redox reactions are applicable to light energy conversion in particular, exploitation of solar light depends on the successful prevention of thermal back transfer of electrons from DQ^- to D^+. Here micellar systems due to their two-phase character offer some interesting possibilities, which are presently being examined. In particular it seems worthwhile to pursue in more detail the $CO_3{}^{2-}$ oxidation to $CO_3{}^-$ by excited quinones, since $CO_3{}^-$ in its subsequent reactions is known to yield oxygen.[30] Hence in a system containing quinone and carbonate, oxygen evolution from water by visible light becomes feasible. Studies in this direction are now under way.

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Molecular Design by Cycloaddition Reactions. 30.[1] Photochemical Cycloadditions of Quadricyclane to Aromatic Hydrocarbons and *o*-Quinones. First Example of Photochemical Pericyclic [$4\pi + 2\sigma + 2\sigma$] Addition

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Abstract: The photochemical pericyclic [$4\pi + 2\sigma + 2\sigma$] additions of anthracene, acridine, and some 1,2-quinones to quadricyclane were extensively investigated and compared with those of norbornadiene. The structures of these adducts were determined by spectral inspections. The reaction mechanisms for these adducts are discussed in connection with the theory of polar cycloaddition reaction on the basis of configuration interaction analyses.

Many useful examples showing the application of the simple and powerful generalized selection rules for pericyclic reactions have been reported.[2,3] To the best of our knowledge, the photochemical allowed [$4\pi + 2\pi(2\sigma) + 2\pi(2\sigma)$] cycloaddition has no precedent in the chemical literature.

It was of interest to examine the possibility of the mode of [$4\pi + 2\sigma + 2\sigma$] cycloaddition both from a synthetic and a theoretical point of view. Quadricyclane seemed to be a good model for this purpose. By contrast, regio- and stereospecific thermal allowed [$2\pi + 2\sigma + 2\sigma$] cycloaddition reactions[4] and metal-catalyzed [$2\pi + 2\sigma$] cycloaddition reactions of quadricyclane have been investigated.[5] On the other hand, Murov and Hammond[6] have reported that quadricyclane is a very effective quencher of the fluorescence of aromatic hydrocarbons such as anthracene and naphthalene, and suggested that the electronic energy of the aromatic hydrocarbons is efficiently transferred to vibrational energy of quadricyclane followed by isomerization to norbornadiene. Solomon et al.[7] have described that the fluorescence quenching of aromatic hydrocarbons by quadricyclane could proceed via a charge-transfer complex. In spite of these efforts, the possibility of chemical product formation has not been excluded, since Yang et al.[8] and the present authors[9] have shown tht some aromatic hydrocarbons undergo highly efficient photocycloadditions with several cyclic dienes and trienes resulting in chemical product formation through a significant pathway for the decay of the exciplexes.

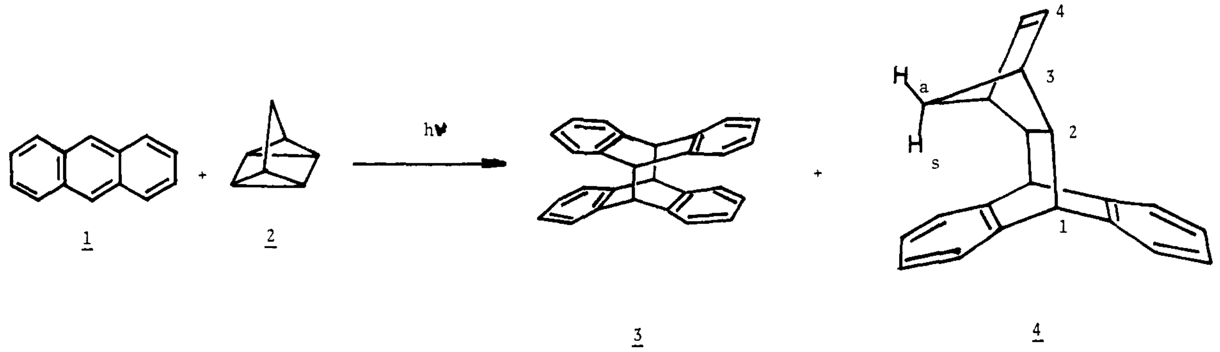
We have recently communicated the photochemical reaction between aromatic hydrocarbons and quadricyclane.[10] These results are discussed in detail in this paper in comparison with the previous works[7,8] and with further additional data that we have obtained.

Table I. Photocycloaddition of Aromatic Hydrocarbons to Quadricyclane and Norbornadiene

Compd	Quencher[a]	Solvent	Reaction Time, h	$k_q\tau_0$ l./mol	1:1 adduct (yield %)
Anthracene	Q	C_6H_6	6	12.2	15
	Q	CH_3CN	6		2.5
	Q	EtOH	6		13
	Q	CH_2Br_2	6		None
	NB	C_6H_6	6		None
9-Methyl-	Q	C_6H_6	2	6.34	7.5
	NB	C_6H_6	2.5		None
9,10-Dimethyl-	Q	C_6H_6	5	2.40	21.5
	NB	C_6H_6	6		None
9,10-Dibromo-	Q	C_6H_6	6.5	35.77	8
	NB	C_6H_6	8		None
9-Cyano-	Q	C_6H_6	4	82.43	3.5
	NB	C_6H_6	5	1.33	2
Naphthalene	Q	C_6H_6	6	48.0	None
	NB	C_6H_6	6		None

[a] Q = quadricyclane, NB = norbornadiene.

Scheme I



Results

Photochemical Pericyclic Reactions. With Anthracene, Substituted Anthracenes, and Naphthalene. When a solution of anthracene (**1**) and a large excess of quadricyclane (**2**) in benzene was irradiated with a high-pressure mercury lamp (100-W) in a Pyrex vessel under argon at 20 °C for 6 h (Scheme I), anthracene was rapidly consumed. After removal of the anthracene photodimer **3** (68%) which precipitated during the irradiation, careful chromatography of the photolysis mixture on silica gel using benzene-*n*-hexane as eluent gave the 1:1 adduct **4** in 15% yield. Interestingly, similar irradiation under the same conditions in the presence of methylene bromide (external heavy-atom effect) resulted in the quantitative formation of the dimer **3**, conversion to norbornadiene (**5**) (20%), and recovery of **2** (80%), and no 1:1 adduct was detected. The structure of the adduct **4** was deduced from elemental analysis, mass spectrum (M^+ 270), and its NMR data. The NMR spectrum of the adduct **4** exhibited signals of two bridged methylene protons at δ −0.19 (d, 1 H, syn H-13, J = 10.5 Hz), and 0.68 (d, 1 H, anti H-13, J = 10.5 Hz), methine protons at δ 2.02 (d, 2 H, H-2 and H-7, J = 1.0 Hz) and 2.41 (d, 2 H, H-3 and H-6, J = 1.8 Hz), benzylic methine protons at δ 4.04 (d, 2 H, H-1 and H-8, J = 1.0 Hz), olefinic protons at δ 6.03 (d, 2 H, H-4 and H-5, J = 1.8 Hz), and aromatic protons at δ 6.92–7.18 (m, 8 H). Appearance of the higher methylene proton signal was attributable to the anisotropy of benzene moiety, which was to be expected for the exo isomer by molecular models. Thus, the adduct was concluded to be the exo $[4\pi + 2\sigma + 2\sigma]$ cycloadduct **4**. It is to be noted that both the thermal and photochemical reactions of **1** and norbornadiene (**5**) gave no 1:1 adduct even under more drastic conditions or a much longer time.

Substituent effects for the photocycloaddition were also examined, and these results are summarized in Table I. Most impressive was the result that 9-cyanoanthracene reacted with norbornadiene (**5**) to give a dimer (76%) together with a 1:1 adduct (2%).

When a solution of naphthalene (**6**) and **2** in benzene was irradiated under the same conditions through a Corex filter, extensive isomerization of **2** to norbornadiene (**5**) was observed, and no 1:1 adduct was detected (cf. Table I).

To obtain further information about these photochemical pericyclic reactions, we carried out fluorescence quenching experiments; the fluorescence of anthracene (**1**) and naphthalene (**6**) was efficiently quenched by **2** and linear Stern–Volmer plots were obtained for the quenching reactions. The rate constant for the quenching reaction of anthracene (3.1×10^9 l. mol^{-1} s^{-1}) is about the same as that of naphthalene (3.2×10^9 l. mol^{-1} s^{-1}). This observation was consistent with the results of Murov and Hammond.[6] The $k_q\tau_0$ values for the quenching reactions are also listed in Table I.

With Acridine. Irradiation of acridine (**7**) and quadricyclane (**2**) in benzene afforded an isomeric mixture of 1:1 adducts of **8** and **9** in a moderate yield (Scheme II). The NMR of the reaction mixture showed the ratio of 5:2. Similar irradiation of acridine (**7**) and norbornadiene (**5**) under the same conditions gave also the isomeric 1:1 adducts **8** and **9** in the ratio of 5:1. A pure sample of **8** was isolated by chromatography on alumina followed by recrystallization, but isomer **9** decomposed slowly upon chromatography or the attempted purification. The structures of the isomers were determined by NMR data. A significant shielding effect by the anisotropy of the benzene moiety for methylene bridge protons in **8** is observed at δ −0.08 (1 H, d, J = 9.0 Hz) and 0.9 (1 H, d, J = 9.0 Hz). By contrast, compound **9** showed methylene protons at δ

Scheme II

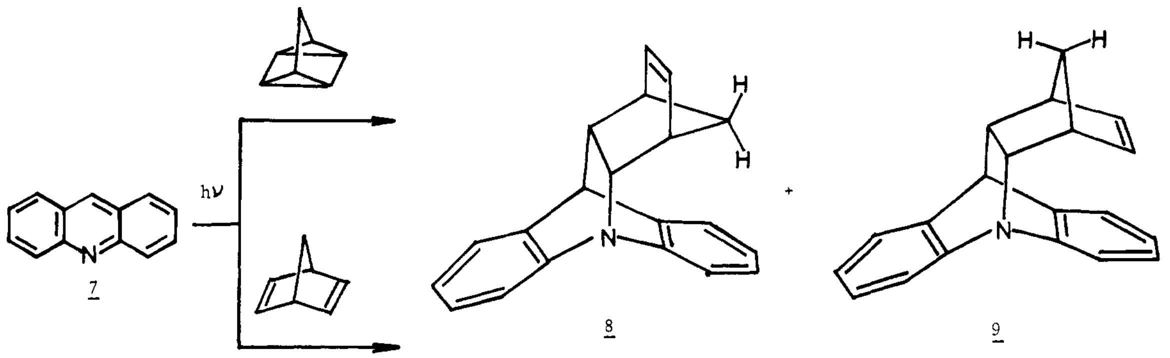


Table II. Solvent Effect and Sensitizing Effect in Photocycloaddition of Acridine to Quadricyclane and Norbornadiene

Quencher^a	Solvent	Sensitizer	Total yield of 1:1 adducts (%)
Q	C_6H_6	None	55
NB	C_6H_6	None	50
Q	C_6H_6-t-BuOH	None	40
NB	C_6H_6-t-BuOH	None	41
Q	C_6H_6	Biacetyl	11
NB	C_6H_6	Biacetyl	14
Q	$CHCl_3$-CH_2Br_2	None	None
NB	$CHCl_3$-CH_2Br_2	None	None
Q	EtOH	None	Trace^b
NB	EtOH	None	Trace^b

[a] Q = quadricyclane; NB = norbornadiene. [b] Only photoreductive products were detected.

1.2-1.3 (2 H, multiplet). The endo isomer could not show such an anisotropic shielding effect of the aromatic ring by inspection of the stereo model. Thus, structures **8** and **9** were assigned to be exo and endo 1:1 adducts, respectively.

Furthermore, the results of these photoadditions in various solvents are summarized in Table II.

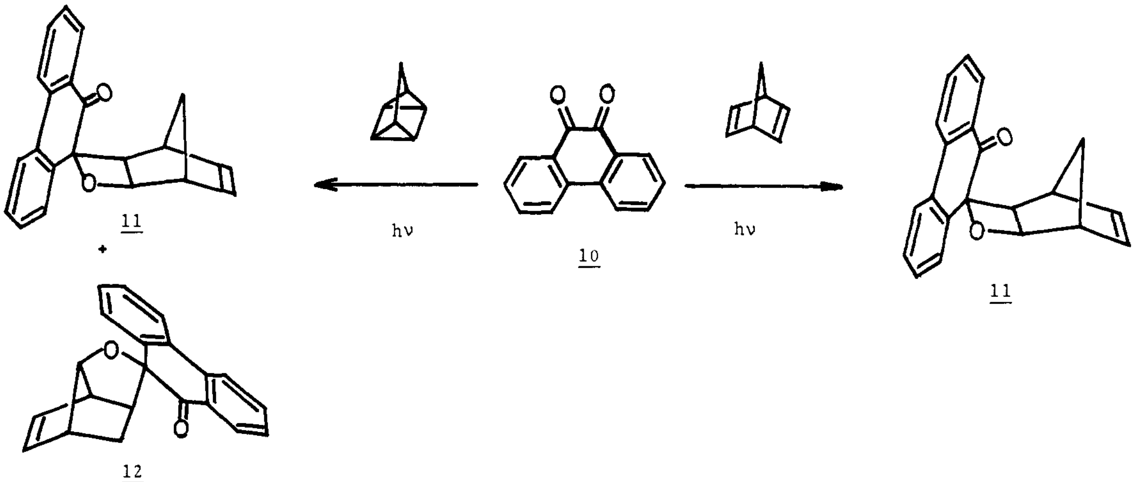
As shown in Table II, the total yield of the 1:1 adducts **8** and **9** decreased for the photoaddition reactions in the presence of biacetyl and methylene bromide. Most significantly, the photoproduct formations are affected by the polarity of a protic solvent. These striking effects of solvents are discussed later. Besides, no interconversions of norbornadiene to quadricyclane were observed during the irradiation; the reaction was monitored by NMR in periods of 30 min, 1 h, and 3 h. All adducts obtained as above apparently arose from the photochemically induced reaction. In fact, no reactions occurred when a solution of acridine and **2** or **5** in benzene was refluxed for a much longer time.

With 9,10-Phenanthrenequinone, Acenaphthenequinone, and Tetrachloro-*o*-benzoquinone. Irradiation of a solution of 9,10-phenanthrenequinone (**10**) and a large excess of quadricyclane (**2**) in benzene with a high-pressure mercury lamp in a Pyrex vessel for 3 h gave adducts **11** and **12** with a ratio of 2:3 in about 57% yield. On the other hand, similar irradiation of **10** and norbornadiene (**5**) under same conditions gave only **11** in a moderate yield. Compound **11** was identified as an *exo*-keto oxetane structure by the spectral data. The ir spectrum of **11** showed a carbonyl absorption at 1710 and 1690 (shoulder) cm^{-1}. The NMR spectrum of **11** exhibited bridged methylene protons at δ 1.30 (d, 1 H) and 2.53 (d, 1 H) with coupling constant of 9.0 Hz, bridgehead protons at δ 2.46 (br s, 1 H) and 3.23 (br s, 1 H), two methine protons at δ 4.72 (dd, 1 H, J = 5.0 and 1.5 Hz) due to influence of the oxygen atom and 2.54 (dd, 1 H, J = 5.0 and 1.5 Hz), two olefinic protons at δ 5.90 (m), and aromatic protons at δ 7.25-8.00 (m, 8 H).

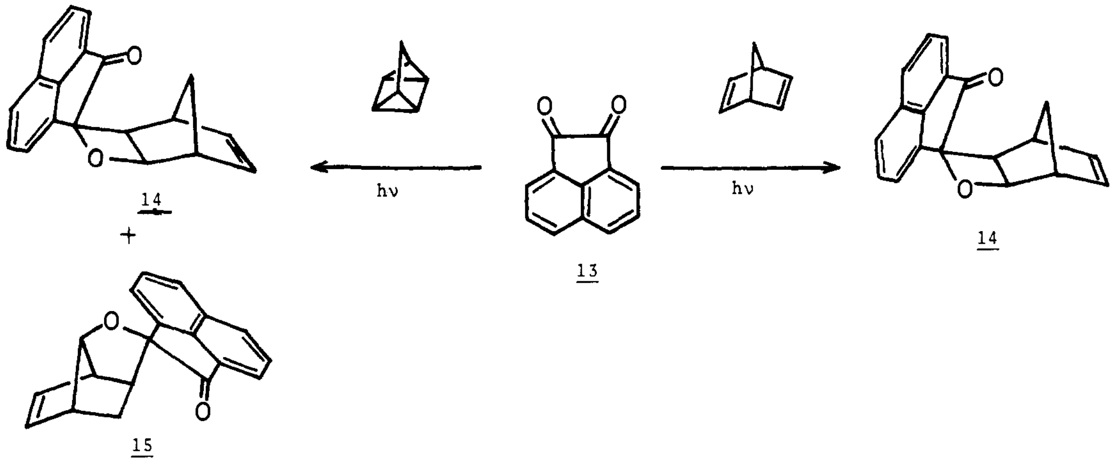
Compound **12** was identified as a photorearrangement product. The IR spectrum of **12** showed a carbonyl absorption at 1700 cm^{-1}. The NMR spectrum of **12** showed signals of a slightly split singlet at δ 4.45 (1 H) attributable to bridged methine proton by influence of the oxygen atom. Furthermore, the characteristic signals at δ 1.17 and 1.88 were assigned to *endo*- and *exo*-methylene protons, respectively, which are in accord with the chemical shifts of those of the norbornene system, and the large coupling constant of 12 Hz is also attributable to the geminal protons. Thus, the adduct **12** was concluded to the structure of 8-oxatricyclo[4.3.0.0^{3,7}]-non-4-ene, as depicted in Scheme III.

Analogously, the photoaddition of acenaphthenequinone (**13**) to quadricyclane (**2**) under above conditions gave a mixture of keto oxetane **14** and photorearrangement product **15**,

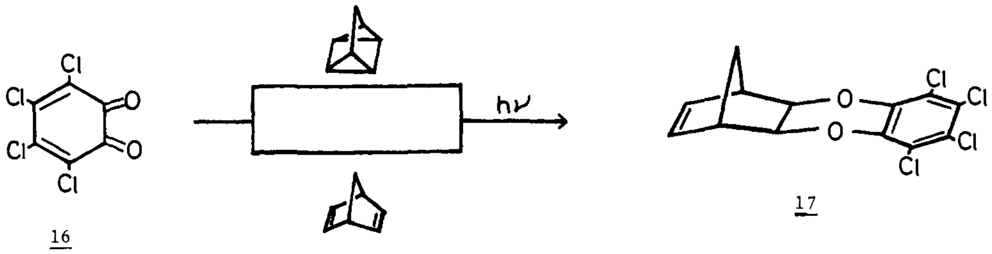
Scheme III



Scheme IV



Scheme V



but with norbornadiene (**5**) only the adduct **14** was isolated (Scheme IV).

By contrast, irradiation of tetrachloro-*o*-benzoquinone (**16**) and quadricyclane or norbornadiene in benzene with a high-pressure mercury lamp in a Pyrex vessel through an iodine-carbon tetrachloride filter solution (>400 nm) gave only a 1:1 adduct (**17**), which was identified as an *exo-cis*-dioxene compound, in a moderate yield (Scheme V).

Discussion

The formation of photoproduct **4** may be rationalized as a photochemical pericyclic $[4\pi + 2\sigma + 2\sigma]$ addition between the π,π^* singlet excited anthracene and quadricyclane. By contrast, one interesting implication comes from consideration of the fact that the photochemical product could not be detected from the quenching of naphthalene by quadricyclane, which resulted in extensive isomerization of quadricyclane to norbornadiene. Since the anthracene has a higher electron affinity than the naphthalene, there is a difference in the charge-transfer character of the excited intermediates.

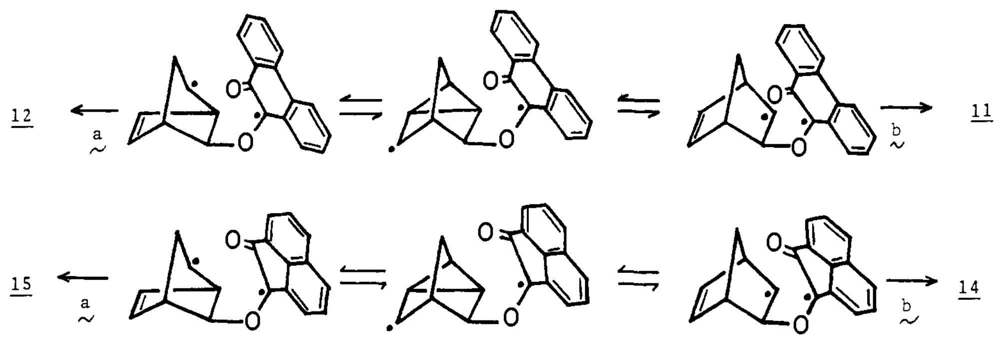
On the other hand, the light-induced addition of 1,3-dienes to anthracene has been visualized as a photochemical allowed [4s + 4s] reaction and the degree of stereoselectivity suggests that the reaction is concerted, but 9-cyanoanthracene added to 1,3-dienes stereospecifically in a [4s + 2s] manner.[8] In this connection, it is explained in terms of a polar photocycloaddition reaction and that the orbital symmetry approach can be used with many photochemical problems such as the effect of substituents on the mechanism and stereochemistry of photochemical pericyclic reactions.[11]

Interestingly, as shown in Table I, the photochemical cycloaddition reaction of 9-cyanoanthracene (relatively lower energy LUMO) and norbornadiene led to the formation of the [4 + 2] adduct, and this formation is in sharp contrast to no formation of the photoadduct in the reaction of unsubstituted anthracene and norbornadiene; it is suggested that the 9-cyanoanthracene LUMO (or SOMO (singly occupied molecular orbital)) and the norbornadiene HOMO interactions are expected to be more predominant than the 9-cyanoanthracene LUMO (or SOMO) and the norbornadiene LUMO interactions. By contrast, it could also be explained as a result of a two-step mechanism via a singlet biradical intermediate with stabilization of a polar contributing structure by the introduction of cyano group in the excited anthracene molecule; the intermediate undergoes ring closure faster than bond rotation or radical rearrangement.

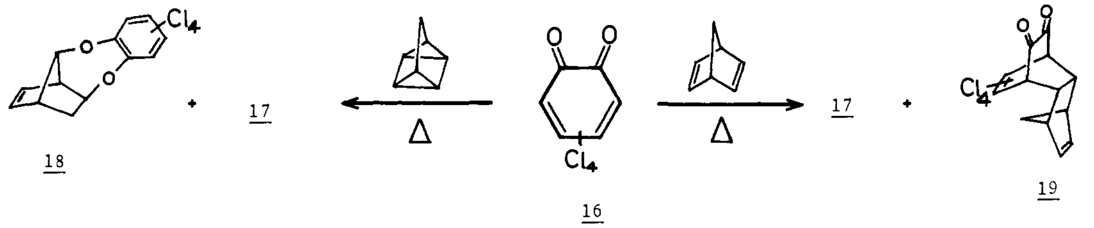
Variable amounts of exo and endo$[4\pi + 2\sigma + 2\sigma]$ adducts **8** and **9** were obtained from the photoaddition of acridine and quadricyclane. It is interesting that quadricyclane does not quench appreciably the fluorescence of acridine. On the other hand, the photoreduction of acridine in the presence of several hydrogen atom donors has been investigated;[12] it is suggested that the primary reactant is a low-lying n,π^* singlet of acridine, which lies lower in energy than the fluorescent π,π^* singlet. While acridine is nonfluorescent in benzene and other hydrocarbons, it fluoresces strongly in alcohols. Addition of small amounts of alcohol or water to hydrocarbon solutions of acridine facilitates the appearance of fluorescence. As shown in Table II, the total yields of the 1:1 adducts **8** and **9** decreased considerably for the reaction in the presence of *tert*-butyl alcohol, which indicated that the fluorescent π,π^* singlet is not the reactive species for the photoaddition pathway, and in the presence of biacetyl, which is known to be a sensitizer of acridine.[13] Furthermore, the external heavy-atom effect suggests a singlet mechanism for the addition process. Thus, it is likely that the n,π^* singlet of acridine is the reactant in an important decay path for the photocycloaddition reaction. In addition, the photoproduct formations were affected by the polarity of the solvent; upon irradiation with quadricyclane in a protic solvent such as ethanol, acridine gave only the photoreductive products[14] and no 1:1 adduts were detected. Similar results were observed in the photocycloaddition of acridine with norbornadiene to give the exo and endo $[4\pi + 2\pi]$ adducts as shown in Table II.

The photocycloadditions involving the carbonyl or dicarbonyl groups are also examined through the use of interaction diagrams by Epiotis;[11,15] the ability of the carbonyl group to interact with double bonds via its π or n electrons leads to either

Scheme VI



Scheme VII

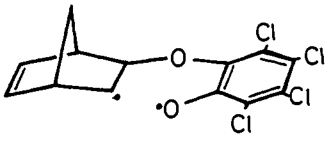


concerted or stepwise photocycloaddition.

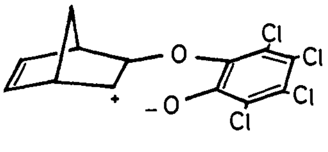
The light-induced addition of phenanthrenequinone or acenaphthenequinone to norbornadiene resulted in the formation of the keto oxetane ([2π + 2π] adduct) **11** or **14**. However, similar addition to quadricyclane resulted in the formation of a mixture of the keto oxetane **11** or **14** and the photorearrangement product **12** or **15**. Probably, these mixtures are the products of exo attack of the quinone n,π* triplet[16] on quadricyclane, leading to the set of biradicals, which are capable of rebonding in two pathways a and b as shown in Scheme VI.

An increase in the electron accepting ability of the dicarbonyl 4π component such as tetrachloro-*o*-benzoquinone (**16**) is expected to result in an increase in the [4π + 2π] stereoselectivity of the photoaddition;[11,15] both the HOMO and the LUMO energy levels are lower when *o*-benzoquinone is tetrasubstituted.[17]

Indeed, the results obtained with the photoaddition of tetrachloro-*o*-benzoquinone (**16**) to norbornadiene (**5**) gave only exo [4π + 2π] adduct (**17**); a stronger interaction for the photoaddition occurs between the LUMO (or SOMO) of the quinone (SA symmetry) and the HOMO of norbornadiene (SA symmetry) than the interaction of the quinone LUMO (or SOMO) and norbornadiene LUMO, and leads to the stabilization of the $[_{\pi}4_s + {}_{\pi}2_s]$ transition state, as illustrated in Figure 1. It is also explained that the adduct **17** might be formed by a polarized biradical approaching a zwitterion[18] via the n,π* singlet, which thus undergoes ring closure faster than bond rotation or rearrangement of the radical.



[A]



[B]

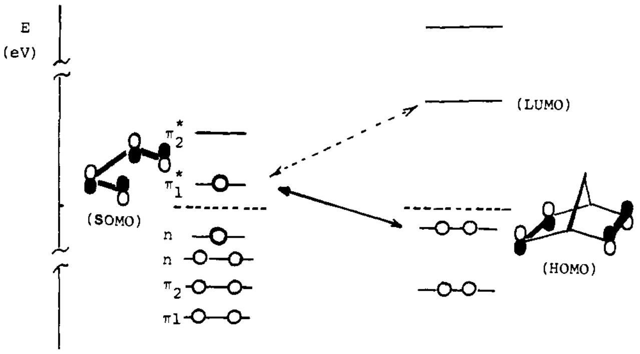


Figure 1. Interaction diagram illustrating the photocycloaddition of a strong electron acceptor dicarbonyl compound and a electron donor alkene. Crucial interactions are indicated by solid arrows and lead to the stabilization of the s + s transition state. The diagrams are schematic.

On the other hand, the addition of **16** to quadricyclane gave also the same adduct which could be formed by the formal [4π + 2σ + 2σ] manner if the reaction is concerted. It is to be noted that no keto oxetane and photorearrangement product were detected for the photoaddition reactions, and no interconversions of quadricyclane to norbornadiene were observed during the irradiation, by NMR analyses. In addition, the product **17** apparently arose from the photochemically induced reaction, since a striking contrast between thermal cycloaddition reactions of quadricyclane and that of norbornadiene to tetrachloro-*o*-benzoquinone (**16**) has been examined,[19] and the several products were isolated as shown in Scheme VI; the thermal cycloaddition of **16** to quadricyclane gave a main product **18** together with **17**, but the same addition to norbornadiene gave compound **19** as a major product, as shown in Scheme VII.

Finally, it is noteworthy that this is the first case where anthracene, acridine, and tetrachloro-*o*-benzoquinone react photochemically with quadricyclane to give the [4π + 2σ + 2σ] adducts. The substituent effects on the photochemical reactivity are valuable probes of the symmetry-forbidden process by the Woodward-Hoffmann analyses for the photochemical pericyclic reactions.

Experimental Section

Melting points are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Fluorescence spectra were determined with a Hitachi MPF-2A fluorescence spectrophotometer. NMR spectra were taken with a JEOL C-60 XL spectrometer with tetramethylsilane as internal standard. IR spectra were taken with a JASCO-IR-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV.

General Procedure for Photocycloaddition of Anthracene and Quadricyclane or Norbornadiene. A solution of anthracene and a large excess of quadricyclane or norbornadiene in various solvents was irradiated for 6 h with a 100-W high-pressure mercury lamp fitted with a Pyrex filter under argon at room temperature. After the precipitated anthracene dimer was filtered off, the solvent was removed under reduced pressure. The residual solid was chromatographed on a silica gel column using *n*-hexane. These results are summarized in Table I.

(a) A solution of **1** (0.53 g) and **2** (2.76 g) in benzene (50 ml) was irradiated for 6 h. Workup gave the adduct **4** (0.12 g) and the dimer **3** (0.36 g): **4**, mp 157-160 °C, colorless prisms; NMR δ (CCl$_4$) −0.19 (d, 1 H, J = 10.5 Hz), 0.68 (d, 1 H, J = 10.5 Hz), 2.02 (d, 2 H, J = 1.0 Hz), 2.41 (d, 2 H, J = 1.8 Hz), 4.04 (d, 2 H, J = 1.0 Hz), 6.03 (d, 2 H, J = 1.8 Hz), 6.92-7.18 (m, 8 H). Anal. Calcd for $C_{21}H_{18}$: C, 93.69; H, 6.31. Found: C, 93.43; H, 6.57.

(b) A solution of **1** (0.5 g) and **2** (2.8 g) in acetonitrile (50 ml) was irradiated under the same conditions. Workup gave the adduct **4** (0.02 g) and the dimer **3** (0.34 g).

(c) A solution of **1** (0.5 g) and **2** (2.7 g) in ethanol (150 ml) was irradiated under the same conditions. Workup gave the adduct **4** (0.1 g) and the dimer **3** (0.38 g).

(d) A solution of 9-methylanthracene (0.58 g) and **2** (2.76 g) in benzene (50 ml) was irradiated for 2 h. Workup gave exo 1:1 adducts of 9-methylanthracene and quadricyclane (0.1 g, colorless needles, mp 131-132 °C; NMR (CDCl$_3$) δ −0.20 (d, 1 H, J = 9.0 Hz), 0.67 (d, 1 H, J = 9.0 Hz), 1.70 (d, 1 H, J = 8.7 Hz), 1.88 (s, 3 H), 2.12 (dd, 1 H, J = 8.7 and 3.0 Hz), 2.47 (br s, 2 H), 4.08 (d, 1 H), J = 3.0 Hz), 6.08 (br s, 2 H), 7.00-7.30 (m, 8 H). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.77; H, 7.11.), and the dimer (0.335 g).

(e) A solution of 9,10-dimethylanthracene (0.15 g) and quadricyclane (1.4 g) in benzene (50 ml) was irradiated under the same conditions. Workup gave exo 1:1 adducts of 9,10-dimethylanthracene and quadricyclane (0.055 g, mp 179-180 °C, colorless needles; NMR (CDCl$_3$) δ −0.19 (d, 1 H, J = 9.0 Hz), 0.65 (d, 1 H, J = 9.0 Hz), 1.81 (s, 2 H), 1.90 (s, 6 H), 2.53 (s, 2 H), 6.08 (s, 2 H), 7.30-7.07 (m, 8 H). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.57; H, 7.49), and the dimer (0.11 g).

(f) A solution of 9,10-dibromoanthracene (0.504 g) and quadricyclane (2.76 g) in benzene (50 ml) was irradiated. Workup gave recovery of 9,10-dibromoanthracene (0.39 g), and the endo 1:1 adduct (0.05 g, mp 171-174 °C, colorless needles); NMR (CDCl$_3$) δ 1.52 (s, 1 H), 1.76 (s, 1 H), 1.92 (s, 2 H), 3.30 (s, 2 H), 5.90 (s, 2 H), 7.60-7.35 (m, 4 H), 8.33-8.10 (m, 4 H). Anal. Calcd for $C_{21}H_{10}Br_2$: C, 58.91; H, 3.77. Found: C, 58.87; H, 3.85.

(g) A solution of 9-cyanoanthracene (0.58 g) and quadricyclane (2.76 g) in benzene (50 ml) was irradiated. Workup gave the dimer (0.335 g), and exo 1:1 adducts of 9-cyanoanthracene and quadricyclane: 0.03 g, mp 162-165 °C, colorless needles; NMR (CDCl$_3$) δ −0.23 (d, 1 H, J = 9.0 Hz), 0.80 (d, 1 H, J = 9.0 Hz), 1.98 (br s, 1 H), 2.65 (d, 1 H, J = 9.0 Hz), 2.77 (br s, 1 H), 3.30 (dd, 1 H, J = 9.0 and 3.0 Hz), 4.17 (d, 1 H, J = 3.0 Hz), 5.91 (s, 2 H), 7.20 (m, 6 H), 7.60 (m, 2 H). Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.49; H, 5.69; N, 4.54.

(h) A solution of 9-cyanoanthracene (1.0 g) and norbornadiene (11 g) in benzene (100 ml) was irradiated. Workup gave the dimer (0.75 g) and endo 1:1 adducts of 9-cyanoanthracene and norbornadiene: 0.03 g, mp 174-176 °C, colorless needles; NMR (CDCl$_3$) δ 1.30 (dd, 2 H, J = 5.5 and 10.8 Hz), 1.73 (dd, 1 H, J = 10.8 and 2.4 Hz), 2.67 (dd, 1 H, J = 10.8 and 2.4 Hz), 2.73 (dd, 1 H, J = 2.4 and 4.5 Hz), 3.15 (ddd, 1 H, J = 2.4, 3.5, and 4.5 Hz), 4.08 (d, 1 H, J = 3.5 Hz), 5.94 (m, 2 H), 7.20 (m, 6 H), 7.58 (m, 2 H). Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.61; H, 5.81; N, 4.61.

Photochemical Reaction of Naphthalene with Quadricyclane. A solution of naphthalene (0.51 g) and quadricyclane (3.96 g) in benzene (50 ml) was irradiated for 6 h with a 100-W high-pressure mercury lamp fitted with a Corex filter under argon at room temperature. Workup as described above gave only recovery of naphthalene (0.5 g) and 96% conversion to norbornadiene, and no 1:1 adduct was detected.

General Procedure for Photocycloaddition of Acridine and Quadricyclane or Norbornadiene. A solution of acridine (3 mmol) and quadricyclane or norbornadiene (30 mmol) in various solvents (50 ml) in the absence or in the presence of biacetyl (30 mmol) was irradiated with a 100-W high-pressure mercury lamp fitted with a Pyrex filter under argon at room temperature. The solvent was removed under reduced pressure. The residual solid was chromatographed on an alumina column using benzene and then analyzed by NMR or preparative TLC (alumina plate).

These results are summarized in Table II. **8**: mp 135 °C, colorless prisms; NMR (CDCl$_3$) δ −0.08 (d, 1 H, J = 9.0 Hz), 0.90 (d, 1 H, J = 9.0 Hz), 2.22 (dd, 1 H, J = 7.5 and 3.0 Hz), 2.48 (br s, 1 H), 2.67 (br s, 1 H), 3.32 (d, 1 H, J = 7.5 Hz), 4.06 (d, 1 H, J = 3.0 Hz), 6.06 (m, 2 H), 7.12 (m, 8 H). Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.32; N, 5.16. Found: C, 88.73; H, 6.59; N, 4.93. **9**: mp 115-120 °C, pale yellow prisms; NMR (CDCl$_3$) δ 1.23 (d, 1 H, J = 7.0 Hz), 1.29 (d, 1 H, J = 7.0 Hz), 2.35 (br s, 1 H), 2.55 (dd, 1 H, J = 7.5 and 3.0 Hz), 2.91 (br s, 1 H), 3.36 (d, 1 H, J = 7.5 Hz), 4.08 (d, 1 H, J = 3.0 Hz), 6.22 (m, 2 H), 6.61 (m, 8 H).

Photocycloaddition of Phenanthrenequinone and Quadricyclane. A solution of phenanthrenequinone (0.65 g) and quadricyclane (2.67 g) in benzene (50 ml) was irradiated for 3 h under the same conditions as described above. Workup gave **11** (0.21 g) and **12** (0.32 g): **11**, mp 179-180 °C, pale yellow prisms; IR (KBr) 1710, 1690 (sh) cm^{-1}; NMR (CDCl$_3$) δ 1.30 (d, 1 H, J = 9.0 Hz), 2.46 br s, 1 H), 2.53 (d, 1 H, J = 9.0 Hz), 2.54 (dd, 1 H, J = 5.0 and 1.5 Hz), 3.23 (br s, 1 H), 4.72 (dd, 1 H, J = 5.0 and 1.5 Hz), 5.90 (m, 2 H), 7.25-8.00 (m, 8 H); **12**, mp 224-225 °C, colorless prisms; IR (KBr) 1700 cm^{-1}; NMR (CDCl$_3$) δ 1.17 (dd, 1 H, J = 12.0 and 6.0 Hz), 1.88 (dd, 1 H, J = 12.0, 5.0 Hz), 2.24 (dd, 1 H, J = 6.0 and 2.0 Hz), 2.84 (m, 1 H), 3.19 (m, 1 H), 4.45 (dd, 1 H, J = 2.2 and 2.2 Hz), 5.11 (ddd, 1 H, J = 6.0, 3.5, and 1.6 Hz), 6.11 (dd, 1 H, J = 6.0, 3.5 Hz), 7.25-7.90 (m, 8 H).[20] Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.79; H, 5.49.

Photocycloaddition of Phenanthrenequinone and Norbornadiene. A solution of phenanthrenequinone (0.65 g) and norbornadiene (2.67 g) in benzene (50 ml) was irradiated for 3 h under the same conditions. Workup gave **11** (0.54 g). Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.89; H, 5.55.

Photocycloaddition of Acenaphthenequinone and Quadricyclane. A solution of acenaphthenequinone (0.55 g) and quadricyclane (2.67 g) in benzene (50 ml) was irradiated for 3 h under the same conditions. Workup gave **14** (0.17 g) and **15** (0.26 g). **14**: mp 119-120 °C, colorless prisms; IR (KBr) 1720 cm^{-1}; NMR (CDCl$_3$) δ 1.75 (d, 1 H, J = 9.0 Hz), 2.58 (d, 1 H, J = 4.2 Hz), 2.95 (d, 1 H, J = 3.0 Hz), 3.03 (d, 1 H, J = 9.0 Hz), 3.30 (dd, 1 H, J = 3.0 and 1.5 Hz), 5.17 (dd, 1 H, J = 4.2 and 1.5 Hz), 5.88 (dd, 1 H, J = 6.0 and 3.0 Hz), 6.15 (dd, 1 H, J = 6.0 and 3.0 Hz), 7.50-8.10 (m, 6 H). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15. Found: C, 83.25; H, 5.25. **15**: mp 165-166 °C, colorless prisms; IR (KBr) 1715 cm^{-1}; NMR (CDCl$_3$) δ 1.03 (dd, 1 H, J = 12.0 and 6.0 Hz), 2.21 (dd, 1 H, J = 6.0 and 2.0 Hz), 2.63 (dd, 1 H, J = 12.0 and 5.5 Hz), 3.00 (m, 1 H), 4.28 (m, 1 H), 4.47 (dd, 1 H, J = 2.0 and 2.0 Hz), 5.75 (ddd, 1 H, J = 6.0, 3.2, and 1.5 Hz), 6.25 (dd, 1 H, J = 6.0 and 3.2 Hz), 7.6-8.1 (m, 6 H).[20] Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15. Found: C, 83.34; H, 5.10.

Photocycloaddition of Acenaphthenequinone and Norbornadiene. A solution of acenaphthenequinone (0.55 g) and norbornadiene (2.67 g) in benzene (50 ml) was irradiated for 3 h under the same conditions. Workup gave **14** (0.386 g).

Photocycloaddition of Tetrachloro-*o*-benzoquinone and Quadricyclane. A solution of tetrachloro-*o*-benzoquinone (0.1 g) and quadricyclane (0.36 g) in benzene (20 ml) was irradiated for 1 h with 0.5% iodine-CCl$_4$ filter solution under argon at room temperature. Workup described above gave **17** (0.02 g): mp 148-149 °C (lit.[19] mp 149 °C).

Photocycloaddition of Tetrachloro-*o*-benzoquinone and Norbornadiene. A solution of tetrachloro-*o*-benzoquinone (0.1 g) and norbornadiene (0.3 g) in benzene (20 ml) was irradiated under the same conditions as described above. Workup gave **17** (0.03 g).[19]

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Photochemical Reactions in Organized Monolayer Assemblies. 4. Photodimerization, Photoisomerization, and Excimer Formation with Surfactant Olefins and Dienes in Monolayer Assemblies, Crystals, and Micelles[1,2]

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Abstract: An investigation of the photoreactions of surfactant derivatives of 4-stilbazole and 1-phenyl-4-(4-pyridyl)-1,3-butadiene in various media is reported. It is found that in the solid state (with differences depending upon the negatively charged counterion) excimer fluorescence and dimerization are the dominant photoprocesses. The same processes occur in condensed monolayer assemblies; in addition, cis to trans isomerization of the surfactant stilbazole occurs but not the reverse. In contrast, for both micelles (with cetyltrimethylammonium bromide) and solutions only cis-trans isomerization and monomer fluorescence are observed; although there is some evidence of photocyclization, no dimers or excimers could be detected even at high concentrations. The differences between the solid state and monolayer behavior and that in solutions and micelles are attributed largely to the influence of packing phenomena in the former systems where all evidence points to a highly condensed structure. The prominent occurrence of excimer due to a preference for packing into dimeric sites in the condensed monolayers is consistent with the behavior observed for several other chromophores in assemblies of this sort. The contrast between the behavior of these surfactant molecules in condensed monolayers and micelles is significant since it indicates merely orienting chromophores at a hydrophilic-hydrophobic interface are insufficient to force bimolecular interactions.

Introduction

Olefins and dienes such as the stilbenes and diaryl-1,3-butadienes have been found to undergo a variety of different photoprocesses including cis-trans isomerization,[4-7] cyclization to phenanthrenes and related polycyclic aromatic hydrocarbons,[8-11] dimerization, and excimer and exciplex formation.[12-17] Although these processes have been found to occur to varying extents under different conditions in solution and in the solid state, relatively little is known about the specific influence of molecular environment on the individual photoprocesses. Much recent work has focused on the use of organized structures such as crystals,[15-18] "cracked" dimers,[19] or micelles[20-21] to elucidate details of photoprocesses and their control by molecular environment. In our own investigations we have used organized monolayer assemblies both to probe mechanistic details of photoreactions and to modify the normal solution behavior.[1,2,22,23] Recently we reported results of a preliminary investigation of a surfactant stilbene derivative prepared by N-alkylation of *trans*-4-stilbazole with the hydrophobic octadecyl group.[2] In studies of this molecule in solution, monolayer assemblies, and in crystals, it was found that its photobehavior was extremely dependent upon molecular environment. In the present paper we report results of an extended investigation of the stilbazole derivative and a similar diaryl-1,3-butadiene in a variety of media including monolayer assemblies, solids, and micelles. Results of this study emphasize the dominant role environment can play in controlling the photochemistry of these chromophores and suggest possibilities for use of the solid state and monolayer assemblies to prepare other species not obtainable in solution. An interesting aspect of this study is the finding that rather large differences exist between results obtained in micelles and in condensed monolayers. The present study emphasizes the importance of packing effects in controlling behavior in both crystals and condensed monolayers.