

PHOTOCYCLOADDITION REACTION OF 1,4,5,8-TETRAAZAPHENANTHRENE
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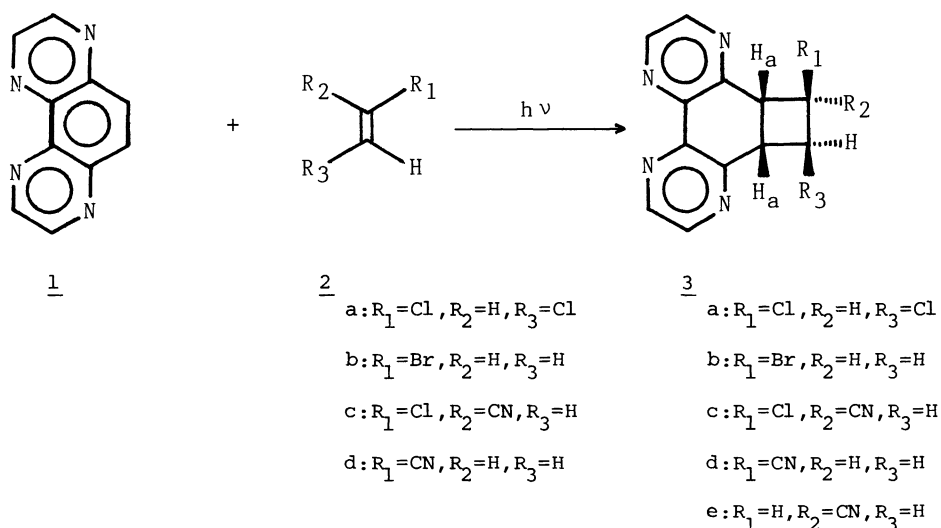
Irradiation of 1,4,5,8-tetraazaphenanthrene with some olefins such as trans-1,2-dichloroethylene, vinyl bromide, acrylonitrile, and 2-chloroacrylonitrile gave [2+2] cycloadducts. The stereochemistry of cycloadducts, quantum yield measurements, sensitization, and quenching studies indicate the reaction to proceed through a triplet excited state.

Many [2+2] photocycloaddition reactions are known to occur via the intermediacy of exciplex,¹⁾ but direct evidence for this mechanistic pathway, triplet exciplex in particular, is sparse.²⁾ One of the most convincing evidence for the exciplex mechanism in the photochemical [2+2] cycloaddition reactions is the photoaddition of phenanthrene with dimethyl fumarate which has been extensively studied.³⁾ However, relatively little is known about the photocycloaddition reaction of the heterocyclic phenanthrenes with olefins. It is predicted that the photochemical behavior of these compounds should be different from that of phenanthrene due to the presence of (n, π^*) state. We report here the photocycloaddition reaction of 1,4,5,8-tetraazaphenanthrene (TAP), a phenanthrene analogue containing four nitrogen atoms, with olefins through a triplet excited state.

Irradiation of a chloroform solution of TAP(1) and trans-1,2-dichloroethylene(2a) with 300 nm UV light yielded only one 1:1 cycloadduct(3a) in quantitative yield.⁴⁾ Short-wavelength irradiation of 3a gives rise to the starting material, TAP. This suggests the compound 3a to be a [2+2] cycloadduct. The NMR spectra of 3a exhibits a symmetrical AA'XX' splitting pattern for the cyclobutane ring protons indicating the cis stereochemistry for the two carbon-chlorine bonds although the absolute stereochemistry of the 1:1 cycloadduct (3a) is not definitely determined.⁵⁾ Irradiation of a chloroform solution of TAP(1) in the presence of excess vinyl bromide (2b) and 2-chloroacrylonitrile (2c) with 300 nm UV light led to the formation of only one cycloadduct 3b and 3c in quantitative yields, respectively,⁶⁾ while two isomeric cycloadducts 3d and 3e in 1:3 ratio were obtained with acrylonitrile (2d).⁷⁾ Stereochemical assignments are based on the NMR data.

LC analysis and NMR spectroscopy revealed that this photocycloaddition reactions proceed stereoselectively. This is due to the repulsion of π -electron cloud of pyrazine ring in TAP with halogen atom electron cloud. Therefore, only 3a, 3b, 3c were formed from 2a, 2b, 2c in quantitative yields, respectively. In

particular, the formation of only 3a from 2a indicates that this reaction proceeds via a diradical intermediate in which rotation of C-C bond precedes ring closure. The stereochemical assignments of 3d and 3e were based on the chemical shift of the proton (R_2) in 3d which is located in the shielding zone of anisotropic pyrazine ring. The photocycloaddition to 2d favors the formation of the endo adduct, 3e, which is stabilized by the overlap interaction of π -orbitals of CN triple bond and pyrazine ring in TAP.



Some olefins such as 2,3-dimethyl-2-butene, methyl crotonate, dimethyl fumarate, p-chlorocinnamionitrile, fumaronitrile, tetracyanoethylene, and 3-chloro-1-propene did not yield any photoproducts.

TAP shows very weak fluorescence ($\Phi_f = 0.001$) and laser flash photolysis study in methanol indicated the efficient intersystem crossing from the excited singlet state to the triplet state ($\Phi_{isc} = 0.95$). The fluorescence of TAP was not quenched by the olefins such as trans-1,2-dichloroethylene which yield photocycloadducts while dimethyl fumarate and fumaronitrile quench the

Table 1. The effect of benzophenone on the photocycloaddition reaction of TAP with trans-1,2-dichloroethylene at 366 nm^{a)}

Concentration of benzophenone/M	A/A_0 ^{b)}	Φ
0	1.0	0.038
0.01	0.52	0.039
0.025	0.30	0.036
0.05	0.18	0.034
0.10	0.09	0.029

a) Concentration of TAP is $3 \times 10^{-3} \text{M}$.

b) Fractions of photons absorbed by TAP in this condition.

Table 2. The effect of xanthone on the photocycloaddition reaction of TAP with trans-1,2-dichloroethylene at 366 nm^{a)}

Concentration of xanthone/M	A/A_0 ^{b)}	Φ
0	1.0	0.038
0.001	0.76	0.040
0.003	0.52	0.044
0.01	0.25	0.045
0.03	0.10	0.042

a) Concentration of TAP is $3 \times 10^{-3} \text{M}$.

b) Fractions of photons absorbed by TAP in this condition.

fluorescence of TAP without yielding any photoproducts. No singlet exciplex emission was detected. These data suggest the photocycloaddition reaction to proceed from the triplet excited state.

The quantum yields of photocycloaddition reaction decrease as the concentration of benzophenone, a triplet sensitizer, increases (Table 1) indicating that all the benzophenone triplets do not generate effectively the TAP triplets. It is very likely that the self-quenching of benzophenone triplets is efficient at high benzophenone concentration. In contrast to the sensitized photocycloaddition reaction by benzophenone, the quantum yields of photocycloaddition reaction increase slightly as the concentration of xanthone, a triplet sensitizer, increases (Table 2) while azulene quenches the photocycloaddition reaction very efficiently (Table 3) giving the slope/intercept ratio of $3,370 \text{ M}^{-1}$ in the Stern-Volmer plot. It is, therefore,

Table 3. The azulene effect on the photocycloaddition reaction of TAP with trans-1,2-dichloroethylene at 366 nm ^{a)}

Concentration of azulene/M	ϕ	ϕ^0/ϕ
0	0.038	1.0
1×10^{-4}	0.028	1.36
2×10^{-4}	0.021	1.81
4×10^{-4}	0.016	2.38

a) Concentration of TAP is $3 \times 10^{-3} \text{ M}$.

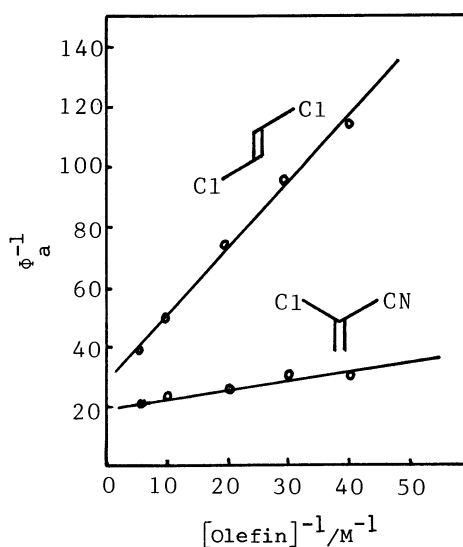
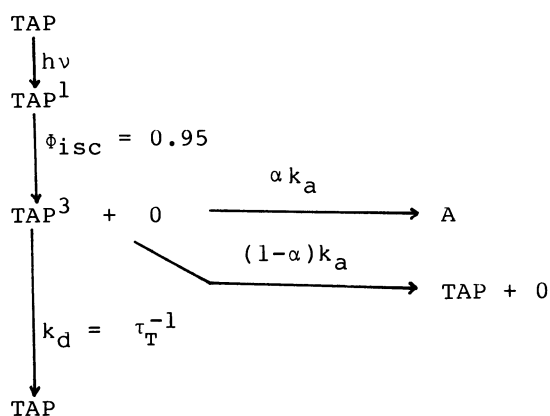


Fig.1. Variation in quantum yield for triplet cycloadduct formation with olefin concentration.



Scheme 1.

concluded that the photocycloaddition reaction of TAP with trans-1,2-dichloroethylene proceeds from the triplet excited state of TAP.

$$\frac{1}{\phi_a} = \frac{1}{\alpha} \left(1 + \frac{1}{k_a \tau_T [O]} \right) \quad (1)$$

The Scheme 1 can be written for the photocycloaddition reaction of TAP with olefins where O,A represent olefin, adduct, respectively. The relationship between ϕ_a^{-1} and $[O]^{-1}$ is given by Eq. 1. A good linear relationship was obtained in the plots of ϕ_a^{-1} vs. $[O]^{-1}$ as shown in Figure 1, supporting the mechanistic scheme and the photocycloaddition reaction between TAP and olefins occurs via a triplet excited state of TAP.

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References

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- 2) R.A. Caldwell, *J. Am. Chem. Soc.*, **95**, 1690 (1973).
- 3) D. Creed, R.A. Caldwell, and M.M. Ulrich., *J. Am. Chem. Soc.*, **100**, 5831 (1978).
- 4) 3a: White crystals, mp 190-191 °C; ^1H NMR(CDCl_3) δ 4.5(2H,d, J=4 Hz), 4.9(2H,d, J=4 Hz), 8.7(4H,q); MS(m/e) 278(M^+); IR(KBr) 3040,2950,1400, 1250, 965,885, and 760 cm^{-1} . UV(EtOH) λ_{max} (log ϵ) 270 nm(3.79), 322(4.09). Found: C,51.59; H,2.92; N,19.8%. Calcd for $\text{C}_{12}\text{H}_8\text{N}_4\text{Cl}_2$: C,51.64; H,2.89; N,20.10%.
- 5) The stereochemistry of 1:1 cycloadducts 3a, b, c, d, e was tentatively assigned by the NMR spectra.
- 6) 3b: White crystals; ^1H NMR(CDCl_3) δ 2.90-3.40(2H,m), 4.05-4.70(3H,m), 8.6(4H,q); MS(m/e) 288(M^+); IR(KBr) 3045,2980,2940,1410,1355, and 865 cm^{-1} . Found: C,49.91;H,3.20;N,19.91%. Calcd for $\text{C}_{12}\text{H}_9\text{H}_4\text{Br}$: C,49.85;H,3.14; N,19.38%.
- 3c: Slightly yellow crystals; ^1H NMR(CDCl_3) δ 3.1-3.6(2H,m),4.1-4.9(2H,m), 8.6(4H,q); MS(m/e) 269(M^+); IR(KBr) 3060,2960,2260,1410,1100, and 880 cm^{-1} . Found: C,57.79;H,3.14;N,25.80%. Calcd for $\text{C}_{13}\text{H}_8\text{N}_5\text{Cl}$: C,57.89;H,2.99; N,25.97%.
- 7) 3d: White crystals; ^1H NMR(CDCl_3) δ 2.60-3.55(3H,m), 4.1-4.55(2H,m), 8.6(4H,q); MS(m/e) 235(M^+); IR(KBr) 3020,2980,2940,2250,1450, and 1260 cm^{-1} . Found: C,66.29;H,3.90;N,29.61%. Calcd for $\text{C}_{13}\text{H}_9\text{N}_5$: C,66.37;H,3.86;N,29.77%.
- 3e: White crystals; ^1H NMR(CDCl_3) δ 2.45-3.40(2H,m), 3.70-4.55(3H,m), 8.6(4H,q); MS(m/e) 235(M^+); IR(KBr) 3020,2980,2950,2250,1480,1415, and 1110 cm^{-1} . Found: C,66.28;H,3.92;N,29.65%. Calcd for $\text{C}_{13}\text{H}_9\text{N}_5$: C,66.37;H,3.86; N,29.77%.

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