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Photolysis of 3-phenyl-4-phenylethynylcyclobut-3-en-*trans*-1,2-dicarboxylic acid dimethyl ester in methanol [1]

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Abstract

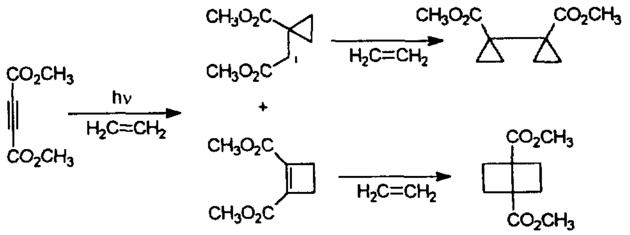
The photolysis of 3-phenyl-4-phenylethynylcyclobut-3-en-*trans*-1,2-dicarboxylic acid dimethyl ester (PPCB) in methanol yields 1:1 adducts (**1a–1d**, **2a** and **2b**) and an acetylene reduction product (**3**). The major products are **2a** and **2b** under neutral conditions, whereas **1a** and **1b** are the major products under acidic conditions and/or in the presence of electron donors, such as 1,4-dimethoxybenzene. The fluorescence of PPCB decreases as the concentration of sulphuric acid is increased. Azulene quenching studies suggest that **1a–2b** are formed from the singlet excited state, whereas the triplet excited state yields **3**. The formation of the photoadducts **1a–1d** can be correlated with the atomic charge of excited PPCB, suggesting an exciplex and a carbocation, rather than carbenoid, intermediate in the reaction.

Keywords: Methanol; 3-Phenyl-4-phenylethynylcyclobut-3-en-*trans*-1,2-dicarboxylic acid dimethyl ester; Photolysis

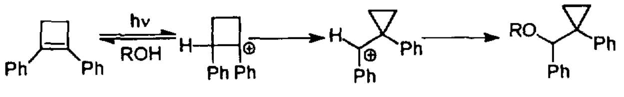
1. Introduction

The photoreaction of conjugated polyynes with olefins gives cyclobutene photoadducts as major products. The addition of unsymmetrical olefins, such as acrylonitrile, methyl acrylate and ethyl vinyl ether, to the triplet excited state of some polyynes yields regioselective [2+2]-type photoadducts as major products [1].

The photoreactions of 1,4-diphenyl-1,3-butadiyne (DPB) with dimethyl fumarate (DMFu) [2] and 2,3-dimethyl-2-butene (DMB) [3] were carried out as model reactions of polyynes with olefins to obtain photoadducts possessing cyclopropane rings. Two intermediates, carbene and carbocation, are possible in connection with the formation of cyclopropane rings. Owsley and Bloomfield [4] reported that the photoaddition of ethylene to dimethyl acetylenedicarboxylate generated bicyclopropyl compounds via a cyclopropyl carbene and bicyclo[2.2.0]-hexanyl derivative.



When a solution of 1,2-diphenylcyclobutene in methanol is irradiated, cyclopropyl and cyclobutyl compounds are generated [5]. This addition reaction, which may involve the rearrangement of the cyclobutyl cation to the cyclopropyl cation, proceeds exclusively via the excited singlet state.



In the photoreaction of DPB with DMB, two primary and one secondary photoadduct are obtained [3]. One of the primary photoadducts is the 1:2 adduct possessing two cyclopropane rings, which is probably formed from a carbene intermediate. This reaction is quenched with methanol, yielding only one cyclopropane and ether moiety from methanol insertion.

The photoreaction of DPB with DMFu yields a primary 1:1 and two secondary 1:2 photoadducts [2]. One of the 1:2

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[1] This paper is dedicated to Professor Pill-Soon Song on the occasion of his 60th birthday.

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photoadducts is generated from the singlet excited state of the primary photoadduct and possesses cyclopropane and oxirane rings. The other product is formed in the triplet manifold and contains two cyclopropane rings. We proposed that these photoadducts are formed from singlet and triplet carbenes, but attempts to detect or trap these carbene intermediates in cryogenic conditions have not been successful. If the primary photoadduct DPB–DMFu photoreacts with DMFu through this mechanism, a propargylene derivative will be formed as an intermediate, which is expected to be detected or trapped by the reported methods [6].

We have carried out the photolysis of 3-phenyl-4-phenylethynylcyclobut-3-en-*trans*-1,2-dicarboxylic acid dimethyl ester (PPCB), the primary photoadduct between DPB and DMFu, in methanol to provide an insight into the mechanism of formation of the secondary photoadducts in the photoaddition reaction of DPB with DMFu. However, no photoadduct containing a cyclopropane ring could be detected.

In this study, we investigated the addition of methanol to the excited states of PPCB in various conditions to test the involvement of carbocation intermediates rather than carbene intermediates in the photoaddition reaction of polyynes to olefins.

2. Experimental details

2.1. Instruments

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AM-300 and AC-200 spectrometers with chemical shifts being referenced against tetramethylsilane as internal standard or the signal of the solvent $CDCl_3$. UV absorption spectra were recorded on a Shimadzu 3100S spectrometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5895A GC-MS by the electron impact (EI) method. High-resolution mass spectra were determined with a JEOL JMS-DX 303 mass spectrometer. Fourier transform IR (FTIR) spectra were recorded on a Bomem MB-100 spectrometer in KBr pellets or NaCl cells. High-performance liquid chromatography (HPLC) was performed on a Waters Associates model 244 liquid chromatograph (Mildford, MA) equipped with a model 6000A solvent delivery system, model 440 UV absorbance detector fixed at 254 nm and model U6K universal injector. A Lichrosorb SI-60 column was used for preparative analyses.

2.2. Materials

Methanol was purified with $CuSO_4$ followed by fractional distillation prior to use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia) were used for HPLC and UV absorption spectra. PPCB was prepared by the reported method [2].

2.3. Irradiation of PPCB in methanol

A deaerated solution of PPCB (5 mmol l^{-1}) in methanol was irradiated with 300 nm UV light in a Rayonet photochemical reactor (model RPR-208) equipped with RUL 300 nm lamps. After irradiation for 12 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts (**1a**–**1d**, **2a**, **2b** and **3**) were isolated by column chromatography using hexane–ethyl acetate (3:1, v/v) as eluent. The products were purified by normal phase HPLC using hexane–ethyl acetate–dichloromethane (8:1:80, v/v/v) as eluent. Isolated yields: **1a**–**1d**, trace amounts; **2a**, 1.4%; **2b**, 1.2%; **3**, 0.6%.

Compound **1a**: $\delta_H(CDCl_3$, 200 MHz): 7.61–7.24 (10H, m), 6.59 (1H, d, $J=5.1$ Hz), 4.69 (1H, dd, $J=8.2$ and 5.1 Hz), 3.82 (3H, s), 3.70 (3H, s), 3.69 (1H, d, $J=8.2$ Hz), 3.07 (3H, s); $\delta_C(CDCl_3$, 50 MHz): 199.4, 171.1, 169.4, 139.6, 133.6, 128.7, 128.4, 128.2, 127.7, 127.4, 126.7, 101.0, 100.0, 87.2, 52.6, 52.2, 52.2, 51.5, 42.9; λ_{max}(MeOH) (nm): 263.3; ν_{max}(NaCl) (cm^{-1}): 3061.5, 2951.9, 1954.3, 1736.0, 1494.1, 1443.1, 1283.3, 1192.7, 1103.6, 1034.9, 732.2, 698.3; *m/z* (70 eV): 378 (M^+, 1.5%), 318 ($M^+-HCO_2CH_3$, 38.9%), 287 ($M^+-HCO_2CH_3-OCH_3$, 29.6%); calculated M^+ for $C_{23}H_{22}O_5$: 378.1467; found: 378.1452.

Compound **1b**: $\delta_H(CDCl_3$, 200 MHz): 7.57–7.25 (10H, m), 6.57 (1H, d, $J=4.9$ Hz), 4.65 (1H, dd, $J=8.2$ and 4.9 Hz), 3.82 (3H, s), 3.77 (1H, d, $J=8.2$ Hz), 3.64 (3H, s), 3.11 (3H, s); $\delta_C(CDCl_3$, 75 MHz): 200.3, 171.5, 169.4, 139.2, 133.3, 128.9, 128.4, 128.3, 127.9, 127.3, 126.9, 101.0, 100.0, 87.6, 52.4, 52.3, 52.3, 51.4, 43.0; λ_{max}(MeOH) (nm): 263.6; ν_{max}(NaCl) (cm^{-1}): 2938.3, 2850.8, 1954.9, 1736.8, 1446.0, 1443.1, 1281.6, 1195.8, 1100.0, 1034.6, 735.1, 698.6; *m/z* (70 eV): 378 (M^+, 0.2%), 318 ($M^+-HCO_2CH_3$, 23.2%), 287 ($M^+-HCO_2CH_3-OCH_3$, 19.4%); calculated M^+ for $C_{23}H_{22}O_5$: 378.1467; found: 378.1457.

Compound **1c**: $\delta_H(CDCl_3$, 200 MHz): 7.57–7.24 (10H, m), 6.53 (1H, d, $J=5.0$ Hz), 4.27 (1H, dd, $J=8.1$ and 4.9 Hz), 3.98 (1H, d, $J=8.1$ Hz), 3.75 (3H, s), 3.32 (3H, s), 3.30 (3H, s); $\delta_C(CDCl_3$, 50 MHz): 199.0, 170.5, 169.9, 137.1, 133.6, 128.8, 128.5, 128.2, 127.8, 127.5, 127.1, 103.1, 101.0, 89.1, 52.6, 52.4, 51.7, 51.3, 41.1; λ_{max}(MeOH) (nm): 264.2; ν_{max}(NaCl) (cm^{-1}): 2950.1, 1953.6, 1735.9, 1440.0, 1300.1, 1195.8, 1084.3, 1029.1, 741.5, 696.9; *m/z* (70 eV): 378 (M^+, 0.6%), 318 ($M^+-HCO_2CH_3$, 14.6%), 287 ($M^+-HCO_2CH_3-OCH_3$, 28.9%); calculated M^+ for $C_{23}H_{22}O_5$: 378.1467; found: 378.1473.

Compound **1d**: $\delta_H(CDCl_3$, 200 MHz): 7.52–7.22 (10H, m), 6.59 (1H, d, $J=5.0$ Hz), 4.25 (1H, dd, $J=7.8$ and 5.0 Hz), 4.00 (1H, d, $J=7.8$ Hz), 3.70 (3H, s), 3.30 (3H, s), 3.16 (3H, s); $\delta_C(CDCl_3$, 50 MHz): 199.0, 170.8, 169.8, 136.9, 133.5, 128.8, 128.6, 128.2, 127.8, 127.3, 127.3, 103.0, 100.6, 88.7, 52.5, 52.5, 52.0, 51.7, 41.0; λ_{max}(MeOH) (nm): 263.9; ν_{max}(NaCl) (cm^{-1}): 2949.6, 1955.7, 1736.1, 1439.2, 1297.4, 1194.7, 1076.0, 1028.7, 739.6, 697.0; *m/z* (70 eV):

378 (M^+, 0.6%), 318 ($M^+-HCO_2CH_3$, 34.1%), 287 ($M^+-HCO_2CH_3-OCH_3$, 34.7%); calculated M^+ for $C_{23}H_{22}O_5$: 378.1467; found: 378.1482.

Compound **2a**: δ_H($CDCl_3$, 200 MHz): 7.70–7.22 (10H, m), 5.96 (1H, s), 4.09 (1H, d, J = 1.8 Hz), 3.97 (1H, d, J = 1.8 Hz), 3.74 (3H, s), 3.68 (3H, s), 3.49 (3H, s); δ_C($CDCl_3$, 50 MHz): 171.7, 171.6, 150.7, 140.1, 134.9, 133.9, 132.5, 129.1, 128.8, 128.4, 128.4, 127.6, 127.5, 117.1, 58.0, 52.3, 52.3, 45.2, 45.1; λ_{max}(MeOH) (nm): 332.0; ν_{max}(NaCl) (cm^{-1}): 3023.3, 2950.1, 2846.4, 1733.1, 1446.5, 1350.1, 1256.5, 1165.8, 1079.1, 1028.9, 758.9, 694.7; m/z (70 eV): 378 (M^+, 4.1%), 287 ($M^+-HCO_2CH_3-OCH_3$, 30.8%), 259 ($M^+-HCO_2CH_3-OCH_3-CO$, 75.3%); calculated M^+ for $C_{23}H_{22}O_5$: 378.1467; found: 378.1454.

Compound **2b**: δ_H($CDCl_3$, 200 MHz): 7.36–7.05 (10H, m), 6.00 (1H, s), 4.03 (1H, d, J = 2.0 Hz), 3.79 (1H, d, J = 1.8 Hz), 3.71 (3H, s), 3.69 (3H, s), 3.59 (3H, s); δ_C($CDCl_3$, 50 MHz): 171.6, 171.3, 149.9, 143.3, 135.3, 133.1, 132.2, 128.8, 128.8, 128.0, 128.0, 127.1, 126.3, 106.7, 55.6, 52.2, 52.0, 46.0, 45.8; λ_{max}(MeOH) (nm): 313.4, 254.2; ν_{max}(NaCl) (cm^{-1}): 2946.7, 1734.2, 1439.4, 1348.7, 1246.0, 1176.0, 1079.1, 1028.9, 757.5, 695.7; m/z (70 eV): 378 (M^+, 21.5%), 287 ($M^+-HCO_2CH_3-OCH_3$, 61.8%), 259 ($M^+-HCO_2CH_3-OCH_3-CO$, 81.4%); calculated M^+ for $C_{23}H_{22}O_5$: 378.1467; found: 378.1483.

Compound **3**: δ_H($CDCl_3$, 300 MHz): 7.42–7.24 (10H, m), 6.76 (1H, d, J = 11.9 Hz), 6.53 (1H, d, J = 11.9 Hz), 3.97 (1H, s), 3.87 (1H, d, J = 1.8 Hz), 3.69 (3H, s), 3.36 (3H, s); δ_C($CDCl_3$, 75 MHz): 171.9, 171.2, 141.6, 136.9, 136.6, 134.3, 133.2, 129.0, 128.5, 128.0, 127.7, 126.8, 121.5, 52.2, 51.8, 46.7, 46.6; λ_{max}(MeOH) (nm): 310.2; ν_{max}(NaCl) (cm^{-1}): 3019.3, 2952.5, 1733.1, 1440.7, 1222.9, 1027.8, 1079.1, 1028.9, 762.5, 696.4; m/z (70 eV): 348 (M^+, 12.9%), 316 (M^+-CH_3OH, 35.6%), 257 ($M^+-HCO_2CH_3-OCH_3$, 24.0%), 229 ($M^+-HCO_2CH_3-OCH_3-CO$; 100.0%); calculated M^+ for $C_{22}H_{20}O_4$: 348.1362; found: 348.1370.

2.4. Irradiation of PPCB in methanol in the presence of sulphuric acid, sodium methoxide, 1,4-dimethoxybenzene or 1-cyanonaphthalene

Four irradiation tubes were filled with 0.005 M PPCB solution in methanol plus 0.050 M sulphuric acid (I), 0.10 M sodium methoxide (II), 0.10 M 1,4-dimethoxybenzene (III) and 0.10 M 1-cyanonaphthalene (IV). All four solutions were purged with nitrogen gas and irradiated with 300 nm UV light in a Rayonet photochemical reactor (model RPR-208) equipped with RUL 300 nm lamps. After irradiation for 12 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts (**1a**–**1d**, **2a**, **2b** and **3**) were isolated by column chromatography using hexane–ethyl acetate (3:1, v/v) as eluent. The products were purified by normal phase HPLC using hexane–ethyl acetate–dichloromethane (8:1:80, v/v/v) as eluent. Isolated yields: I: **1a**, **1b**, **1c**, **1d** and **3** were obtained in 5.9%, 4.7%, 1.8%, 1.2% and 2.0% yields respectively; II: **2a**, **2b** and **3** were obtained in 0.6%, 0.7% and 1.5% yields respectively; III: **1a**, **1b**, **1c**, **1d**, **2a**, **2b** and **3** were obtained in 6.1%, 6.5%, 1.8%, 2.4%, 1.7%, 1.9% and 1.9% yields respectively; IV: no **1a**–**3** were obtained.

2.5. Fluorescence quenching

The fluorescence spectra of PPCB were obtained in the presence of various concentrations of sulphuric acid in methanol. The Stern–Volmer constants ($k_q\tau_F$) were obtained from the Stern–Volmer plot

$$\Phi_F^0/\Phi_F = 1 + k_q\tau_F[\text{quencher}]$$

2.6. Effect of azulene on the photolysis of PPCB

PPCB solutions in Pyrex cells containing various concentrations of azulene ($(0\text{–}3.0)\times10^{-4}$ mol l^{-1}) were degassed with argon gas and irradiated in a merry-go-round apparatus with 300 nm UV light. Quantitative analysis was carried out by HPLC using Lichrosorb SI-60 and hexane–ethyl acetate–dichloromethane (32:1:320, v/v/v) as eluent. UV absorption by azulene was calibrated.

2.7. X-Ray structure determination

A suitable crystal of **1b** for X-ray diffraction was obtained by cutting a large colourless crystal grown from slowly cooled hexane–Et_2O solution. Reflection data were collected on an Enraf-Nonius CAD4TSB diffractometer with graphite-monochromated Mo Kα radiation at 20 °C. Accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centred reflections in the range $10.25 \leq \theta \leq 15.66$ (SET4). All data were collected with the $\omega/2\theta$ scan mode and were corrected for Lp effects. No absorption correction was applied. The structure of the compound was solved by direct methods (SHELXS-86). Non-hydrogen atoms were refined by full-matrix least-squares techniques (SHELXL-93) with anisotropic displacement parameters. Methyl and phenyl hydrogen atoms were placed at their geometrically calculated positions ($d_{CH} = 0.960$ Å for methyl hydrogens, $d_{CH} = 0.930$ Å for aromatic hydrogens) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.5U(C_{methyl})$ and $1.2U(C_{aromatic})$). The final R_1 and weighted ωR_2, where $R_1 = \Sigma[F_O - F_C]/\Sigma F_O$ and $\omega R_2 = [\Sigma[\omega(F_O^2 - F_C^2)^2]/\Sigma[\omega(F_O^2)^2]]^{1/2}$, were 0.0695 and 0.1910 respectively for 2644 reflections with $F_O > 4.0\sigma(F_O)$. All calculations were performed on an IBM RISC/6000 workstation.

3. Results and discussion

Photolysis of PPCB in methanol for 12 h yields seven photoadducts, corresponding to 3-methoxy-3-phenyl-4-

phenylvinyliden-cyclobutan-1,2-dicarboxylic acid dimethyl ester (**1a**–**1d**), 3-(1-methoxy-2-phenylvinyl)-4-phenylcyclobut-3-en-1,2-dicarboxylic acid dimethyl ester (**2a** and **2b**) and 3-phenyl-4-styrylcyclobut-3-en-1,2-dicarboxylic acid dimethyl ester (**3**) (Fig. 1). The structures of the photoproducts were determined by various physical methods. All the data indicate the presence of an allene moiety in **1a**–**1d** ($\delta_H \sim 6.5$ in ^{1}H NMR; $\delta_C \sim 100$, 101 and 200 in ^{13}C NMR; $\nu \sim 1950$ cm^{-1} in IR). The existence of an allenyl proton and allenyl carbon was verified by ^{1}H–^{13}C heterocorrelation spectroscopy (COSY) of **1a**. The stereochemistry of **1a**–**1d**, **2a** and **2b** was assigned by nuclear Overhauser effect (NOE) experiments as shown in Fig. 2. X-Ray crystallography of crystalline **1b** yielded the structure shown in Fig. 3 in agreement with the stereochemistry of **1a**–**1d** derived from NOE data.

The Stern–Volmer plot of Φ^0/Φ vs. [azulene] ([Az]) shows that the singlet excited state of PPCB gives **1a**–**2b** and the triplet excited state gives **3**. Fig. 4 shows almost constant quantum yields for **1b** and **2b** with varying azulene concentration, suggesting that the photoadducts **1a**–**2b** are formed only from the singlet excited state. The effect of azulene on the photolysis of PPCB in methanol shows a linear Stern–Volmer plot for the formation of **3**. A large Stern–Volmer constant ($k_q\tau$) of 2200 M^{-1} strongly suggests a triplet state to be the reactive state for **3**.

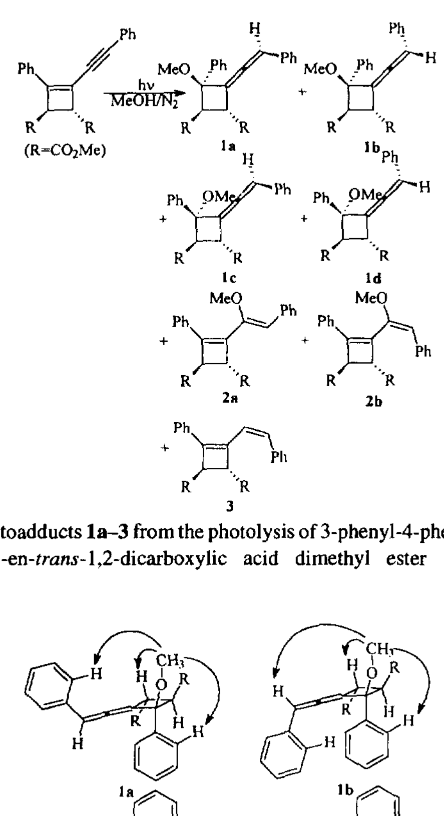


Fig. 1. Photoadducts **1a**–**3** from the photolysis of 3-phenyl-4-phenylethynylcyclobut-3-en-*trans*-1,2-dicarboxylic acid dimethyl ester (PPCB) in methanol.

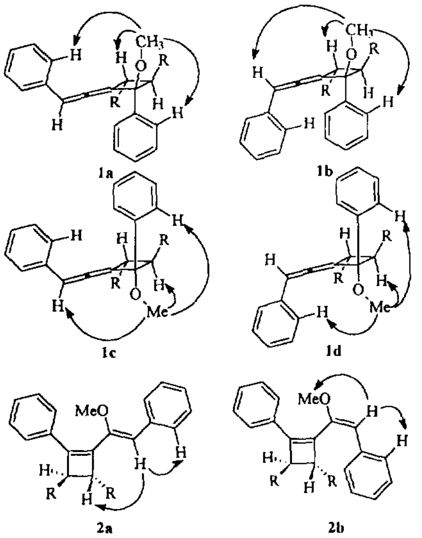


Fig. 2. Results of 300 MHz NOE experiments for photoadducts **1a**–**2b** (R ≡ CO$_2$Me).

The fluorescence of PPCB is quenched by sulphuric acid in methanol ($k_q\tau_F = 0.299$ M^{-1}), and the formation of **1a**–**1d** is increased as the sulphuric acid concentration is increased, confirming that **1a**–**2b** are produced via the singlet excited state of PPCB. In the presence of sulphuric acid or electron donors, such as 1,4-dimethoxybenzene, the formation of **1a**–**1d** is increased, while that of **2a** and **2b** is decreased. As shown in Table 1, the yields of all products are decreased in the presence of sodium methoxide or electron acceptors. Photolysis of pure **2a** and **2b** in methanol does not yield **1a**–**1d** in the presence or absence of sulphuric acid. Compounds **2a** and **2b** are rapidly interconvertible, photochemical interconversion being about twofold faster than thermal interconversion in methanol. The degree of photochemical and thermal interconversion decreases and **2a** and

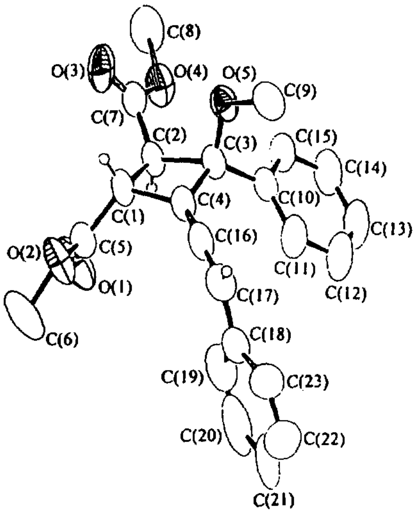


Fig. 3. ORTEP (Oak Ridge thermal ellipsoid plot) diagram of photoadduct **1b**.

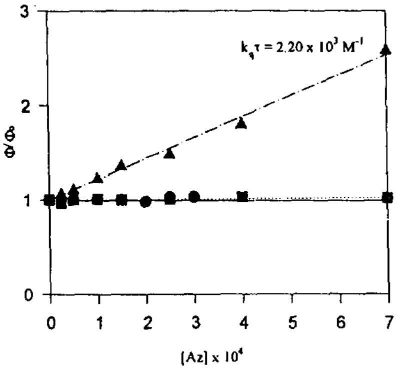


Fig. 4. Azulene quenching of the photolysis of PPCB in methanol to afford **1b** (●), **2b** (■) and **3** (▲).

Table 1
Isolated yields of photoadducts **1a–3** in the presence of additives [a]

Additive	Convergence yield (%)	Isolated yield (%)		
		1a–1d	**2a, 2b**	**3**
–	20.4	Trace amounts	1.4, 1.2	0.6
H_2SO_4	44.6	5.9, 4.7, 1.8, 1.2	–	2.0
DMBz [b]	53.9	6.1, 6.5, 1.8, 2.4	1.7, 1.9	1.9
NaOMe	85.6	–	0.6, 0.7	1.5
CN [c]	63.9	–	–	–

[a] Isolated yields were estimated after irradiation for 12 h.
[b] 1,4-Dimethoxybenzene.
[c] 1-Cyanonaphthalene.

2b are slowly decomposed in methanol solution in the presence of sulphuric acid.

The atomic charges of PPCB were calculated from AM1 and PM3 hamiltonians contained within the MOPAC program (Table 2). The calculated and experimental data clearly indicate that the electron density in the excited singlet state is highest at the C(4) position of PPCB. All the photoproducts can be obtained simultaneously only when the C(4) position is protonated (or hydrogen abstracted) in the excited state. A plausible mechanism for the formation of photoadducts **1a–1d**, involving protonation at the C(4) position of PPCB, is proposed.

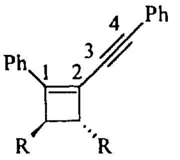
However, the C(4) position of the singlet excited state of PPCB is not basic enough to abstract a proton from methanol, although the electron density is highest in this position. The photoproducts were formed only in trace amounts in methanol, indicating that the rate-determining step is the protonation step in the formation of **1a–1d**. An increase in acidity or the addition of an electron donor to increase the atomic charge on C(4) enhances the protonation of PPCB. As shown in Table 2, the C(4) atomic charge in doublet states, formed in the presence of electron donors, is increased significantly. This is exemplified by the increased yields of **1a–1d** in the presence of sulphuric acid or 1,4-dimethoxybenzene (Table 1). However, the yields of **2a** and **2b** are decreased under the same conditions. The results indicate that a concerted reaction is responsible for the formation of **2a** and **2b**, not a stepwise route of protonation followed by methanol addition.

A plausible mechanism for the photolysis of PPCB in methanol is shown in Scheme 1. The singlet excited state has zwitterionic character; the yields of **1a–1d** are increased on addition of sulphuric acid, whereas those of **2a** and **2b** are decreased since the addition of methanol is a concerted process. Calculations utilizing the PM3 hamiltonian contained in the HYPERCHEM program show that the cyclobutyl cation is more stable than the vinyl cation by about 5.5 kJ mol^{-1}. The triplet excited state has diradical character and abstracts hydrogen from methanol to afford **3**.

It has been reported that anti-Markownikoff-type adducts of aromatic olefin–nucleophiles are obtained through photoinduced electron transfer [7]. However, no anti-Markownikoff-type adducts could be obtained under the experimental conditions used.

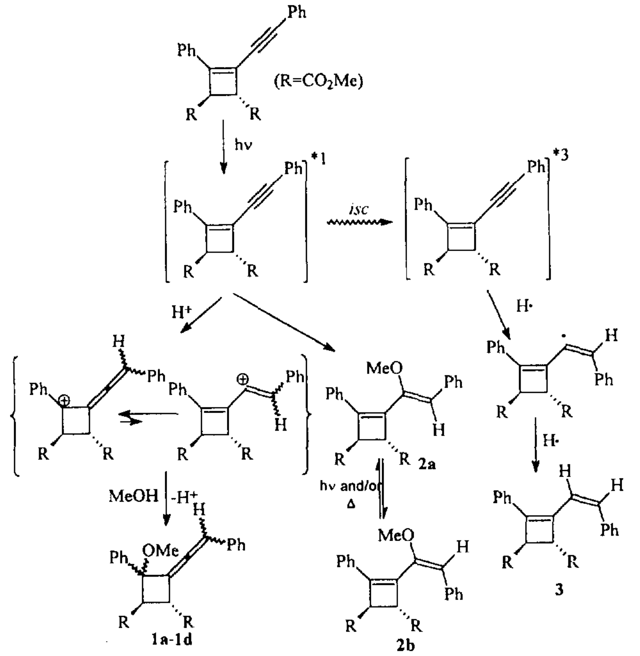
Allenyl-type adducts **1a/1c** and **1b/1d** are obtained in methanol in a ratio of approximately 3:1. Semiempirical molecular orbital calculations using the HYPERCHEM system (PM3 method) were carried out to estimate the stabilities and optimized structures of the adducts and cationic intermediates. The optimized structure of the cationic intermediates is almost planar, but tilted by about −3.74° and 2.88° in the case of **1a** and **1c** respectively. The difference between

Table 2
Estimated atomic charges of PPCB obtained from the AM1 and PM3 hamiltonians contained within the MOPAC program



	Atomic charge			
	C(1)	C(2)	C(3)	C(4)
GS [a]	−0.0446	0.0186	−0.0982	−0.0777
	(−0.0409)	(0.0049)	(−0.0921)	(−0.0726)
TS	Not obtained			
	(−0.0721)	(−0.0083)	(−0.0746)	(−0.0790)
SS	−0.0655	−0.0176	−0.0736	−0.1085
	(−0.0368)	(−0.0544)	(−0.0069)	(−0.1199)
DS(−1)	−0.1872	−0.1070	−0.0354	−0.2656
DS(+1)	0.0663	0.1246	−0.1420	0.0973

The values in parentheses were estimated from the AM1 hamiltonian.
[a] GS, ground state; TS, triplet excited state; SS, singlet excited state; DS, doublet state.



Scheme 1. Plausible mechanism for the photoreaction of PPCB with methanol.

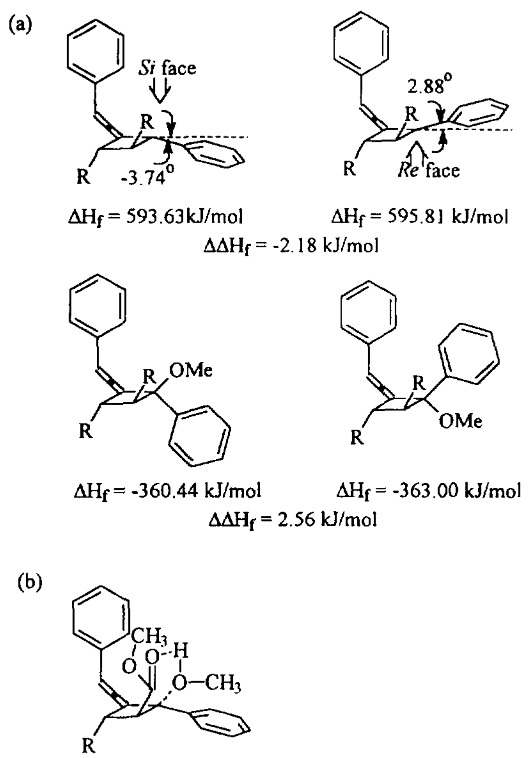
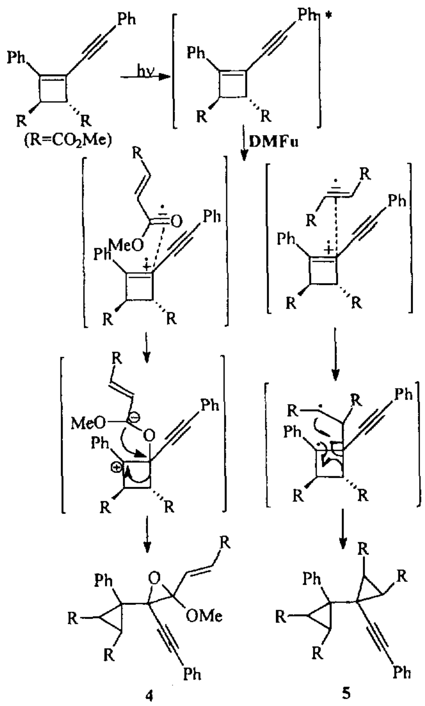


Fig. 5. (a) Estimated improper torsion angle and heat of formation of **1a**, **1c** and their cationic intermediates in the optimized geometry calculated from the RHF/PM3 hamiltonian contained within the HYPERCHEM program; (b) hydrogen bond formation of **1a** with methanol ($R \equiv CO_2Me$).

the heats of formation of the cationic intermediates of **1a** and **1c** is -2.18 kJ mol^{-1}, and 2.56 kJ mol^{-1} in the case of **1a** and **1c**. The formation of **1a** is more favourable if we consider the energy of the cationic intermediates only, but the adjacent carbomethoxy group makes *Re* face attack of methanol preferable to *Si* face attack, and thus the yield of **1a** may be lower than that of **1c**. The reason for the formation of allenyl adducts is probably a result of hydrogen bond formation between the adjacent carbomethoxy group and methanol making *Si* face attack more favourable than *Re* face attack as shown in Fig. 5.

Fumaronitrile ($E^0_{1/2}$(red) = 1.36 eV) and excited PPCB in dichloromethane show a weak exciplex emission in the range 450–580 nm, suggesting that a PPCB–DMFu exciplex may be formed although no exciplex emission was observed in dichloromethane. In the presence of DMFu ($E^0_{1/2}$(red) $= -1.54$ eV) or 1,4-dicyanobenzene ($E^0_{1/2}$(red) $= -1.54$ eV), the yields of **1a–3** are decreased and no photoadduct of PPCB–DMFu in methanol is observed. It seems that photoaddition occurs through a geminate radical ion pair, and that the addition of DMFu$^{\bullet -}$ to the most positive position of PPCB$^{\bullet +}$, followed by skeletal rearrangement, affords photoadducts, such as **4** and **5**, in non-polar solvents (as shown in Table 2, the C(2) position of PPCB$^{\bullet +}$ has the most positive character). This reaction is suppressed in methanol solution,



Scheme 2. Plausible mechanism for the photocycloaddition of PPCB with DMFu.

which may be due to dissociation of the geminate radical ion pair. Considering all the data, a plausible mechanism involving an exciplex and carbocation, rather than carbene, intermediate is proposed in Scheme 2.

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