



Photoaddition of 1,4-diphenyl-1,3-butadiyne to dimethyl fumarate: a novel exciplex mechanism

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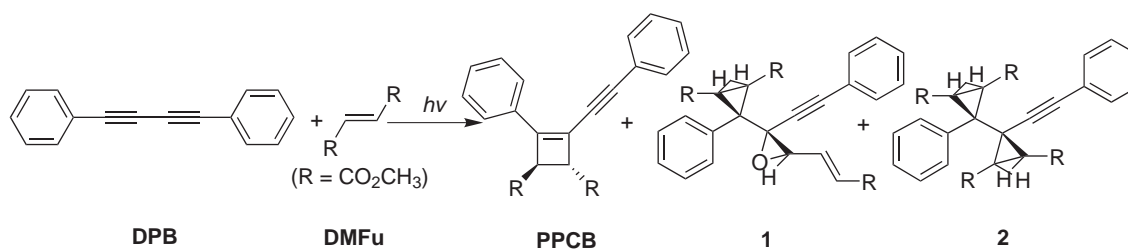
Abstract—Irradiation of 1,4-diphenyl-1,3-butadiyne with dimethyl fumarate yields novel oxirane and cyclopropane adducts as secondary products through a geminate radical ion pair type exciplex mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

Irradiation of conjugated polyalkynes with simple olefins normally yields [2+2] type cycloaddition products, cyclobutenes, through cumulene-type triplet excited states.¹ The regio- and site-selectivity of the reaction are dependent upon the kind of terminal groups and the number of conjugated triple bonds of polyalkynes, and on the electronic character of the substrate olefins. The electron deficient olefins are more reactive than the electron rich olefins.

We have, however, reported a novel photocycloaddition reaction of 1,4-diphenylbutadiyne (**DPB**) with dimethyl fumarate (**DMFu**) yielding oxirane and cyclopropane adducts along with a normal cyclobutene adduct.^{2,3} The formation of oxirane and cyclopropane adducts is very interesting, and the mechanism of the reaction is studied by carbene trapping, solvent and temperature effects, laser flash photolysis and pulse radiolysis (Scheme 1).

Carbene intermediates were initially suggested for the formation of cyclopropane and oxirane products, the singlet state carbene reacting only with C=O double bond to afford **1** while the triplet state carbene reacting only with C=C double bond of **DMFu** to give **2**. The carbene intermediate has previously been suggested for the photocycloaddition reaction of dimethyl acetylene dicarboxylate with ethylene,⁴ for the photopolymerization of conjugated polyalkynes⁵ and for the photoadditions of alkenes to alkynes.⁶

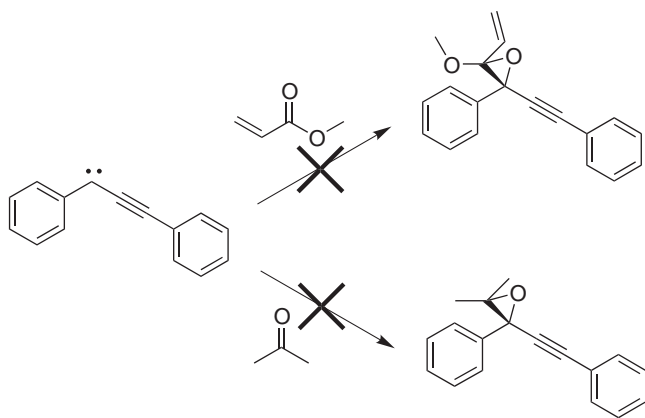
Every attempt to detect or trap these carbene intermediates in the photoaddition of **DPB** to **DMFu** under the cryogenic conditions, however, was not successful.^{7,8} Methanol, a good carbene quencher, was added to trap the possible carbene intermediates without success.⁹ Photolysis of the primary product, 3-phenyl-4-phenylethynylcyclobut-3-en-*trans*-1,2-dicarboxylic acid dimethyl ester (**PPCB**), in methanol was carried out for



Scheme 1.

Keywords: butadiyne; photoaddition; exciplex; carbene; solvent effect.

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Scheme 2.

12 h to test OH insertion of the carbene suggested or the rearrangement of carbocation generated by protonation of cyclobutene to cyclopropane.¹⁰ The photolysis, however, yielded seven photoadducts, six via the singlet excited state, and one reduction product from the triplet excited state. Neither carbene insertion product nor carbocation rearrangement to give cyclopropane was observed suggesting that carbene or carbocation intermediates are not involved in the reaction.¹¹ Irradiation of **PPCB** and **DMFu** in the presence and absence of pyridine, an efficient carbene quencher,¹² gave the same products in the same ratio and no carbene was trapped by pyridine.

When a model carbene, 1,3-diphenyl propargylene, was generated in the presence of methyl acrylate or acetone, carbene addition to C=O double bond to form oxirane ring was not observed excluding any carbene intermediate in the formation of the oxirane adduct. Furthermore, the photoreaction of the primary photoadduct, **PPCB**, with other olefins such as 2,3-dimethyl-2-butene

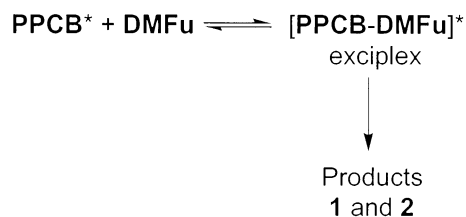
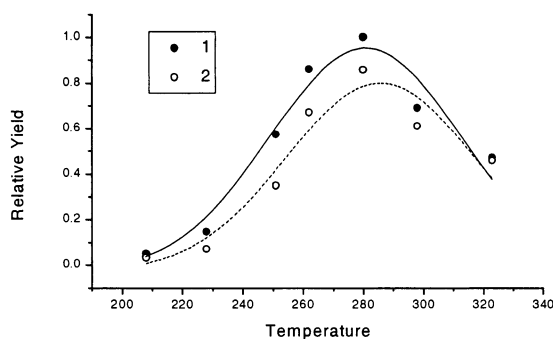
(**DMB**) and acrylonitrile (**AN**) generated normal bicyclobutene product(s) only without giving any cyclopropane or oxirane derivatives. No cyclopropane derivative was obtained from the photolysis of **PPCB** alone. These results clearly exclude a carbene or carbocation mechanism for the photoreaction of **PPCB** with **DMFu** to give oxirane and cyclopropane adducts¹³ (Scheme 2).

The fluorescence of **PPCB** was efficiently quenched by electron deficient olefins. Fumaronitrile ($E_{1/2}^{\circ}(\text{red}) = 1.36 \text{ eV}$) quenched the fluorescence of **PPCB** in dichloromethane very efficiently and a weak exciplex emission was observed in the range 450–480 nm. **DMFu** and 1,4-dicyanobenzene also quenched the fluorescence of **PPCB** efficiently suggesting the formation of **PPCB-DMFu** exciplex although no exciplex emission was observed in dichloromethane.¹⁴ The yields of methanol-**PPCB** adducts are decreased in the presence of **DMFu** ($E_{1/2}^{\circ}(\text{red}) = -1.54 \text{ eV}$) or 1,4-dicyanobenzene ($E_{1/2}^{\circ}(\text{red}) = -1.54 \text{ eV}$) since the excited singlet state of **PPCB** is quenched efficiently by the olefins competing with methanol addition. No photoadduct of **PPCB-DMFu** was observed in methanol suggesting the **PPCB-DMFu** photoreaction to proceed through a geminate radical ion pair type exciplex adding **DMFu** to most positive position of **PPCB** followed by skeletal rearrangement to give photoadducts **1** and **2** in nonpolar solvents. This is strongly supported by the solvent effects on the reaction. The relative yields (relative quantum yields) of **1** and **2** decreased in the polar solvents probably due to the efficient charge separation and rapid dissociation of the geminate radical ion pair to give starting materials in polar solvents like methanol¹⁵ (Table 1).

When the photolysis of **PPCB** and **DMFu** solution was carried out above 15°C, the yields of **1** and **2** decreased as the temperature is raised as shown in Fig. 1.¹⁶ Dissociation of the exciplex formed becomes more

Table 1. Dielectric constants and relative yields of **1** and **2** in various solvents

Solvents	Diethyl ether	THF	Dichloromethane	Methanol	Acetonitrile
Dielectric constant	4.20	7.58	8.93	32.66	35.94
Relative yield of 1	1	0.91	0.77	0.14	0.008
Relative yield of 2	1	0.86	0.69	0.10	0.007

Figure 1. Temperature effects on the formation of **1** and **2**.

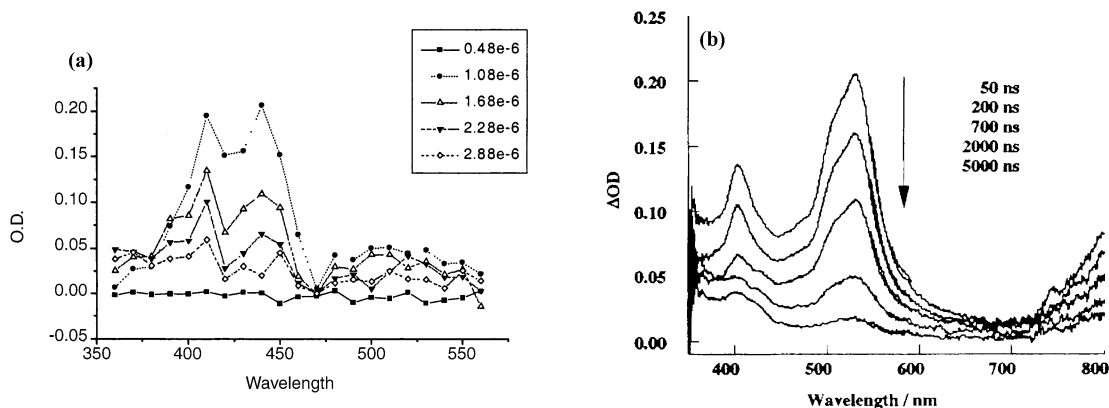


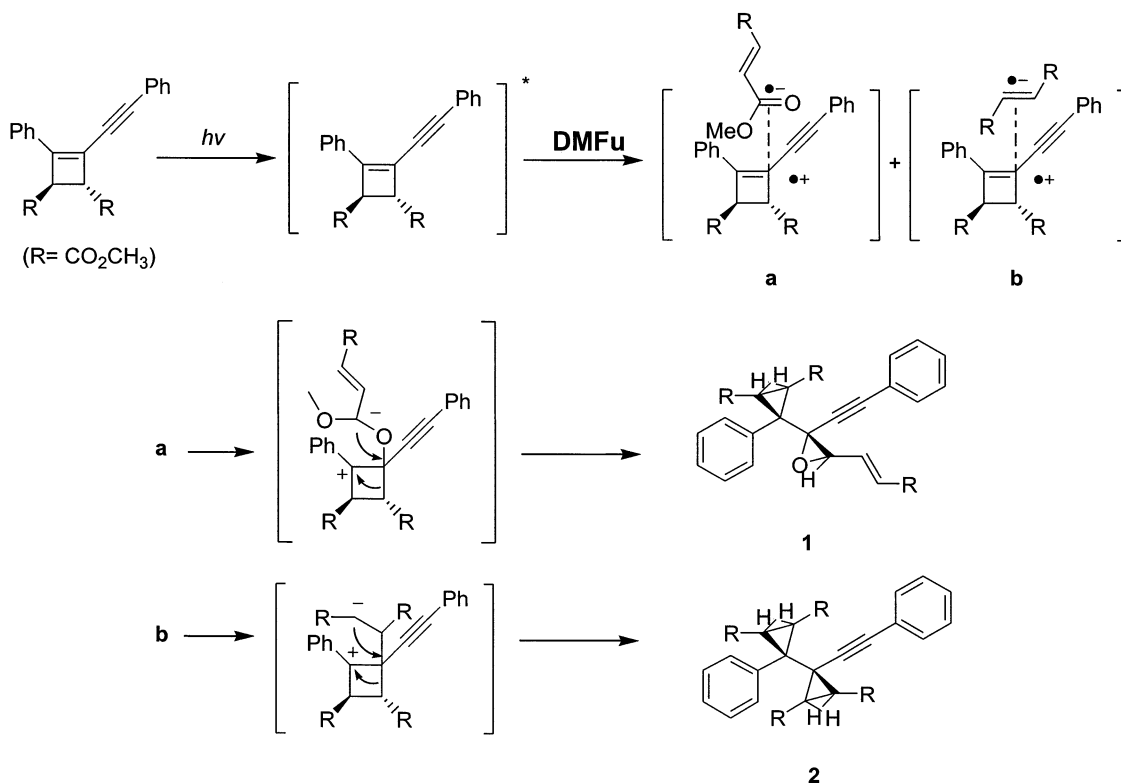
Figure 2. Transient absorption spectra of **PPCB**: (a) flash excitation of **PPCB** at 355 nm in the presence of **DMFu** in dichloromethane. (b) Transient absorption spectra after pulse radiolysis of **PPCB** in dichloromethane at room temperature.

efficient than the addition reactions to give **1** and **2** at high temperatures, leading to the negative temperature effect which is typical of an exciplex mechanism.¹⁷

Laser flash photolysis of **PPCB** in dichloromethane or acetonitrile shows triplet–triplet absorption at 440 nm while the mixture of **PPCB** and **DMFu** (Fig. 2a) shows peaks at 510, 440 and 410 nm which are attributed to **PPCB**^{•+}, triplet state of **PPCB**, and **DMFu**^{•-}, respectively. The peak at 410 nm was identified as the radical anion of **DMFu** as reported¹⁸ and the 440 nm peak is due to the triplet–triplet absorption as observed in the photolysis of **PPCB** alone in dichloromethane. The peak at ca. 510 nm can be assigned to **PPCB** which is formed by electron transfer from **PPCB**^{*} to **DMFu** leading to the exciplex [**PPCB**^{•+}–**DMFu**^{•-}]^{*}. Excitation

of **PPCB**–**DMFu** solution in acetonitrile showed stronger absorption peak at 510 nm by **PPCB**^{•+} due to the extensive charge separation and stabilization of radical ion pair, [**PPCB**^{•+}–**DMFu**^{•-}]^{*}, in polar solvents. These results strongly indicate that 510 nm peak in laser flash photolysis and pulse radiolysis is due to **PPCB**^{•+}, and an exciplex is formed along with the triplet excited state of **PPCB** in the photolysis of **PPCB** with **DMFu**.^{19,20}

This was strongly supported by pulse radiolysis results. The **PPCB**^{•+} was generated by time resolved pulse radiolysis of **PPCB** in dichloromethane at room temperature.²¹ An absorption peak at 510 nm was observed immediately after the pulse radiolysis of **PPCB** in dichloromethane (Fig. 2b) due to **PPCB**^{•+}. It decayed



Scheme 3.

according to the second-order reaction rate equation with the half-lifetime of 700 ns. No formation of a new peak was observed during the decay indicating the **PPCB**^{•+} to be a stable unimolecular radical cation. The decay corresponds to the neutralization of **PPCB**^{•+} with Cl[−] generated in the initial radiolytic processes of dichloromethane.

The exciplex mechanism as shown in Scheme 3 is proposed for the photoreaction of **PPCB** with **DMFu** based on all the experimental data.

Acknowledgements

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- 1**: ¹H NMR (300 MHz, CDCl₃), δ = 7.37–7.26 (m, 10H), 6.80/6.27 (d/d, *J* = 15.6 Hz, 1H/1H), 4.28/4.19 (d/d, *J* = 9 Hz, 1H/1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.36 (s, 3H), 3.26 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ = 170.86, 169.41, 165.79, 143.27, 136.30, 131.73, 128.56, 128.15, 127.97, 127.65, 125.97, 124.50, 122.28, 105.81, 92.16, 85.60, 82.44, 54.96, 52.04, 51.90, 51.77, 51.66, 51.27, 42.34 ppm; MS (70 eV), *m/e* = 490 (M⁺, 1.5%). **2**: ¹H NMR (300 MHz, CDCl₃), δ = 7.44–7.11 (m, 10H), 4.03/3.97 (d/d, *J* = 9.10 Hz, 1H/1H), 4.23/3.97 (d/d, *J* = 9.43 Hz, 1H/1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.73 (s, 3H), 3.67 (s, 3H), 3.10 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ = 171.66, 170.87, 170.72, 170.58, 137.90, 132.30, 132.21, 129.12, 128.93, 128.76, 128.44, 128.09, 127.43, 122.96, 91.50, 85.14, 55.64, 52.96, 52.82, 52.35, 47.78, 46.45, 46.14, 44.70, 44.25 ppm; MS (70 eV), *m/e* = 490 (M⁺, 3.1%).
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- Temperature effect: After irradiation for 30 min with medium pressure mercury arc lamp, samples were analyzed by HPLC. During the irradiation, temperature was controlled utilizing mixtures of various solvents and dry ice. Solvent effect: Relative yields of photoadducts **1** and **2** were obtained in the same experimental conditions (same temperature, reaction time, and concentration).
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- Time resolved differential absorption spectra on the nanosecond time scale were obtained with the 355 nm third harmonic, 6 ns pulse from a Continuum Nd-Yag laser. The probe light after the reaction cell was focused into the entrance slit of a 320 nm monochromator. The concentration of solution was adjusted to give ca. 1.0 absorbance at the wavelength of excitation.
- The intensity of the 510 nm peak was dramatically enhanced in polar solvents such as acetonitrile.
- Pulse radiolysis was carried out at the Osaka University by Professor T. Majima.