in increased yields. Interestingly, the photoadditions of 9,10-disubstituted anthracenes (R = R′ Me and Ph) gave exclusive formations of the corresponding ene-type products in good yields. While the methyl group is an electron-donating group to aromatic systems, 9- or 10-phenyl may not be the donor group. These results might be attributed to the steric interaction between the 9-phenyl group and the 1- and 8-position perihydrogens to cause the phenyl group to be noncoplanar with the anthracene ring. Thus, the exclusive formations of the ene-type $[{}_\pi4 + {}_\pi6 + {}_\sigma2]$ products are readily understandable in terms of the steric interaction over the orbital interaction. The quantum yields (Φ_{-1}) of the consumption of substituted anthracenes in the

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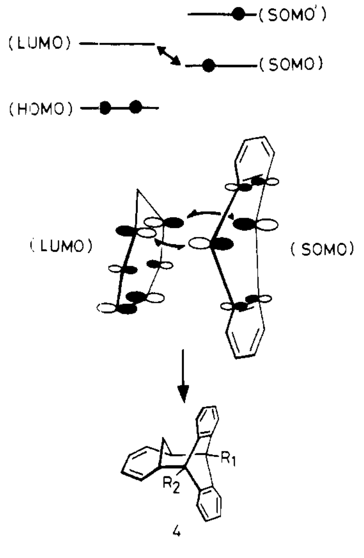
[10] Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1957**, *79*, 352–356.

[11] Yang, N. C.; Srinivasachar, K. *J. Chem. Soc, Chem. Commun.* **1976**, 48–49.

[12] Murov, S.; Hammond, G. S. *J. Chem. Phys.* **1968**, *72*, 3797–3801.

Scheme II



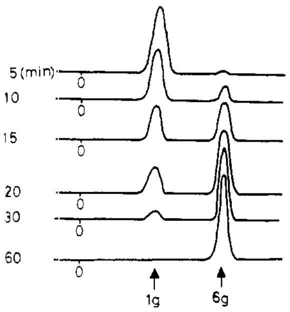


Figure 2. TLC change with the lapse of time for the photoaddition reaction of 9,10-dicyanoanthracene (**1g**) and cyclohepta-1,3,5-triene (monitored by an Iatron TH-10 TLC analyzer).

presence of a large excess of cyclohepta-1,3,5-triene were determined and were summarized in Table IV.

As can be seen in Table IV, the lower quantum yields obtained with 9-phenyl- and 9,10-diphenylanthracenes could then be taken as an indication that the steric interactions appear to be a significant inhibitory influence.

On the other hand, it might be explained that the highly symmetrical geometry of the resulting structure (4) is related to the preference of $[_{\pi}4 + {}_{\pi}6]$ cycloaddition over $[_{\pi}4 + {}_{\pi}4]$ cycloaddition between the interaction of the anthracene SOMO and the triene LUMO by a high-lying SOMO of anthracene.

We schematically consider the possible representation of an important orbital interaction in Scheme II.

Recently Yang et al.[11] reported that the photocycloaddition of 9-cyanoanthracene, with an electron-accepting ability by the MO prediction, to cyclohepta-1,3,5-triene yielded the $[_{\pi}4 + {}_{\pi}2]$, $[_{\pi}4 + {}_{\pi}4]$, and $[_{\pi}4 + {}_{\pi}6]$ cycloadducts in dual reaction pathways. We have also reinvestigated the same photocycloaddition of 9-cyanoanthracene to cyclohepta-1,3,5-triene under the same conditions as described above which afforded the $[_{\pi}4 + {}_{\pi}2]$ and $[_{\pi}4 + {}_{\pi}4]$ cycloadducts together with a small amount of the ene-type product. Surprisingly, the same photoadditions of 9,10-dicyanoanthracene, with a more powerful electron-accepting ability by the MO prediction, to cyclohepta-1,3,5-triene gave a perispecific $[_{\pi}4 + {}_{\pi}2]$ cycloadduct in good yield. The reaction was monitored with an Iatron TH 10 TLC analyzer, but no isomeric products could be detected during the irradiation as shown in Figure 2. Figure 3 shows the Stern–Volmer plots for fluorescence quenching of 9,10-dicyano- and 9,10-dibromoanthracenes by cyclohepta-1,3,5-triene in benzene, from which $K_q\tau_s$ was calculated; these values are listed in Table V.

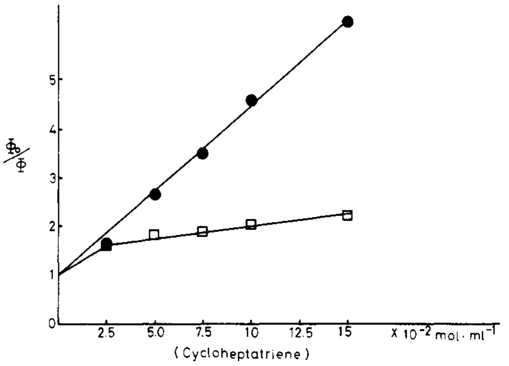


Figure 3. Stern–Volmer plots of fluorescence quenching of 9,10-dicyanoanthracene (●) or 9,10-dibromoanthracene (□) by cyclohepta-1,3,5-triene.

Table V. Fluorescence Quenching of 9,10-Disubstituted Anthracenes by Cyclohepta-1,3,5-triene

compd	$K_q\tau_s$[a]	Ex[b]	Em[c]
1g	36.81	402	460
1h	35.20, 3.13	364	434

[a] Values given are in M^{-1} at ambient temperature. [b] Ex = excitation light, in nanometers. [c] Em = emission light, in nanometers.

Table VI. Solvent Effect on Photocycloaddition of 9,10-Dicyanoanthracene with Cyclohepta-1,3,5-triene[a]

solvent[c]	yield[b] of $[_{\pi}4 + {}_{\pi}2]$ adduct **6**, %	solvent[c]	yield[b] of $[_{\pi}4 + {}_{\pi}2]$ adduct **6**, %
n-hexane	58	acetone	59
benzene	63	ethylene glycol-dimethyl ether	61

[a] Irradiation was carried out under nitrogen at room temperature. [b] Yields are calculated on the basis of an internal standard (1-cyanonaphthalene). [c] Volume 150 mL, 0.001 M **1g** and 0.01 M **2**.

The efficient quenching of fluorescence in the case of the photoaddition reaction of 9,10-dicyanoanthracene by cyclohepta-1,3,5-triene suggests that the addition proceeds via the singlet excited state of 9,10-dicyanoanthracene. Furthermore, as shown in Table VI, the photoaddition reaction was found unchanged in various solvents.

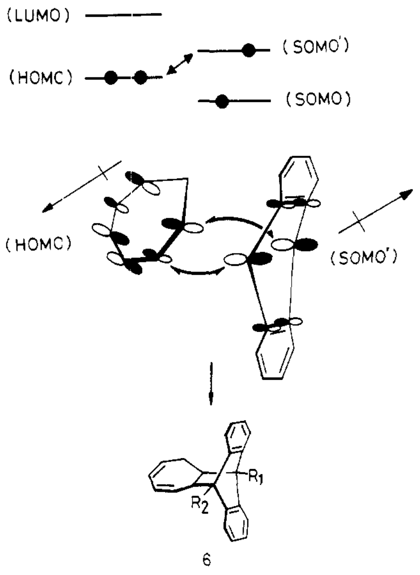
From the experimental results, it is concluded that the $[_{\pi}4 + {}_{\pi}2]$ cycloadduct could arise from the dominant interaction by intermolecular charge-transfer excitation from the triene HOMO to the singlet excited anthracene SOMO′ and might be allowed by the dipole–dipole interaction[11] (Scheme III).

By contrast, the quenching effects of fluorescence of 9,10-dibromoanthracene by cyclohepta-1,3,5-triene may suggest that the photoaddition proceeds via two different excited states (the singlet and triplet states). The bromine substituent exerts a heavy-atom effect on the aromatic system to promote intersystem crossing, which may suggest that the addition proceeds via the triplet excited states as depicted in Scheme IV.

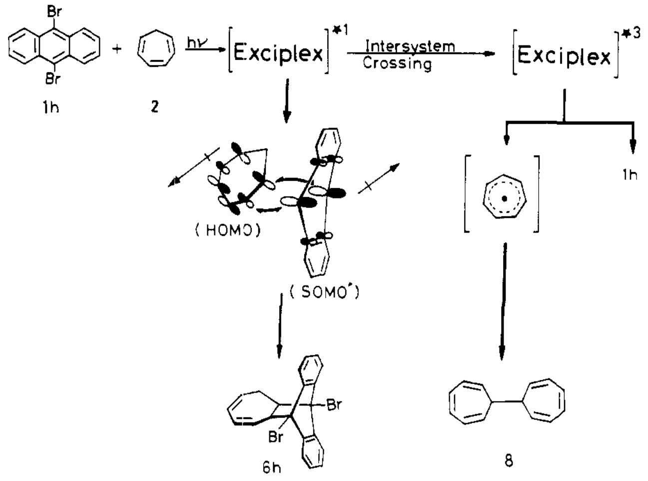
Indeed, the product distributions of ditropyl (**8**) remarkably decreased in the presence of the triplet quencher (*trans*-piperylene) as shown in Table VII. However, the formation of the $[_{\pi}4 + {}_{\pi}2]$ cycloadduct remained constant within experimental error. Probably, the $[_{\pi}4 + {}_{\pi}2]$ cycloadduct might be formed via the excited singlet state.

Finally, it is to be noted that the substituent effects on the photochemical reactivity are valuable probes of the

Scheme III



Scheme IV



symmetry-forbidden process by the Woodward–Hoffmann analyses for the photochemical pericyclic reactions.

Experimental Section

The melting points were measured with a Yanagimoto micro melting 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 Me_4Si as an internal standard; chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO DS-701 G 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. Relative fluorescence intensities were measured with a Hitachi MPF 4 spectrofluoromer. The excitation wavelength was adjusted to obtain maximum emission. The samples were degassed by nitrogen before the measurements were made. The lamp used was a xenon arc lamp (Usio UXL 150 DS). Quantum yields were measured by using a merry-go-round apparatus to assure uniform irradiation of test and actinometric samples. The product distributions were measured by using an Iatron TH-10 TLC analyzer.

General Procedure for Photocycloaddition of Substituted Anthracenes and Cyclohepta-1,3,5-triene. A solution of various anthracene derivatives and a large excess of cyclohepta-1,3,5-triene in various solvents was irradiated several times with a 100-W high-pressure mercury lamp fitted with an I_2–CCl_4 filter solution under nitrogen at room temperature. After the consumption of starting materials was confirmed by UV spectrophotometry, the solvent was removed under reduced pressure at room temperature. The residual solid was chromatographed on a silica gel column by using various solvent mixtures.

Table VII. Quenching Effect in Photocycloaddition of 9,10-Dibromoanthracene with Cyclohepta-1,3,5-triene in the Presence of Triplet Quencher

irradn time, min	product ratio[a,d]			
	[$_\pi 4 + {}_\pi 2$] adduct		ditropyl	
	none[c]	add[b]	none[c]	add[b]
60	0.86	0.90	0.039	0.050
120	0.92	0.90	0.077	0.058
240	1.09	0.88	0.288	0.067

[a] Measured with an Iatron TH-10 TLC analyzer on the basis of an internal standard. [b] Quencher added was *trans*-piperylene. [c] No quencher added. [d] The relative amount of internal standard (2-methoxynaphthalene) was taken as 1 in each case.

Photochemical Reaction of 9-Methylanthracene with Cyclohepta-1,3,5-triene. A solution of **1a** (0.3 g) and **2** (1.5 g) in benzene (20 mL) was irradiated by the above procedure. The same workup gave the adducts **4a** and **7a** and the anthracene photodimer (0.16 g). The first fractions gave 0.04 g (9%) of **4a** as colorless crystals, mp 68–70 °C (ethanol). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.66; H, 7.45. The second fractions gave 0.03 g (7%) of adduct **7a** as colorless crystals, mp 74–76 °C (ethanol). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.61; H, 7.01.

Photochemical Reaction of 9-Phenylanthracene with Cyclohepta-1,3,5-triene. A solution of **1b** (0.5 g) and **2** (1.2 g) in benzene (40 mL) was irradiated by the above procedure. The same workup gave the adducts **4b** and **7b**. The first fractions gave 0.26 g (38%) of adduct **4b** as yellow plates, mp 108–109 °C (ethanol). Anal. Calcd for $C_{27}H_{22}$; C, 93.60; H, 6.40. Found: C, 93.45; H, 6.33. The second fractions gave 0.15 g (22%) of adduct **7b** as yellow crystals, mp 112–114 °C (ethanol). Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.68; H, 6.42.

Photochemical Reaction of 9,10-Dimethylanthracene with Cyclohepta-1,3,5-triene. A solution of **1c** (0.3 g) and **2** (1.2 g) in benzene (50 mL) was irradiated by the above procedure. The same workup gave the adduct **7c** (0.31 g, 69%) as colorless crystals, mp 139–140 °C. Anal. Calcd for $C_{23}H_{22}$; C 92.57; H, 7.43. Found: C, 92.61; H, 7.55.

Photochemical Reaction of 9,10-Diphenylanthracene with Cyclohepta-1,3,5-triene. A solution of **1d** (0.5 g) and **2** (1.45 g) in benzene (80 mL) was irradiated by the above procedure. The same workup gave the adduct **7d** (0.46 g, 73%) as yellow plates, mp 178–179 °C (ethanol). Anal. Calcd for $C_{33}H_{26}$, C, 93.80; H, 6.20. Found: C, 93.67; H, 6.28.

Photochemical Reaction of 9-Cyanoanthracene with Cyclohepta-1,3,5-triene. A solution of **1f** (0.3 g) and **2** (1.4 g) in benzene (120 mL) was irradiated by the above procedure. The same workup gave the adducts **5f** (0.12 g, 28%),[11] **6f** (0.14 g, 32%),[11] and **7f** (0.017 g, 4% as colorless crystals from ethanol): mp 136–138 °C; IR (Nujol) 2260 (CN) cm^{-1}. Anal. Calcd for $C_{22}H_{17}N$; C, 89.46; H, 5.80; N, 4.74. Found: C, 89.09; H, 5.83; N, 4.62.

Photochemical Reaction of 9,10-Dicyanoanthracene with Cyclohepta-1,3,5-triene. A solution of **1g** (0.3 g) and **2** (1.45 g) in benzene (150 mL) was irradiated by the above procedure. The same workup gave the adduct **6g** (0.27 g, 63%) as colorless crystals: mp 158–159 °C; IR (Nujol) 2265 (sh, CN) cm^{-1}. Anal. Calcd for $C_{23}H_{16}N_2$; C, 86.22; H, 5.03; N, 8.74. Found: C, 85.90; H, 4.94; N, 8.52.

Photochemical Reaction of 9,10-Dibromoanthracene with Cyclohepta-1,3,5-triene. A solution of **1h** (0.3 g) and **2** (1.5 g) in benzene(100 mL) was irradiated by the above procedure. The same workup gave the adducts **6h** (0.22 g, 58%) and **8** (0.24 g, 81%). For **6h**: mp 185–187 °C (ethanol); yellow crystals; IR (Nujol) 3080, 3005, 1600, 1440, 745 cm^{-1}. Anal. Calcd for $C_{21}H_{16}Br_2$: C, 58.87; H, 3.74; Br, 37.39. Found: C, 58.62; H, 3.79; Br, 37.57.

A solution of crude 8 (0.2 g) and tetracyanoethylene (0.14 g) in benzene (6 mL) was stirred at 60 °C for 10 min. The solvent was evaporated under reduced pressure, and the residue was recrystallized from ethanol-benzene (10:1) to give the 1:1 adduct **10**: 0.25 g (74%); mp 216-217 °C; IR (Nujol) 2260 (CN) cm^{-1}; NMR δ (CDCl$_3$) 1.10 (m, 1 H, H-1), 1.59 (m, 1 H, H-2), 1.68 (m, 1 H, H-1′), 3.86 (m, 2 H, H-3, H-6), 5.20 (dd, 2 H, J = 9.0, 4.3 Hz, H-2′, H-7′), 6.16 (dd, 2 H, J = 9.0, 3.0 Hz, H-3′, H-6′), 6.38 (d, 2 H, J = 4.4 Hz, H-4, H-5), 6.60 (t, 2 H, J = 3.0 Hz, H-4′, H-5′). Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.42; H, 4.51; N, 18.06. Found: C, 77.28; H, 4.68; N, 18.01.

Quantum Yield Determination. A solution of **1a-h** (0.0087 mmol) and **2** (10 mmol) in benzene (100 mL) was prepared. The solution in a Pyrex tube was degassed with nitrogen and irradiated at 3650 Å by use of a filter. The light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker.[5]

The consumption of **1a-h** was monitored by UV spectroscopy by use of the 0-0 absorption band (λ_{max}; see Table IV). Several measurements were taken at different conversions (<10% conversion), and the average value was used. The results were shown in Table IV.

Fluorescence Quenching. Samples (3 mL) containing 2.4 × 10^{-5} M anthracene derivatives **1g** and **1f** and varying concentrations of cyclohepta-1,3,5-triene (**2**) in benzene were placed in optical path length quartz cells (1 × 1 cm). The intensities were measured three times for each cell, and an average value for each sample was used. The results are shown in Figure 3 and Table V.

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Registry No. 1a, 779-02-2; **1b**, 602-55-1; **1c**, 781-43-1; **1d**, 1499-10-1; **1e**, 120-12-7; **1f**, 1210-12-4; **1g**, 1217-45-4; **1h**, 523-27-3; **2**, 544-25-2; **3a**, 36773-81-6; **3e**, 1627-06-1; **4a**, 75378-73-3; **4b**, 75378-74-4; **4e**, 75378-75-5; **5e**, 42916-01-8; **5f**, 59410-57-0; **6f**, 59410-56-9; **6g**, 75378-76-6; **6h**, 75378-77-7; **7a**, 75378-78-8; **7b**, 75378-79-9; **7c**, 75378-80-2; **7d**, 75378-81-3; **7f**, 75378-82-4; **8h**, 831-18-5; **10**, 75400-72-5; tetracyanoethylene, 670-54-2.

Mechanism of the Photochemical Wolff Rearrangement. The Role of Conformation in the Photolysis of α-Diazo Carbonyl Compounds

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Investigation of photochemical processes of several α-diazo carbonyl compounds reveals that the Wolff rearrangement to form ketene takes place directly from the singlet excited state of the *s-Z* conformer whereas the excited state of the *s-E* conformer dissociates nitrogen to generate singlet carbonyl carbene, which either undergoes characteristic carbenic reactions, e.g., insertion and 1,2-hydrogen shift, or gives rise to ketene. The migratory aptitude as well as the relative efficiency of other competing reactions from singlet carbene is shown to be an important factor in determining which reaction pathway is favored. Substantial amounts of singlet carbene can be formed even under sensitized conditions, presumably via intersystem crossing from initially formed triplet carbene.

The photochemistry of α-diazo carbonyl compounds has received much attention recently both from chemists interested in the nature and mechanisms of the reactions undergone by these species[1] and from others interested in using them as labeling reagents for active sites of enzymes.[2] Thus, carbenes produced upon irradiation of α-diazo carbonyl compounds have been known to undergo insertion and/or addition reactions and hence to be useful reactive intermediates for introduction of the carbonylmethylene group. The photolysis is, however, often accompanied by the Wolff rearrangement (WR) which has diminished the utility of these compounds as a ketocarbene source. The WR, on the other hand, has found wide use as the crucial step in the Arndt-Eistert synthesis.[3] It has also attracted much interest industrially[4] as a photoresist process. It is very important to elucidate, then, the exact nature which controls the two competitive pathways in the photolysis of α-diazo carbonyl compounds. Although the WR has been the subject of numerous mechanistic investigations,[1] a satisfactory rationalization of this reaction has not yet been achieved. Involvement of free ketocarbene in the WR was first reported by Wolff[5] and is still favored by many authors, although there are few direct proofs for the intermediacy of ketocarbene. More recently, Kaplan and Meloy[6] proposed a one-step, concerted rearrangement by studies of hindered internal rotation about the C-C bond in diazo ketones. They have suggested that diazo ketones exist as an equilibrium mixture of *s-Z* and *s-E* forms and that only the *s-Z* form is responsible for the WR with migration accompanying loss of nitrogen due to stereoelectronic reasons. There is evidence,[7] on the other hand, that under certain conditions some diazo compounds are protonated and that therefore the WR takes place in the diazonium ion. Despite the wealth of data which has been

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