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Photocycloadditon Reaction of *trans*-Cinnamonitrile Derivatives with Tetramethylethylene

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Stereospecific [2+2] cycloadducts are obtained as major products when *trans*-cinnamonitrile derivatives are irradiated with excess tetramethylethylene. The fluorescence quenching studies, weak exciplex fluorescence, and sensitization by benzophenone suggest that this stereospecific photochemical cycloaddition reaction involves singlet exciplex intermediate formed between cinnamonitrile derivatives and tetramethylethylene.

Introduction

The photocycloaddition reactions of compounds which are the type of $C_6H_5CH=CXY$ with tetramethylethylene (TME) and other olefins have been reported with much attention.[1-3] Thier mechanism usually involves singlet excited state of the $C_6H_5CH=CXY$ with ground state of olefins giving an exciplex and the stereochemistry of products is retention. The triplet state of the $C_6H_5CH=CXY$ produced by sensitization gives only *cis* ⇌ trans isomerization and no cycloadduct is observed from the triplet state.[4]

In order to investigate the mechanism of and the substituent effects on the cycloaddition reaction of *trans*-cinnamonitrile derivatives, fluorescence quantum yields, fluorescence quenching by olefins, and sensitization by benzophenone of the compounds are studied.

Experimental

Materials. *trans*-Cinnamonitrile derivatives (*m*-Br, *m*-Cl, *p*-Cl, *m*-OCH₃, *p*-OCH₃, *p*-CH₃, *m*-NO₂, *p*-NO₂) were synthesized from corresponding *trans*-cinnamic acids (Aldrich Chemical Co.) by the method reported.[5] Other *trans*-cinnamonitrile derivatives (*p*-Br, *p*-N, N-dimethyl amino) were synthesize from modified Wittig reaction in which the corresponding benzaldehydes were treated by the carbanion of diethyl cyanomethanephosphonate synthesized from triethyl phosphonate and 2-chloroacetonitrile (Aldrich Chemical Co.).[6,7] These *trans*-cinnamonitrile derivatives were separated by column chromatography and recrystallized from n-hexane and methanol. Tetramethylethylene (99⁺%, gold level) (TME) and methylcrotonate were obtained from Aldrich Chemical Co. and used without further purification. Fumaronitrile was also obtained from Aldrich Chemical Co. and purified by recrystallization and sublimation. All the solvents such as chloroform, methanol, cyclohexane were obtained from Merck Chemical Co..

Spectra. ¹H NMR spectra were measured on Varian T-60A and Varian 80A spectrometers against tetramethylsilane internal standard in deuterated chloroform. Ultraviolet-visible spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 267 spectrophotometer using potassium bromide pellets and/or sodium plate. Fluorescence spectra were recorded on an Aminco-Bowman spectrofluorometer with Aminco XY-recorder.

Irradiation of trans-Cinnamonitrile Derivatives and Tetramethylethylene. *trans*-Cinnamonitrile and TME in chloroform solution were deoxygenated by bubbling dry nitrogen through the solution for 0.5-1 h and irradiated for 25-50 hrs in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co.) Model RPR-208 or RPR-100 equipped with eight 300 nm UV lamps.

Irradiated samples were analyzed by silica gel TLC utilizing *n*-hexane-dichloromethane or *n*-hexane - ethyl ether mixture as a developing solvent. The major product was isolated by preparative TLC.

Determination of Fluorescence Quantum Yields and Fluorescence Quenching by Olefins. Fluorescence quantum yields (ϕ_f^s) of *trans*-cinnamonitrile derivatives in dilute solution[8] were determined by eq. (1)

$$\frac{\phi_f^s \cdot OD}{\phi_f^r \cdot OD} = \frac{\phi_f^s \, \varepsilon_s c_s dI_0}{\phi_f^r \, \varepsilon_r c_r dI_0} = \frac{\text{area under fluo. peak}^s}{\text{area under fluo. peak}^r} \quad (1)$$

in which the subscript *s* means *trans*-cinnamonitrile derivatives, *r* means *p*-terphenyl or dimethoxycoumarin (DMC) as references, and OD means the optical density. The approximation of $cdI_0 \simeq I_a$ for OD < 0.05 is used. The relative fluorescence quantum yields of *trans*-cinnamonitrile derivatives were determined by measuring the weight of area under the fluorescence bands.

In order to determine the Stern-Volmer constants $(k_q \cdot \tau)$ of fluorescence quenching, the fluorescence spectra of *trans*-

cinnamonitrile derivatives (5×10^{-5} mole) containing 0, 2 × 10^{-2}, 4×10^{-2}, 6×10^{-2}, 8×10^{-2} and 10^{-1} mole of olefins (TME, fumaronitrile, methyl crotonate) were obtained in chloroform at room temperature with respect to excitation at 290 nm.

Triplet Sensitization by Benzophenone. trans-Cinnamonitrile derivatives ($10^{-3}M$), TME($5 \times 10^{-2}M$) and benzophenone were dissolved in chloform. The UV absorbance of benzophenone at 300 nm was five times that of *trans*-cinnamonitriles. The solution was irradiated by the same method as used in the direct irradiation. The photoproducts were separated by preparative TLC or column chromatography.

Results and Discussion

Photoreaction of trans-Cinnamonitrile Derivatives with TME.
The major photoproducts formed between *trans*-cinnamonitrile derivatives (1) and TME (2) in chloroform is isolated by preparative TLC and their structures are determined on the basis of spectral data; the appearance of four new methyl proton resonance peaks in the region of 0.6 - 1.6 and methine protons in the cyclobutane ring as two doublets (2.8-3.2, 1H, *d*, AB; 3.4-3.8, 1H, *d*, AB), the disappearance of vinyl proton peaks in *trans*-cinnamonitrile derivatives, the disappearance of C = C stretching bands at about 1640 cm^{-1}, the 10-15 cm^{-1} blue shift
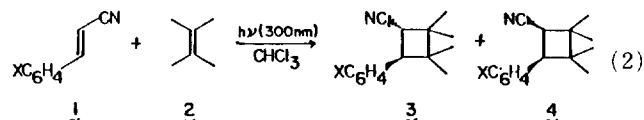
$$X: \text{a. H; b. m-Br; c. m-Cl; d. m-OCH}_3; \text{ e. p-Br ; f. p-Cl;}$$
$$\text{g. p-OCH}_3; \text{ h. p-CH}_3; \text{ i. m-NO}_2; \text{ j. p-NO}_2; \text{ k. p-NMe}_2$$

of $\nu_{C\equiv N}$ stretching bands from those of *trans*-cinnamonitrile derivatives, the appearance of cyclobutane ring deformation bands at about 680 - 700 cm^{-1} in the IR spectra, blue shift of λ_{max}^{abs}, and the appearance of benzenoid like bands in the UV spectra as tabulated in Table 2 and 3.

These spectral data indicate the photoproducts to be [2 + 2] cycloadducts. These cycloadducts are obtained as a mixture of stereoisomers (3 and 4) but the single product 3 is obtained when a large excess of TME is used. The ratio of stereoisomers are determined by the integration of NMR resonance peaks of the four methyl protons of cycloadducts 3 and 4.

When **1a, 1b, 1c, 1d, 1e, 1f, 1g** are **1h** are irradiated with TME, *trans*-[2+2] cycloadduct 3 and/or *cis*-[2+2] cycloadduct 4 can be obtained as a major and a minor products, respectively, while **1g** gives a cycloadduct as a minor product only, and **1i, 1j** and **1k** do not give any cycloadduct. When the ratio of **1a, 1f, 1h** to TME are 1/50, two isomeric cycloadducts of **3a** and **4a, 3f** and **4f, 3h** and **4h** are obtained while *trans*-[2+2] cycloadduct of **3b, 3c, 3d, 3e** only are obtained when the ratio of **1b, 1c, 1d, 1e** to TME are 1/130 as shown in Table 1.

When **1g** is irradiated with TME for 80 hrs, *trans*-**1g** and *cis*-**1g** are the major products and a cycloadduct is obtained only as a minor product indicating the *cis* ⇌ *trans* photoisomerization to be the major reaction path. The ratio of *cis*-**1g** to cycloadduct is 4.7/1 as determined by ^{1}H NMR. When **1k** is irradiated with TME, only *cis* ⇌ *trans* photoisomerization reaction is observed and no cycloadduct is obtained. The fluorescence of

TABLE 1: The Ratio of Stereoisomers in Photoreaction Products[a]

trans-Cinnamonitriles	Concentrations of 1	Concentrations of TME	Product ratio (3/4)
1 a	$10^{-3}M$	$5 \times 10^{-2}M$	5/3
1 b	10^{-3}	1.3×10^{-1}	Product 3 only[b]
1 c	10^{-3}	1.3×10^{-1}	Product 3 only
1 d	10^{-3}	1.3×10^{-1}	Product 3 only
1 eq	10^{-3}	1.3×10^{-1}	product 3 only
1 f	1.5×10^{-3}	7.5×10^{-2}	3/1
1 g	1.5×10^{-3}	7.5×10^{-2}	Small amount[c] of cycladducts
1 h	1.5×10^{-3}	7.5×10^{-2}	2/1
1 i	5×10^{-4}	2.5×10^{-2}	No cycloadduct
1 j	5×10^{-4}	2.5×10^{-2}	No cycloadduct
1 k	10^{-3}	1.3×10^{-1}	No cycloadduct

[a] The ratio of cycloadducts were determined by NMR data;
[b] Product 3 only was detected by NMR and gas chromatography:
[c] Cycloadducts were obtained as minor products.

TABLE 2: Spectral Data of *trans*-Cycloadducts

| *trans*-Cycloadducts	NMR (CDCl$_3$)[a]		IR($\nu_{C\equiv N}$; cm^{-1})	UV(λ_{max}^{abs}; nm, CHCl$_3$)		
3 b	3.12 (1H,d,AB)	3.58 (1H,d,AB)	2237	264	271	279
3 c	3.13	3.60	2235	262	269	276
3 d	3.03	3.54	2230		276	283
3 e	3.13	3.52	2230	263	272	279
3 f	3.12	3.60	2230	264	271	279

[a] The chemical shifts of methine protons in the cyclobutane ring.

TABLE 3: Chemical Shifts of Methyl Protons in Cycloadducts[a]

Cycloadducts	Chemical shifts[b] (ppm)			
3 a	0.60	1.00	1.08	1.33
4 a	1.00	1.08	1.17	1.27
3 b	0.77	1.15	1.22	1.47
3 c	0.80	1.20	1.27	1.52
3 d	0.77	1.13	1.22	1.47
3 e	0.73	1.13	1.19	1.45
3 f	0.83	1.23	1.30	1.55
4 f	1.23	1.30	1.35	1.48
3 h	0.87	1.30	1.35	1.60
4 h	1.30	1.35	1.43	1.53

[a] CDCl$_3$ solvent; [b] Protons of each methyl group show single peak only.

methoxy and *p*-N, N-dimethylamino groups are very good elec-
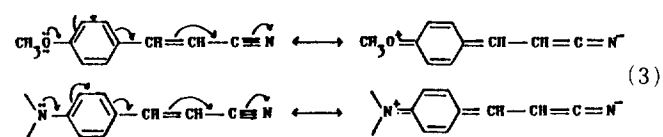
1g and **1k** was not quenched by TME. The intramolecular charge transfer transition is very probable in **1g** and **1k** because *p*-methoxy and *p*-N, N-dimethylamino groups are very good electron donating substituents while cyano group is a strong electron withdrawing group. In the case of *p*-N, N-dimethylamino cinnamonitrile, no cycloadduct is obtained because intramolecular charge transfer is so effective while this charge transfer

character is weaker in *p*-methoxy cinnamonitrile because methoxy group is less electron donating and the compound yields [2 + 2] cycloadducts as minor products besides the major *cis* ⇌ *trans* isomerization products.

The formation of *cis*-[2 + 2] cycloadducts **4a, 4f** and **4h** probably involves two steps when TME concentration is moderately excess. When **la, lf** and **lh** are irradiated, *cis* ⇌ *trans* isomerization reaction competes with cycloaddition reaction to form *cis*-isomers and this *cis*-product yields **4a, 4f** and **4h** on further irradiation. When large excess concentration of TME is used, singlet excited states of **lb, lc, ld**, and **le** encounter with TME molecule before undergoing *cis* ⇌ *trans* isomerization and *trans*-[2 + 2] cycloadducts **3b, 3c** and **3d** only are obtained as shown in Scheme 1.

Fluorescence Studies of trans-Cinnamonitrile Derivatives. Fluorescence quantum yields of *trans*-cinnamonitrile derivatives are measured utilizing *p*-terphenyl[9] or dimethoxycoumarin as standards and are summarized in Table 4. The fluorescence efficiency is low in m-Br, *m*-Cl, and *p*-N, N-dimethylamino-*trans*-cinnamonitriles while *m*-OCH₃-*trans*-cinnamonitrile which has an electron donating substituent gives moderately intense fluorescence. The fluorescence of *trans*-cinnamonitrile, *p*-Br, *p*-OCH₃, *p*-CH₃, *m*-NO₂, and *p*-NO₂-*trans*-cinnamonitrile is too weak to determine the quantum yields. These results are very similiar to those of *trans*-methyl cinnamate derivatives as shown in Table 5. The fluorescence is moderately intense in the compounds with electron donating groups such as *m*-OCH₃, *p*-OCH₃, *m*-OH, *p*-OH and *p*-NMe₂ and compounds with electron withdrawing substituents such as *m*-NO₂, *p*-NO₂, *m*-Cl
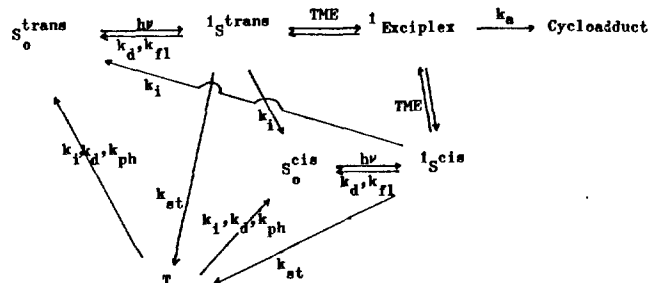
Scheme 1. Mechanism of [2 + 2] Photocycloaddition Reaction.

TABLE 4: Fluorescence Quantum Yields of *trans*-Cinnamonitrile Derivatives in Chloroform

trans-Cinnamonitrile	Φ_f^a
m-Br	4.65×10^{-4}
m-Cl	2.39×10^{-3}
m-OCH₃	7.78×10^{-2}
p-NMe²	2.91×10^{-3b}

ᵃstandard; *p*-terphenyl Φ_f = 0.93 (cyclohexane), λ_{ex} = 290nm.
ᵇstandard; DMC Φ_f = 0.65 (EtOH), λ_{ex} = 370nm.

TABLE 5: Fluorescence Quantum Yields of *trans*-Methylcinnamate Derivatives in Chloroform

trans-Methylcinnamate	Φ_f^a
m-OCH₃	4.05×10^{-2}
p-OCH₃	1.96×10^{-4}
m-OH	2.91×10^{-2}
p-NMe₂	3.95×10^{-3}

ᵃ standard; *p*-terphenyl Φ_f=0.93 (cyclohexane), λ_{ex} = 290nm.

and *p*-Cl show too weak fluorescence to determine their fluorescence quantum yields.

In general, the more electron donating are the substituents, the stronger the fluorescences are exhibited. The meta-substituted cinnamonitrile shows stronger fluorescence than the *para*-substituted cinnamonitrile. The fluorescence quantum yields, however, could not be correlated with any substituent constants.

The results show that the fluorescences of *trans*-cinnamonitrile derivatives and *trans*-methyl cinnamate derivatives are weak or too weak to determine their quantum yields. This may be due to the very high intersystem crossing quantum yields from the singlet state to the triplet state as in the case of cinnamic acid[10] or to very fast internal conversion compared to the fluorescence rate.

The fluorescence of *m*-OCH₃, *m*-Cl and *m*-Br *trans*-cinnamonitriles was quenched by three olefins which have different π-electron densities; fumaronitrile-a π-electron deficient olefin, methyl crotonate-a moderate π-electron deficient olefin, and TME-a π-electron rich olefin. The fluorescence of *trans*-*p*-N,N-dimethylamino cinnamonitrile was not quenched by TME or methyl crotonate because of the strong intramolecular charge transfer transition as shown in eq. 3 but it was quenched to very small extent ($k_q.\tau$ = 1.88) by fumaronitrile, a π-lectron deficient olefin. A plot* of Φ_f^0/Φ_f vs. quencher concentration gave a straight line in agreement with the Stern-Volmer relationship, as shown in Figure 1-3.

$$\Phi_f^0/\Phi_f = 1 + k_q \cdot \tau \, [Q] \qquad (4)$$

The fluorescence spectra of cinnamonitrile derivatives in the presence of excess TME show very weak exciplex peak. The intensity of this fluorescence increases slightly as TME concentrations are increased as shown in Figure 4. This exciplex
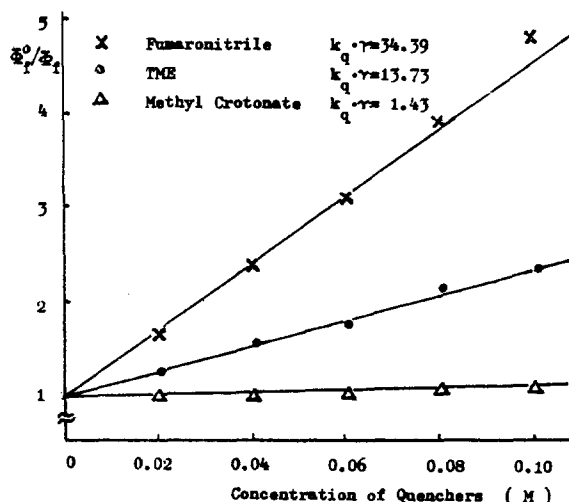

Figure 1. Stern–Volmer plot of fluorescence quenching of *m*-methoxycinnamonitrile.

*The shape of fluorescence envelope remains roughly constant as the intensity is decreased with increasing quencher concentrations. The measurement of Φ_f by peak height should therefore be equivalent to intergration of the area under the fluorescence curves. The plots are obtained by measuring the fluorescence peak heights instead of fluorescence quantum yields.
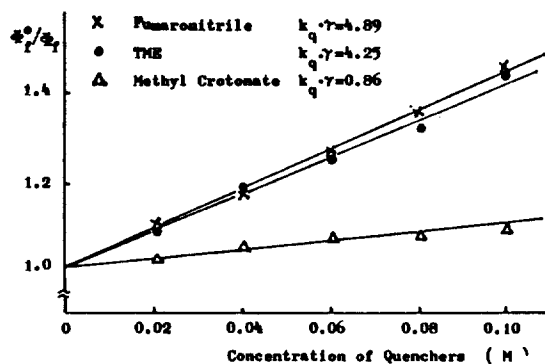
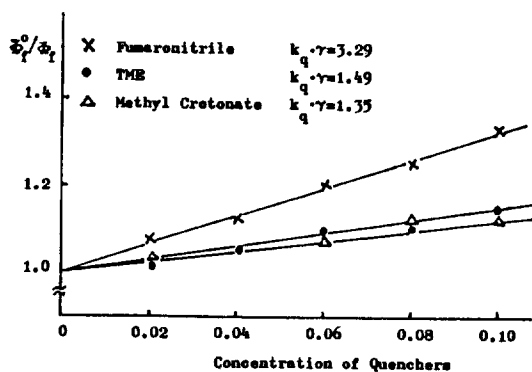**Figure 2.** Stern–Volmer plot of fluorescence quenching of *m*-chlorocinnamonitrile.

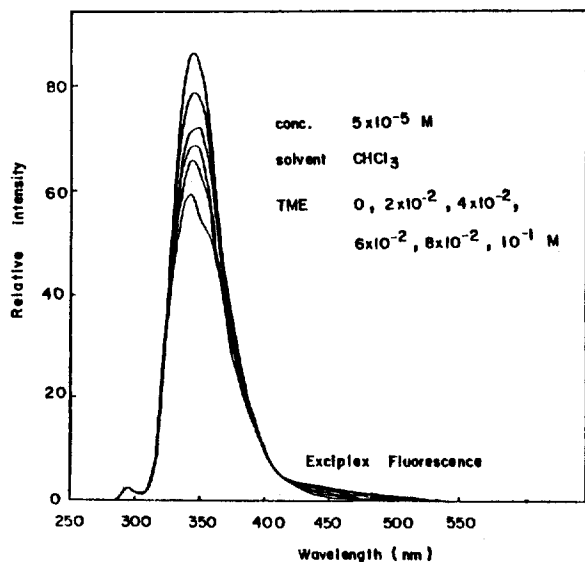**Figure 3.** Stern–Volmer plot of fluorescence quenching of *m*-bromocinnamonitrile.

Figure 4. Fluorescence quenching spectra of trans–*m*-chlorocinnamonitrile by TME.

fluorescence does not appear with π–electron deficient olefins such as fumaronitrile and methyl crotonate. This exciplex fluorescence, therefore, suggests that the photochemical [2 + 2] cycloaddition of trans–cinnamonitrile derivatives with TME involves singlet exciplex intermediate.

Sensitized Reaction by Benzophenone. Irradiation of trans-cinnamonitrile derivatives, TME and benzophenone mixture yields cis⇌trans isomerization products which are formed from the triplet state of cinnamonitrile derivatives and an oxetane

which is formed between the benzophenone triplet state and TME.[11,12] (eq. 5) These results support the singlet exciplex mechanism for the photocycloaddition reaction of cinnamonitrile derivatives.
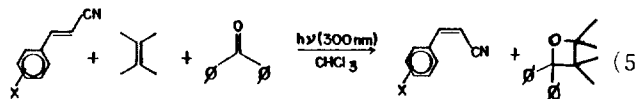
Conclusion

Trans-Cinnamonitrile derivatives undergo [2 + 2] photocycloaddition reactions with TME. The reactions are stereospecific and involve singlet exciplex intermediates as supported by the results of Stern–Volmer plot for the fluorescence quenching, small exciplex fluorescence, and triplet sensitized reaction by benzophenone.

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