effects,[28] might also play a partial role. However, the correlation of the results of our simple treatment with available experimental results[29] seems to be encouraging and could certainly be used as a starting point for more detailed analyses.

Appendix

The crucial orbital coefficients were determined by means of a variety of calculations of a series of representative molecules. Typical olefinic molecules which were calculated included propylene, acrylonitrile, acrolein, fluoroethylene, hydroxyethylene, and aminoethylene and typical butadiene molecules include both the 1 and 2 isomers of cyanobutadiene, carbonylbutadiene, fluorobutadiene, hydroxybutadiene, and aminobutadiene. The generalizations regarding the relative size of the frontier orbital coefficients of various types of olefins and butadienes are based on these calculations and the anomalous cases have been pointed out in footnotes.

Acknowledgment. We are pleased to acknowledge the support of the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(28) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(29) Professor K. N. Houk has used a similar approach in his studies of the regioselectivity of 1,3-dipolar cycloadditions: K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, submitted for publication; K. N. Houk, J. Sims, C. R. Watts and L. J. Luskus, submitted for publication. We thank Professor Houk for informing us of his results prior to publication.

Molecular Design by Cycloaddition Reactions. V.[1] Photochemical and Thermal Cycloaddition Reactions of Anthracene with Cycloheptatriene

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Abstract: Irradiations (Pyrex, >290 nm) of anthracene (**1**) with a large excess of cycloheptatriene (**2**) in benzene or ethanol gave a mixture of formal $[_\pi 6 + _\pi 4]$ (**4**) and $[_\pi 4 + _\pi 4]$ cycloadducts (**5**) in a moderate yield together with an anthracene dimer (**3**). These products are considered to be formed through a biradical intermediate in the excited $\pi-\pi^*$ singlet state. In contrast, the thermal reaction of **1** with **2** afforded only a $[_\pi 4 + _\pi 2]$ cycloadduct (**10**) in a low yield (8%). Catalytic hydrogenations of these adducts, **4**, **5**, and **10**, gave the corresponding tetrahydro derivatives, **6**, **7**, and **11**, respectively. Irradiations (quartz, >220 nm) of these adducts, **4**, **5**, and **10**, resulted in the cycloreversions to anthracene as well as the interconversions between them. Irradiation (Pyrex, >290 nm) of the thermal adduct **10** in benzene gave the valence isomer **12**, while the photoadducts **4** and **5** were stable under the same conditions. The mechanisms for the formation of the products are discussed.

Recently, Hammond and Taylor[2] have reported on the basis of spectroscopic and kinetic studies that an exciplex is formed in the quenching reactions of fluorescence from anthracene and related aromatic compounds with conjugated dienes.

Although the major decay pathway of the exciplex has been suggested to be nonradiative to their components in the ground state, the possibility of the product formation has not been excluded.[2,3] In fact, some of the numerous photochemical cycloaddition reactions of polynuclear aromatic compounds[4] are suggested to follow the modes of decay of excimers and exciplexes as the chemical processes.[5-10]

The photochemical cycloaddition reactions of anthracene with various unsaturated molecules have been documented to give $[_\pi 4 + _\pi 2]$[11-13] and $[_\pi 4 + _\pi 4]$ addition products,[14-16] depending on the nature of the addends and on the reaction conditions. However, there seems to be no studies on the reactions of the conjugated cyclic trienes with anthracene.

As a continuation of our previous reports,[1,17] we have investigated the thermal and photochemical re-

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(1) Part IV of this series: T. Sasaki, K. Kanematsu, Y. Yukimoto, and T. Hiramatsu, submitted to *J. Amer. Chem. Soc.*

(2) (a) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972); (b) G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684, 3687 (1972).

(3) L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

(4) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience, New York, N. Y., 1969, p 171.

(5) (a) T. Sugioka, C. Pac, and H. Sakurai, *Chem. Lett.*, 667, 791 (1972); (b) C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, *ibid.*, 187, 309 (1973).

(6) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 9228 (1972).

(7) N. C. Yang, J. Libman, and M. F. Savitzky, *ibid.*, **94**, 9226 (1972).

(8) T. S. Cantrell, *ibid.*, **94**, 5929 (1972).

(9) K. E. Wilzbach and L. Kaplan, *ibid.*, **93**, 2073 (1971).

(10) D. O. Cowan and R. L. Drislco, *ibid.*, **92**, 6286 (1970).

(11) N. C. Yang, J. Libman, L. Barrette, Jr., M. H. Hui, and R. L. Loeschen, *ibid.*, **94**, 1406 (1972).

(12) (a) G. Kaupp, *Chimia*, 25, 230 (1971); (b) *Angew. Chem., Int. Ed. Engl.*, **11**, 313 (1972).

(13) R. M. Hochstrasser and G. B. Parter, *Quart. Rev., Chem. Soc.*, **14**, 146 (1960).

(14) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 1405 (1972).

(15) G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **11**, 718 (1972).

(16) H. Bouas-Laurent and A. Castellan, *Chem. Commun.*, 1648 (1970).

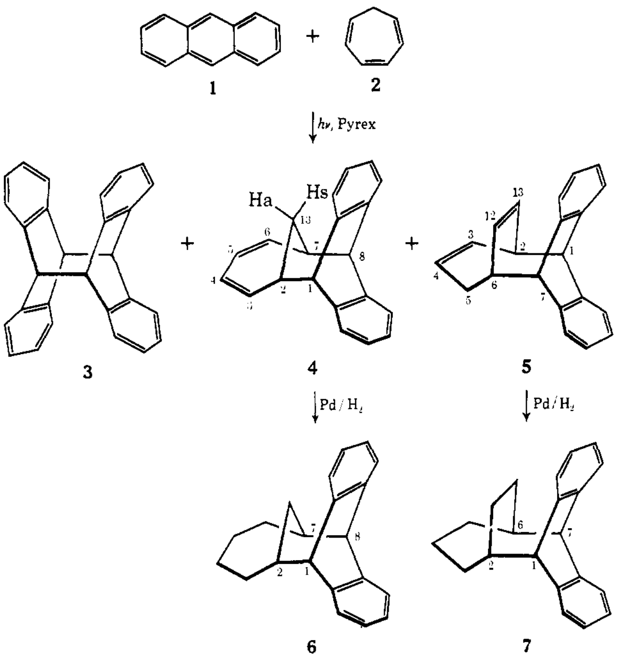
(17) (a) T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc. C*, 2142 (1972); (b) *J. Chem. Soc., Perkin Trans. 1*, 783 (1972).

actions of anthracene with cycloheptatriene as a conjugated triene.

Results

Photochemical Cycloaddition Reactions. When a solution of anthracene (**1**) and a large excess of cycloheptatriene (**2**) in benzene was irradiated with a high-pressure 100-W mercury lamp in a Pyrex vessel under nitrogen at room temperature, anthracene was rapidly consumed. After removal of the anthracene photodimer **3** (30%)[18] precipitated during the irradiation, careful chromatography of the photolysis mixture on silica gel gave two adducts, **4** and **5**, in 34 and 15% yield, respectively (Scheme I). No other 1:1 adducts could be detected by nmr spectroscopy.

Scheme I



The results of the photoadditions in various solvents are summarized in Table I.

Table I. Yields of the Photochemical Cycloadducts[a]

Solvent[c]	Yield (%)[b] Dimer (**3**)	[6 + 4] (**4**)	[4 + 4] (**5**)
Ethanol	32	37	25
Benzene	30	34	15
Chloroform	46	13	6
Methylene chloride	53	9	6

[a] Irradiations were carried out under nitrogen at room temperature for 4 hr. [b] Yields are calculated based on anthracene (**1**) used. [c] 70 ml; 0.012 *M* of **1** and 0.12 *M* of **2**.

The structure of the major product (**4**) was deduced from elemental analysis and spectroscopic data. The mass spectrum displayed a molecular ion peak at *m/e* 270 and prominent fragments at *m/e* 178 (anthracene, base peak) and 91 (tropylium ion, 35%) originating from a retro-Diels–Alder fragmentation. The nmr spectrum ($CDCl_3$) exhibited signals of two bridged methylene protons at δ 1.35 (m, 1 H, syn H-13) and 1.76 (m, 1 H, anti H-13), two equivalent allylic methine protons at δ 2.93 (m, 2 H, H-2 and -7), two equivalent benzylic methine protons at δ 4.20 (d, 2 H, J = 7.2 Hz, H-1 and -8), four vinyl protons at δ 5.25–5.98 (m, 4 H, H-3, -4, -5, and -6), and eight aromatic protons at δ 6.98 (m, 4 H) and 7.20 (m, 4 H), suggesting a highly symmetrical structure. On irradiation at the frequency of H-2 (H-7), the signal of H-1 (H-8) collapsed into a singlet and the signals of H-13 were simplified to an AB-type quartet (J = 14.4 Hz).

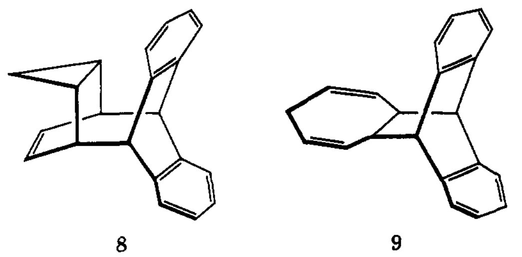


Figure 1.

Additionally, catalytic hydrogenation of **4** in ethanol over palladium on charcoal resulted in the rapid uptake of 2 equiv of hydrogen to give a tetrahydro derivative **6**. The nmr spectrum of **6** was also suggestive of a highly symmetrical structure, and the coupling constant between H-1 (H-8) and H-2 (H-7) was 7.4 Hz. This is to be expected since molecular models show that the dihedral angle for the C_1 (or C_8) and C_2 (or C_7) protons is about 36°.

Thus, the major product was concluded to be a formal $[_{\pi}6 + _{\pi}4]$ cycloadduct (**4**), which is not allowed to arise in a concerted fashion by the orbital symmetry theory,[19] and other conceivable symmetrical structures **8** and **9** could be ruled out (Figure 1).

The structure of the minor product (**5**) was confirmed from the elemental analysis and spectroscopic data. The mass spectrum showed a molecular ion peak at *m/e* 270, and the fragmentation pattern was very similar to that of **4**. The nmr spectrum ($CDCl_3$) revealed signals of two allylic methylene protons at δ 2.24 (m, 2 H, H-5), two nonequivalent allylic methine protons at δ 2.90–3.66 (m, 2 H, H-2 and H-6), two benzylic methine protons at δ 4.30 (d, 1 H, H-7, J = 9.5 Hz) and 4.49 (d, 1 H, J = 9.5 Hz), four vinyl protons at δ 5.20 (m, 2 H, H-3 and H-4), 5.55 (d-d-d, 1 H, H-13 or H-12, J = 9.0, 6.8, and 1.5 Hz) and 5.70 (d-d-d, 1 H, H-12 or H-13, J = 9.0, 6.8, and 1.5 Hz), and eight aromatic ring protons at δ 7.07 (m, 8 H). The presence of two nonequivalent benzylic bridgehead protons permits the conclusion that the structure lacks an element of symmetry.

Furthermore, catalytic hydrogenation of **5** in ethanol over palladium on charcoal proceeded with the rapid uptake of 2 equiv of hydrogen to give a tetrahydro derivative **7**, which had two magnetically equivalent benzylic methine protons [δ ($CDCl_3$) 4.20 (d, J = 12.0 Hz)].

Thus, the minor product was assigned the formal $[_{\pi}4 + _{\pi}4]$ cycloadduct structure (**5**).

Irradiations of **4** and **5** under the same conditions but for a much longer time resulted in no changes, suggesting no interconversoins of these adducts.

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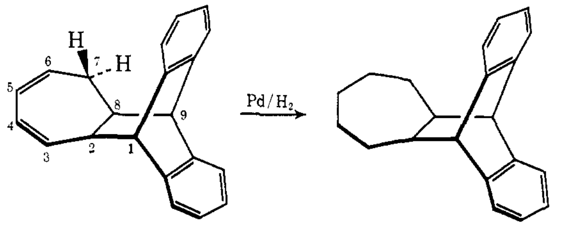
(18) (a) Infrared spectrum identical with spectrum 20684 in Sadler. (b) E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963).

(19) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

Thermal Cycloaddition Reaction. When **1** and a large excess of **2** were heated together in benzene in a sealed tube for 5–6 days at 150–170°, most of anthracene (**1**) was recovered (70%) and only a colorless crystalline product (**10**) was obtained in a very low yield (8%) (Scheme II).

Scheme II

$1 + 2 \xrightarrow{170°}$



10 11

The nature of **10** as a 1:1 adduct was apparent from the elemental analysis and mass spectrum [*m/e* 270 (M^+), 178 (base peak) and 91 (20)]; the fragmentation pattern was very similar to those of **4** and **5**. Structural assignment for **10** was carried out on the basis of the spectroscopic data. The nmr spectrum ($CDCl_3$) revealed signals of allylic methylene protons at δ 1.48 (m, 1 H, H_a-7) and 2.71 (m, 1 H, H_e-7, deshielded by the ring current of a phenyl ring), a methine proton at δ 2.03 (q, 1 H, H-8, J = 11.7 and 6.8 Hz), an allylic methine proton at δ 2.73 (d-d, 1 H, H-2, J = 6.8 and 2.0 Hz), benzylic methine protons at δ 3.87 (s, 1 H, H-9) and 4.15 (d, 1 H, H-1, J = 2.0 Hz), olefinic protons at δ 5.53–6.12 (m, 4 H, H-3, -4, -5, and -6), and aromatic ring protons at δ 7.05 (m, 8 H), suggesting the unsymmetrical structure.

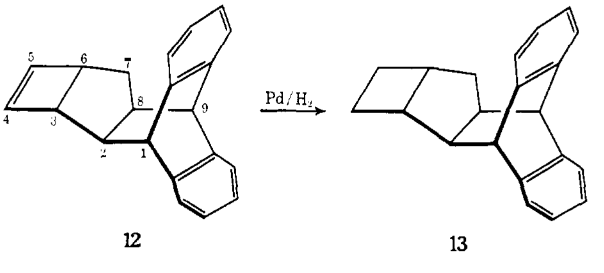
Catalytic hydrogenation of **10** in ethanol over palladium on charcoal resulted in the rapid uptake of 2 equiv of hydrogen to give a tetrahydro derivative **11**. The nmr spectrum of **11** showed a signal of two equivalent benzylic methine protons at δ 3.98 as a singlet.

Thus, the product was concluded to be a symmetry allowed [4 + 2] π cycloadduct (**10**). The nmr and glpc analyses of the crude reaction mixture showed that no other 1:1 adduct could be detected.

Photochemical Conversions of the Cycloadducts. Although both **4** and **5** were not affected, thermal adduct **10** was converted to a new product (**12**) (Scheme III) in 70% yield on irradiation with a high-pressure 100-W mercury lamp in a Pyrex vessel in benzene for 20 hr.

Scheme III

$10 \xrightarrow{h\nu}$



12 13

The nature of **12** as a valence tautomer of **10** was apparent from the elemental analysis and mass spectrum which displayed a molecular ion peak at *m/e* 270. Structural assignment for **12** was made on the basis of the spectroscopic data and chemical conversion. The nmr spectrum ($CDCl_3$) exhibited signals of two methylene protons at δ 1.48 (broad m, 2 H, H-7), two methine protons at δ 2.47 (m, 2 H, H-2 and H-8), two allylic methine protons at δ 3.04 (m, 2 H, H-3 and H-6), two benzylic methine protons at δ 4.02 (d, 1 H, J = 3.8 Hz, H-1) and 4.08 (d, 1 H, J = 2.5 Hz, H-9), two vinyl protons at δ 5.90 (d, 1 H, J = 6.0 Hz, H-4 or H-5) and 5.93 (d, 1 H, J = 6.0 Hz, H-5 or H-4), and eight aromatic ring protons at δ 7.10 (m, 8 H), suggesting the presence of a cyclobutene moiety.

Catalytic hydrogenation of **12** in ethanol over palladium on charcoal rapidly yielded a dihydro derivative (**13**) (no olefinic proton by nmr) after uptake of 1 equiv of hydrogen.

In contrast, irradiations of these adducts through a quartz filter in benzene with a high-pressure mercury lamp led to a marked change in the photochemical behavior.

Irradiation of **4** and **5** resulted in the cycloreversions to the starting materials as the main process and transformations to the isomers (**4**, **5**, **10** and **12**) as the minor processes.

On the contrary, photolysis of **10** afforded mainly a valence isomer (**12**) together with minor cycloreversion products, but the formations of **4** and **5** could not be detected by glpc, tlc, and nmr. The results are summarized in Table II.

Table II. Photolyses of the Adducts[a]

Adduct no.	Product distributions[b,c] (rel yields, %) Anthracene (**1**)	**4**	**5**	**10**	**12**
4	81.5	7.3	3.2	2.1	5.9
5	84.0	3.0	7.2	1.8	5.0
10	8.0			24.5	67.6

[a] 0.02 *M* samples in benzene were irradiated through a quartz filter with a high-pressure 100-W mercury lamp for 3 hr. [b] Total yields were >90%. [c] Based on glpc analyses.

Interconversions of **4**, **5**, and **10** could take place by either stepwise dissociation–recombination processes or a sequence of symmetry allowed processes, but the cycloreversions except for **5** are not symmetry allowed processes.

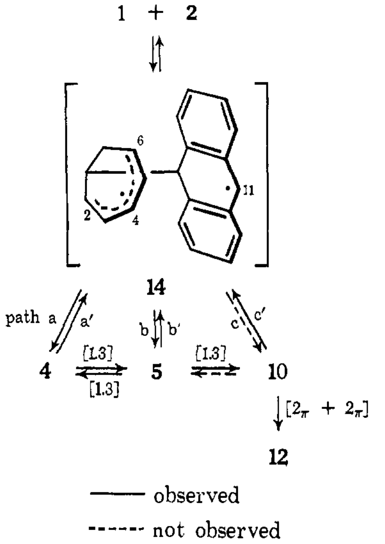
Although the possibility of the competitive concerted isomerization of these adducts cannot be omitted, these results are most readily rationalized by a two-step mechanism *via* a biradical intermediate (see Discussion).

Discussion

The photochemical cycloaddition reaction of **1** with **2** led to the formation of [$_\pi6 + {}_\pi4$] (**4**) and [$_\pi4 + {}_\pi4$] cycloadducts (**5**). The reaction was monitored by nmr spectroscopy, and the ratio of **4** to **5** (6:4 in ethanol) was found unchanged during the irradiation. Under the reaction conditions, the isolated pure products, **4** and **5**, were stable and no interconversions were observed.

While the possibility of the concerted [$_\pi4 + {}_\pi4$] cycloaddition cannot be omitted in the reactions, such observations are readily understandable in terms of a two-step mechanism *via* a biradical intermediate (**14**) which is stabilized by the extensive delocalization in a long enough lifetime for rotation around the σ bond thus formed (see Scheme IV).

Scheme IV



No formation of **10** (path c) is presumed to be a result of an energetically unfavored ring closure compared to paths a and b.

In the biradical intermediate, which must take the more crowded geometry (a sandwich-like approach), the 1,2-ring closure (path c) would give rise to a severe nonbonded interaction between the cycloheptatriene moiety and the benzene ring.[20] The highly symmetrical geometry of the resulting structure (**4**) presumably favors the ring closure at C-6, 11 (path a), which might be related to the preference of $[_{\pi}6 + _{\pi}4]$ cycloaddition over $[_{\pi}4 + _{\pi}4]$ cycloaddition.[21]

The concentration dependence of the triene on the reaction was also investigated and the results are summarized in Table III.

Table III. Concentration Dependence of **2** on the Cycloaddition Reaction[a]

Ratio (**2**/**1**)	Yield (%) of **3**	Rel yield (%)[b] **4**	Rel yield (%)[b] **5**
1	80	59	41
2	77	57.5	42.5
5	43	57	43
12	33	60	40
20	30	59	41

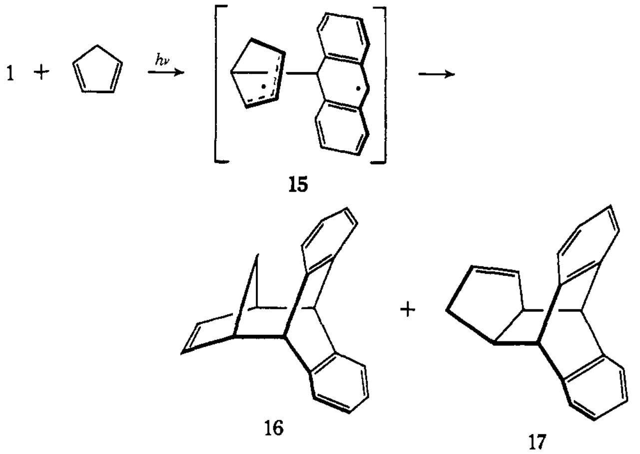
[a] Irradiation was carried out in ethanol under nitrogen at room temperature for 3 hr (using always 0.12 *M* of **1**). [b] Based on nmr analyses after removal of precipitated anthracene dimer **3**.

Obviously, the total yields of 1:1 adducts, **4** and **5**, increased with increase in the concentration of the triene (**2**) and, consequently, that of the anthracene dimer (**3**) decreased. However, the ratio of $[_{\pi}6 + _{\pi}4]$ photoaddition to $[_{\pi}4 + _{\pi}4]$ photoaddition remained constant within experimental error.

These results also support the above mentioned biradical mechanism in which both adducts, **4** and **5**, might arise from the same intermediate (**14**).

It is known that a similar photochemical cycloaddition reaction of **1** with cyclopentadiene proceeds in a two-step mechanism *via* a biradical intermediate (**15**) to give $[_{\pi}4 + _{\pi}4]$ (**16**) and $[_{\pi}4 + _{\pi}2]$ cycloadducts (**17**).[15] While the light-induced addition of cyclohexadiene and acyclic 1,3-dienes to **1** proceeds in a concerted manner to give exclusively the stereospecific $[_{\pi}4 + _{\pi}4]$ adducts[14] (Scheme V).

Scheme V



In connection with these results, the quantum yield (Φ_{-1}) of the consumption of **1** in the presence of a large excess of cycloheptatriene was determined in comparison with those of related systems (Table IV).

Table IV. Quantum Yields of Consumption of **1** in the Presence of Polyolefins

Olefin	Φ_{-1}	Ref
Cyclohexadiene	~0.27	14[a]
Cyclopentadiene	0.065	15
Cycloheptatriene	0.043	This work

[a] The quantum yield was described briefly to be comparable to that of anthracene fluorescence, but no definite value was given.

The quantum yield of consumption of **1** in the presence of **2** ($\Phi_{-1(\text{cycloheptatriene})}$) is comparable to that of cyclopentadiene ($\Phi_{-1(\text{cyclopentadiene})}$), but less than that of cyclohexa-1,3-diene ($\Phi_{-1(\text{cyclohexadiene})}$). This suggests that the reaction mechanism of **1** with **2** is similar to that of **1** with cyclopentadiene, and also supports the biradical mechanism as depicted in Scheme IV.[15] The low values of $\Phi_{-1(\text{cycloheptatriene})}$ and $\Phi_{-1(\text{cyclopentadiene})}$ in comparison with $\Phi_{-1(\text{cyclohexadiene})}$ may be attributed to reverse reaction of the biradical intermediates (**14** and **15**).

On the other hand, the total yields of **4** and **5** markedly decreased in the heavy-atom solvents as shown in Table I. This external heavy-atom effect[22-24] suggests a singlet mechanism for the addition process. Some dienes are known to quench the anthracene singlet *via* the exciplex formation which requires bonding interactions through orbital overlap.[2]

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(20) Since cycloheptatriene is a nonplanar molecule with small barrier of inversion, the thermal cycloaddition could avoid this difficulty by approach of **1** and **2** with less crowded geometry.

(21) However, the reasons underlying these differences in orientation are not fully dissolved at present stage.

(22) B. F. Plummer and D. M. Chihal, *J. Amer. Chem. Soc.*, **93**, 2071 (1971).

(23) N. J. Turro, J. C. Dalton, G. Kavarnos, T. Cole, and P. Scride, *ibid.*, **93**, 1032 (1971), and references cited therein.

(24) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

A large extent of orbital overlap may be attainable between the lowest excited state of **1** and the ground state of **2** because of the energetical proximity and symmetrical accordance between ϕ_8 (**1**) and ϕ_4 (**2**) and/or ϕ_7 (**1**) and ϕ_3 (**2**).

Furthermore, the fluoroescence of anthracene was efficiently quenched by cycloheptatriene. The Stern–Volmer plot for the fluorescence quenching of **1** by **2** in ethanol is shown in Figure 2, from which $K_q\tau_s$ was calculated to be 13.5 M^{-1}.

Thus, it seems plausible that some of the photochemical reactions of **1** with **2** in non-heavy-atom solvents could be initiated by the singlet exciplex formation between **1** and **2** followed by the stepwise σ-bond formation.[25, 26]

The results in Table II are readily understood in terms of the competition between the stepwise cycloreversion and the concerted isomerizations (*i.e.*, [1,3] sigmatropic rearrangement and $[_\pi 2_s + {}_\pi 2_s]$ cycloaddition) or stepwise isomerizations.

A possible mechanism for the photochemical conversions of the adducts is outlined in Scheme IV. The cycloreversion reactions proceed through path a′ and b′ as the main routes for **4** and **5**, but it is not the case for **10**. This difference should be attributable to the presence of a more favored symmetry allowed process (*i.e.*, $[_\pi 2_s + {}_\pi 2_s]$ cycloaddition affording **12**) for **10**.

Interconversions between **4** and **5** could occur by either dissociation–recombination processes *via* biradical intermediate (**14**) or concerted [1,3] sigmatropic rearrangements.

Since path c was shown hardly to occur in the cycloaddition reaction, the tranformation **5** → **10** might take place in an irreversible concerted process. By contrast, thermal reaction of **1** with **2** gave solely the Diels–Alder adduct (**10**) and was unaffected by changing the solvents (benzene, ethanol, and neat). Therefore, the thermal reaction of **1** with **2** is reasonably concluded to be a concerted $[_\pi 4 + {}_\pi 2]$ cycloaddition.

Finally, it should be noteworthy that this is the first case where anthracene reacts photochemically with a cyclic conjugated triene. Further attempts to effect the photochemical and thermal reactions of anthracene with tropone, *N*-alkoxycarbonylazepine, and tropylium ion were all unsuccessful under these conditions.

Experimental Section

Melting points are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyser. Uv spectra were determined with a JASCO ORD-UV-5 spectrometer. Nmr spectra were taken with a JEOL C-60-XL spectrometer and with a Varian A-60 recording 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. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150°. Glpc analyses were performed with a NEVA gas chromatograph Model 1400 and preparative glpc with a Varian Aerograph Model 700 (silicon SE-30).

Photochemical Cycloaddition Reaction of Anthracene (1) with Cycloheptatriene (2). (1) A solution of 0.3 g of **1** and 1.6 g of **2** in 150 ml of ethanol was irradiated for 6 hr with a 100-W high-pressure mercury lamp fitted with a Pyrex filter under nitrogen at room temperature. After the precipitated anthracene dimer **3** (90 mg) was filtered off, the solvent was removed under reduced pressure. The residual solid was chromatographed on a silica gel column using 15% methylene chloride–hexane. The first fractions gave 150 mg (34%) of adduct **4** (R_f 0.44) as colorless crystals: mp 210–203° (ethanol); ir (KBr) 3010, 2910, and 742 cm^{-1}; uv (ethanol) λ_{max} 254 nm (ϵ 4900), 262 (5350), and 274 (4100). *Anal.* Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.75. Found: C, 93.11; H, 6.87. The second fractions gave 65 mg (15%) of adduct **5** (R_f 0.33) as colorless crystals: mp 176–177° (ethanol); ir (KBr) 3000, 2900, 736, and 720 cm^{-1}; uv (ethanol) λ_{max} 272 nm (ϵ 1800), 278 (1700), 280 (2200). *Anal.* Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.75. Found: C, 93.21; H, 6.85. (2) A solution of 150 mg of **1** and 800 mg of **2** in 70 ml of ethanol was irradiated for 4 hr under the same conditions. Aliquots were taken at 1, 2, and 4 hr and found to contain the adducts **4** and **5** in the ratio 58:42, 59:41, and 60:40, respectively (by nmr spectroscopy). After the precipitated dimer **3** (48 mg, 32%) was filtered off, the solvent was removed and the solid residue was chromatographed to give 84 mg (37%) of **4** and 57 mg (25%) of **5**. (3) Irradiation of **1** (150 mg) and **2** (800 mg) in chloroform (70 ml) for 4 hr gave 70 mg (46%) of **3**, 30 mg (13%) of **4**, and 13 mg (6%) of **5**. (4) Irradiation of **1** (150 mg) and **2** (800 mg) in methylene chloride (70 ml) for 4 hr gave 80 mg (53%) of **3**, 20 mg (9%) of **4**, and 13 mg (6%) of **5**.

Hydrogenation of Adduct 4. A solution of 90 mg (0.33 mmol) of **4** in 40 ml of ethanol was hydrogenated over 60 mg of 10% palladium on charcoal at atmospheric pressure until 2 equiv (15 ml) of hydrogen was consumed. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 70 mg (77%) of the tetrahydro derivative **6** as colorless needles: mp 134–136°; ir (KBr) 2880, 1450, and 750 cm^{-1}; nmr ($CDCl_3$) δ 0.51 (m, 1 H), 1.50 (m, 8 H), 2.31 (m, 2 H), 3.70 (d, 2 H, J = 7.4 Hz), and 7.20 (m, 8 H). *Anal.* Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.66; H, 8.14.

Hydrogenation of Adduct 5. A solution of 35 mg (0.13 mmol) of **5** in 30 ml of ethanol was likewise hydrogenated over 20 mg of 10% palladium on charcoal until 2 equiv (6 ml) of hydrogen was consumed. The catalyst was filtered off, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 30 mg (85%) of the tetrahydro derivative **7** as colorless plates: mp 163–164°; ir (KBr) 2900, 1450, and 750 cm^{-1}; nmr ($CDCl_3$) δ 1.40 (m, 10 H), 2.88 (m, 2 H), 4.20 (d, 2 H, J = 12.0 Hz), and 7.12 (m, 8 H). *Anal.* Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.80; H, 8.20.

Thermal Cycloaddition Reaction of 1 with 2. A solution of 0.2 g of **1** and 1.5 g of **2** in 20 ml of benzene was heated at 150–170° in a sealed tube for 5 days. The resulting solution was cooled, and the precipitated anthracene (**1**) (90 mg, 45%) was filtered off. The filtrate was concentrated under reduced pressure and chromatographed on a silica gel column using 15% methylene chloride–hexane. The first fractions consisted of the unreacted anthracene (50 mg, 25%). The second fractions gave 25 mg (8%) of adduct **10** (R_f 0.47) as colorless prisms: mp 164–166°; ir (KBr) 3010, 2920, 1460, 670, and 740 cm^{-1}; uv (ethanol) λ_{max} 248 nm (ϵ 3500), 266 (2420), and 272 (1810); mass spectrum *m/e* 270 (parent), 178, and 91. *Anal.* Calcd for $C_{21}H_{18}$: C, 93.39; H, 6.71. Found: C, 93.16; H, 6.84. The thermal reaction of 0.5 g of **1** and 3.5 g of **2** in the absence of solvent, and in ethanol (20 ml), gave 67 mg (9%) and 60 mg (8%) of the adduct **10**, respectively.

Hydrogenation of Adduct 10. A solution of 80 mg (0.30 mmol) of **10** in 50 ml of ethanol was hydrogenated over 70 mg of 10% palladium on charcoal at atmospheric pressure until 2 equiv (14 ml) of hydrogen was consumed. The catalyst was filtered off, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 65 mg (80%) of the tetrahydro derivative **11** as colorless needles: mp 145–147°; ir (KBr) 2910, 1460, and 760 cm^{-1}; nmr ($CDCl_3$) δ 1.15–1.80 (broad m, 10 H), 2.70 (m, 2 H), 3.98 (s, 2 H), and 7.13 (m, 8 H). *Anal.* Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.88; H, 8.12.

Photolysis of Adducts 4, 5, and 10 through a Pyrex Filter. A solution of 25 mg of **10** in 50 ml of benzene was irradiated for 20 hr with a 100-W high-pressure mercury lamp fitted with a Pyrex filter under nitrogen. After removal of the solvent, glpc analysis of the photolysis mixture showed only one new product as well as a small amount of **10**. Chromatography on a silica gel column using 15% methylene chloride–hexane and recrystallization from ethanol gave 18 mg (70%) of the valence tautomer **12** (R_f 0.56) as colorless crystals: mp 182–183°; ir (KBr) 2910, 1450, 750, and 730 cm^{-1}; uv (ethanol) λ_{max} 266 nm (ϵ 1330) and 273 (1590); *m/e* 270 (parent)

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(25) Then, if two σ bonds were simultaneously formed, the reaction would lead exclusively to the [4 + 4] cycloadduct (see ref 14).

(26) A referee suggests that the formation of **4** and **5** may proceed *via* a common exciplex intermediate. The exciplex may decay *via* a concerted cycloaddition to give **5** and a stepwise addition to give **4**.

and 178. *Anal.* Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.16; H, 6.84.

Irradiation of 30 mg of **4** and 50 mg of **5** for 10 hr under the same conditions resulted in the recovery of unreacted starting materials in quantitative amounts.

Hydrogenation of the Valence Tautomer 12. A solution of 25 mg (0.09 mmol) of **12** in 30 ml of ethanol was hydrogenated over 15 mg of 10% palladium on charcoal at atmospheric pressure until 1 equiv (3 ml) of hydrogen was consumed. The catalyst was filtered off, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 20 mg (80%) of the dihydro derivative **13** as colorless prisms: mp 126–128°; ir (KBr) 2920, 1470, 1460, 750, and 740 cm^{-1}; nmr ($CDCl_3$) δ 1.65 (m, 6 H), 2.05 (m, 4 H), 4.01 (d, 1 H, J = 3.0 Hz), 4.07 (d, 1 H, J = 2.0 Hz), and 7.10 (m, 8 H). *Anal.* Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.45; H, 7.54.

Photolysis of Adducts 4, 5, and 10 through a Quartz Filter. **4**, **5**, and **10** (30 mg) were dissolved with 50 ml of benzene, respectively. Each solution was irradiated for 3.5 hr at room temperature with a 100-W high-pressure mercury lamp fitted with a quartz filter under nitrogen. The solvent was removed under reduced pressure and the residue was analyzed by tlc and glpc. The results are given in Table II.

Quantum Yield Determination. A solution of 1.54 mg (0.0087 mmol) of **1** and 92 mg (1.0 mmol) of **2** in 100 ml of ethanol was prepared. The solution in a quartz tube (3.5 ml) was degassed with nitrogen and irradiated at 3650 Å using a filter. Light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker.[27] The consumption of **1** was monitored by uv spectroscopy using 0–0 band of absorption (λ_{max} 374 nm). Several measurements were taken at different conversions (<10% conversion) and the average value was used. The result was shown in Table IV.

Fluorescence Quenching. Fluorescence intensities were measured with an Hitachi MPF-2A fluorescence photometer, using an excitation wavelength of 374 nm. Samples (3 ml) containing 2.21×10^{-6} M of anthracene (**1**) and varing concentrations of cycloheptatriene (**2**) in ethanol were placed in a quartz cell. The intensities were measured three times for each cell and an average value for each sample was used. The results are shown in Figure 2.

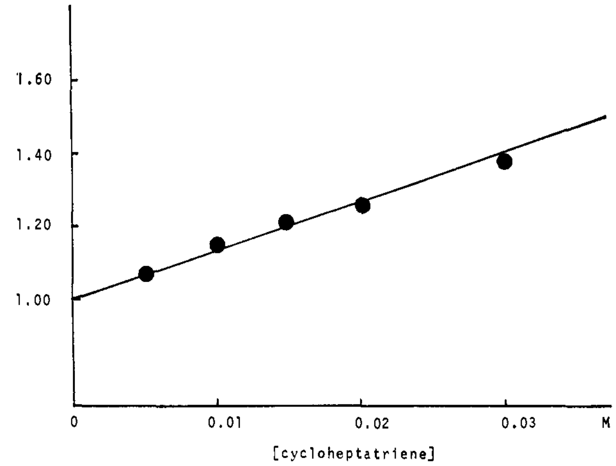

Figure 2. Stern–Volmer plot of fluorescence quenching of anthracene (**1**) by cycloheptatriene (**2**) in ethanol; slope = 13.5 M^{-1}.

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[27] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

Mechanism and Catalysis of 2-Methyl-3-thiosemicarbazone Formation. A Second Change in Rate-Determining Step and Evidence for a Stepwise Mechanism for Proton Transfer in a Simple Carbonyl Addition Reaction[1]

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Abstract: 2-Methyl-3-thiosemicarbazone formation from *p*-chlorobenzaldehyde undergoes a change in rate-determining step at high pH, similar to that at low pH, from rate-determining dehydration of the carbinolamine intermediate to partially rate-determining attack of the nucleophile on the carbonyl group. The attack step is subject to general base catalysis. Brønsted plots for tertiary amines and oxygen anions exhibit breaks for bases of pK_a less than 6. This curvature is consistent with that expected for a simple rate-determining proton transfer reaction between the dipolar addition intermediate $T^{\pm}$ and the catalyzing base. However, the break occurs at a higher pK_a than expected from the estimated pK_a value for $T^{\pm}$ of 3.1. Better agreement is found for a preassociation mechanism with rapid, stepwise proton transfer within an encounter complex after the formation of $T^{\pm}$. According to this mechanism, N–C bond formation within an encounter complex that contains the base catalyst is rate determining with strong bases and there is a change to rate-determining proton transfer with weaker bases. The magnitude of the observed catalytic constants is consistent with that expected for such a mechanism, but is significantly smaller than expected for a concerted mechanism. General acid catalysis of 2-methyl-3-thiosemicarbazide addition to *p*-chlorobenzaldehyde by carboxylic and cacodylic acids closely resembles that observed for the addition of other weakly basic amines (α = 0.2). It is suggested that general acid, unlike general base, catalysis involves some stabilization of the transition state for carbon–nitrogen bond formation by the catalyst.

A growing body of evidence concerning general acid–base catalysis of complex reactions involving proton transfers to or from electronegative atoms suggests that in some cases these proton transfers proceed by discrete steps, rather than by a process that is

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