

[2 + 2]-Photocycloaddition of *N*-Vinylcarbazole to Dimethyl Fumarate

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The [2 + 2]-photocycloaddition of photoexcited *N*-vinylcarbazole (VCZ) with dimethyl fumarate (F) in nonpolar benzene solvent yields an oxetane. This oxetane is subsequently cleaved to give two methoxydiene isomer products. The existence of the exciplex emission, the effect of solvent polarity on the photoproducts, and triplet sensitizer and quencher experiments prove the existence of a singlet exciplex intermediate in the photocycloaddition of VCZ and F.

Oxetane formation *via* [2 + 2]-photocycloaddition of a photoexcited carbonyl compound to an alkene is well known as the Paterno-Büchi reaction.^{1,2} In this cycloaddition, the existence of a biradical intermediate has been postulated from analyses of the product structure. Yang *et al.* further reported the participation of an exciplex prior to biradical formation in the quenching of the ¹n,π* state of acetone by unsaturated compounds.³

On the other hand, oxetane formation during the photocycloaddition of a photoexcited alkene to a ground-state carbonyl compound is very rare.⁴ In this case, however, the participation of an exciplex intermediate has been proved by the observation of the exciplex emission.⁵⁻⁷ In this paper, we report on oxetane formation from photoexcited *N*-vinylcarbazole and dimethyl fumarate *via* an exciplex intermediate, and the subsequent methoxydiene formation. Photopolymerization in this system has already been reported.⁸ In nonpolar benzene solvent, two methoxydiene isomers were produced by the [2 + 2]-photocycloaddition and the subsequent ring cleavage.

Experimental

Materials.—*N*-Vinylcarbazole (VCZ, Nakarai Tesque, Inc.) and dimethyl fumarate (F, Tokyo Kasei Kogyo Co.) were purified by recrystallization several times from methanol and hexane. Acetophenone (Wako Pure Chem. Ind.), as a triplet sensitizer, was purified by distillation under reduced pressure. Naphthalene (Wako), a triplet quencher, was purified by recrystallization. Benzene (Wako) and all other solvents used were dried and purified by distillation.

Photoreaction.—A solution of VCZ (1.0×10^{-2} mol dm⁻³) and F (1.0×10^{-1} mol dm⁻³) in benzene (200 cm³) was deoxygenated by nitrogen bubbling for 35 min. The solution was photoirradiated for 41 h by a 300 W high-pressure mercury lamp (Toshiba) with a Pyrex glass filter at 298 K.^{9,10} In this condition, VCZ was selectively photoexcited by a 334 nm emission line. Products were collected by high-pressure liquid chromatography (Jasco, Trirotar-V) on a silica-gel column (Jasco, Megapak SIL) using ethyl acetate-hexane (2:7, v/v) for elution. The two major products collected were recrystallized from hexane three times and were purified by liquid chromatography. Product **1** had a larger retention time than product **2**. The two methoxydiene isomers (**1** and **2**, *ca.* 10 mg) obtained were identified by MS, NMR and IR spectroscopy. The structure of the two isomers was determined by the ¹H NMR chemical shift of the methoxy group, and by the nuclear Overhauser effects caused by the irradiation at the methoxy peak.

(2E,4E)-5-(9-Carbazolyl)-4-methoxypenta-2,4-dienoic acid 1-methyl ester (**1**): m.p. 138.5 °C (Found: C, 74.4; H, 5.45; O, 15.25; N, 4.95. C₁₉H₁₇O₃N requires C, 74.25; H, 5.58; O, 15.62; N, 4.56%); ν_{\max} (KBr)/cm⁻¹ 2950w, 1710s (CO), 1630m, 1600m, 1490m, 1450s, 1432w, 1424w, 1260w, 1206w, 1152w, 748m and 722m; λ_{\max} (CH₂Cl₂)/nm 339 (ϵ /dm³ mol⁻¹ cm⁻¹ 8350); δ_{H} (400 MHz; CD₂Cl₂; Me₄Si) 3.58 (3 H, s, OCH₃), 3.99 (3 H, s, CO₂CH₃), 6.36 (1 H, s, CH), 6.41 (1 H, d, *J* 15.6, HC=CH), 6.91 (1 H, d, *J* 15.6, HC=CH) and 7.27–8.12 (8 H, m, aromatic); *m/z* 307 (M⁺, 62%), 292 (17, M – CH₃), 248 (16, M – CO₂CH₃), 217 (4, M – CO₂CH₃ – OCH₃), 204 (96, M – CHCOCH₃ – OCH₃), 166 (16, C₁₂H₈N) and 141 (100, M – C₁₂H₈N).

(2E,4Z)-5-(9-Carbazolyl)-4-methoxypenta-2,4-dienoic acid 1-methyl ester (**2**): m.p. 86 °C (Found: C, 74.7; H, 6.1; O, 15.8; N, 4.05. C₁₉H₁₇O₃N requires C, 74.25; H, 5.58; O, 15.62; N, 4.56%); ν_{\max} (KBr)/cm⁻¹ 3655w, 2955w, 1714s (CO), 1622m, 1598m, 1472m, 1450s, 1350m, 1332m, 1300m, 1263m, 1224m, 1192m, 1166m, 1042m, 972m, 750m, 722m and 650m; λ_{\max} (CH₂Cl₂)/nm 351 (ϵ /dm³ mol⁻¹ cm⁻¹ 25 700); δ_{H} (400 MHz; CD₂Cl₂; Me₄Si) 3.23 (3 H, s, OCH₃), 3.79 (3 H, s, CO₂CH₃), 6.81 (1 H, s, CH), 6.36 (1 H, d, *J* 15.2, HC=CH), 7.37 (1 H, d, *J* 15.2, HC=CH) and 7.30–8.10 (8 H, m, aromatic); *m/z* 307 (M⁺, 52%), 292 (38, M – CH₃), 248 (12, M – CO₂CH₃), 217 (6, M – CO₂CH₃ – OCH₃), 204 (96, M – CHCOCH₃ – OCH₃), 166 (9, C₁₂H₈N) and 141 (100, M – C₁₂H₈N).

The reaction quantum yields were determined by the selective photoexcitation of VCZ (4×10^{-4} – 1×10^{-2} mol dm⁻³) in the presence of F (1.0×10^{-1} mol dm⁻³) under the 340 nm monochromatic light ($\Delta\lambda = 19$ nm), whose photon energy was calibrated by potassium ferrioxalate actinometry as 4.3×10^{-6} E s⁻¹.¹¹ For the triplet sensitization experiment, acetophenone (2.0×10^{-1} mol dm⁻³) was selectively excited by 360 nm monochromatic light ($\Delta\lambda = 19$ nm). All samples for the quantum yield measurements were degassed by the freeze-pump-thaw method in a 1 cm quartz cell. The amounts of thermal side products, which were minor, were corrected for by the blank experiments.

Optical Measurements.—The absorption spectra were measured by a UV-200S spectrophotometer (Shimadzu). The emission spectra were obtained with a Hitachi 850 spectrofluorophotometer using a 5 nm slit width. The quantum yield of emission was determined relative to that of quinine sulfate in sulfuric acid.¹² The lifetime of the emission was measured by the single-photon-counting method (PRA Inc., Model 510B). The measurements were made in a degassed 1 cm quartz cell.

Results and Discussion

The fluorescence of ¹VCZ* ($\Phi_f = 0.40$, $\tau_f = 8.2$ ns) was

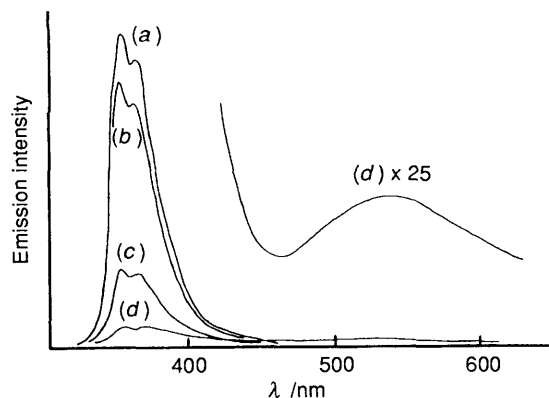


Fig. 1 Fluorescence quenching and exciplex emission of VCZ by the addition of F in benzene solvent at 298 K. $[VCZ] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[F] = 0$ (a), 1.4×10^{-3} (b), 2.0×10^{-2} (c) and 1.0×10^{-1} (d) mol dm^{-3} .

quenched by the addition of F in benzene solvent as shown in Fig. 1. The quenching rate constant determined by the Stern-Volmer plots was almost diffusion-controlled $1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This quenching is considered to be of the electron-transfer type because the free energy change of the reaction estimated by Weller's equation is exothermic by 19.5 kcal mol^{-1} .[†] On quenching, a new broad, structureless, emission band appeared at ca. 520 nm. This band is attributed to the emission of the exciplex formed between VCZ and F in the nonpolar benzene solvent. The lifetime of this exciplex emission was ca. 40 ns, independent of VCZ concentration.

In the previous study, photoirradiation of VCZ with 3-cyanostyrene in benzene gave cyclobutane products.¹⁰ In the present work, however, photoirradiation of VCZ with F gave two methoxydiene isomers **1** and **2**. The quantum yields of **1** and **2** formation were determined as 0.007 and 0.002, respectively. The formation of cyclobutane could not be detected under these experimental conditions. Fig. 2 shows the molecular structures of **1** and **2**. These interesting, unexpected methoxydiene formations are explained by the existence of an oxetane intermediate (X). Initially, the [2 + 2]-photocycloaddition of the C=C bond of VCZ to C=O of F forms an oxetane X, which undergoes ring cleavage to form **1** and **2**, with the loss of formaldehyde. The photoexcited C=C bond of VCZ is likely to attack C=O of F to form oxetane rather than the C=C bond of F to form cyclobutane. The oxetane X could not be isolated, although pyridine was added to the system to keep the solution basic.^{5,6} This oxetane may be photocleaved because the carbazole chromophore of X can also be photoexcited by 334 nm light.^{14,15} The oxetane formation *via* an exciplex, and the subsequent methoxydiene products are important for preparative photochemistry.

Fig. 3 shows the time-conversion plots of photoproducts **1** and **2**. The yields of **1** and **2** increased linearly from the initial stage of photoirradiation. This means that **2** is not produced solely by photoisomerization due to the prolonged photoirradiation of **1** or *vice versa*. The existence of photoisomerizations from **1** to **2** and **2** to **1** was confirmed by the photoirradiation and product analyses of isolated **1** and **2**; the isomerization quantum yields from **1** to **2** and **2** to **1** were determined as 0.05 and 0.04, respectively. However, in the initial stage of the photoaddition of VCZ to F, most of the exciting light is absorbed by the starting material VCZ. Therefore the effect of photoisomerization on the fractions of **1** and **2** is not so large.

The stereochemistry of oxetane X has not been established in this stage of the investigation. As for the conformation of the

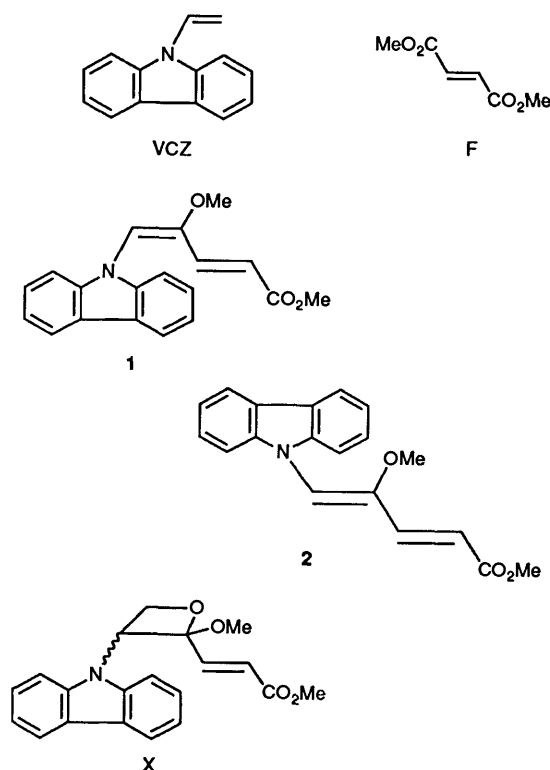


Fig. 2 Structures of VCZ, F, methoxydiene products **1** and **2** and oxetane X

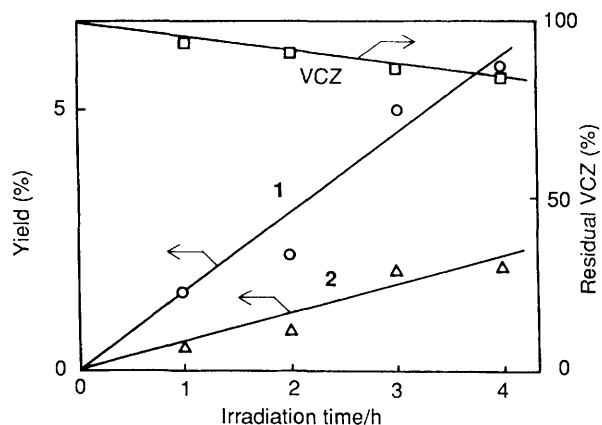


Fig. 3 Time-conversion plots of photoproducts. $[VCZ] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $[F] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$. VCZ was selectively photoexcited by 340 nm monochromatic light in benzene solvent at 298 K.

intermediate exciplex of VCZ and F, the maximum π -orbital overlap is expected. This exciplex conformation is preferable to the formation of X whose carbazolyl and $\text{C}_2\text{H}_2\text{CO}_2\text{Me}$ groups are in the *cis* position. The stereoselective cleavage of *cis*-X leads to *cis*-methoxydiene **1**. The larger formation quantum yield of **1** than that of **2** is consistent with the sandwich structure of the exciplex. At a higher temperature, 75 °C, the ratio of photoproducts **1/2** decreased to 1.2. This suggests the loss of stereoselectivity in the cleavage of X at a higher temperature probably due to the existence of some diradical or zwitterionic intermediate.

The effect of solvent polarity also suggested the participation of the exciplex intermediate in the photocycloaddition of VCZ to F. The exciplex has a large dipole moment and therefore the dissociation to free radical ions becomes predominant in polar solvents.¹⁶ As shown in Fig. 4, the increase of the solvent polarity effectively suppressed the formation of **1** and **2**. In polar

† 1 cal = 4.184 J.

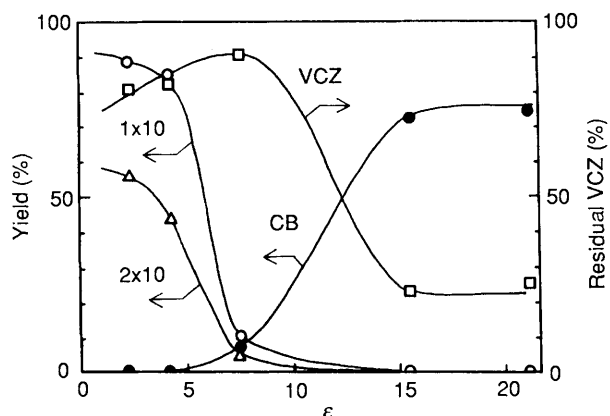
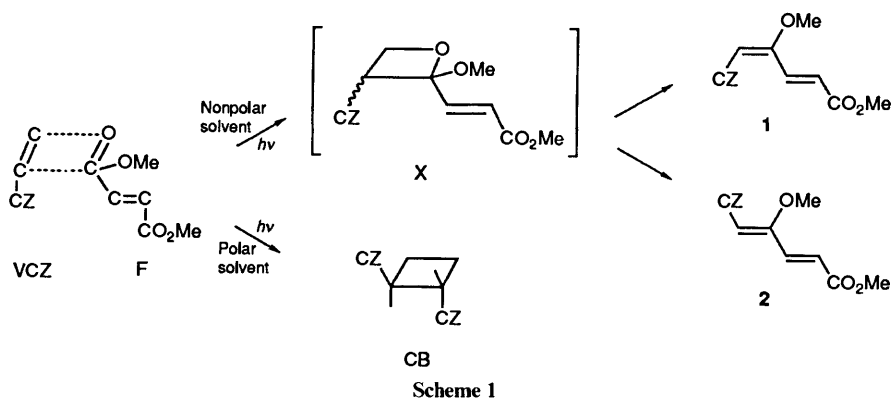


Fig. 4 Solvent polarity effects on photocycloaddition products **1**, **2**, and the *trans*-cyclobutane dimer (CB) at 298 K. Solvents used are benzene ($\epsilon = 2.3$), diethyl ether (4.2), tetrahydrofuran (7.6), methyl ethyl ketone (15.5), and acetone (21.5). $[\text{VCZ}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{F}] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$.

solvents, photoirradiation of VCZ with F gave a large amount of *trans*-1,2-bis(*N*-carbazolyl)cyclobutane dimer (CB) with a trace of polymer.^{8,17} This CB is produced by chain reaction via the radical cation of VCZ; the existence of $\text{VCZ}^{\cdot+}$ was also confirmed by laser photolysis measurements. In polar solvents, the photodissociation of $(\text{VCZ} \cdots \text{F})^*$ exciplex formed free radical ions of $\text{VCZ}^{\cdot+}$ and $\text{F}^{\cdot-}$, which gave CB and polymer, and therefore the formation of **1** and **2** were suppressed.

On using the triplet sensitizer and quencher, the participation of triplet exciplex in the [2 + 2]-photocycloaddition of VCZ with F was excluded. The triplet energies of VCZ, acetophenone, and naphthalene are 70, 74 and 61 kcal mol⁻¹, respectively. Therefore, acetophenone and naphthalene can act as triplet sensitizer and quencher for VCZ, respectively. Acetophenone or naphthalene, whose concentration was properly adjusted for the sufficient sensitization and quenching, was added to the photoreaction system. However, the excitation of acetophenone gave no **1** and **2** formation, and the addition of naphthalene did not quench the product formation. Therefore, we concluded that oxetane X is formed via the singlet exciplex

of VCZ and F. This is consistent with the report of oxetane formation from phenanthrene with F by Farid *et al.*⁶

Scheme 1 summarizes the [2 + 2]-photocycloaddition of VCZ to F, and the subsequent formation of methoxydiene. Photoexcited VCZ forms an exciplex with F, which subsequently gives methoxydiene products via the intermediate oxetane. In polar solvents, however, the photodissociation of the exciplex to free radical ions gives the cyclodimer of VCZ.

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