in Figure 1D. The resonance at δ −16.1 is due to the boratirene.

Analysis of Hydrogen Formed from Addition of Acetic Acid to Irradiated Solutions of Tetraphenylborate. A sealed, degassed solution of sodium tetraphenylborate in DME (1.0 g in 80 mL of solvent) was irradiated (254 nm) in a Rayonet photoreactor for 24 h. After irradiation, the sample was opened in a Vacuum Atmospheric drybox, and then acetic acid (HOAc, 200 μL) or DOAC (98% atom D) was added to the solution. The evolved hydrogen gas was collected in a standard volumetric burette in 10% yield based on complete consumption of tetraphenylborate and the assumption that each mole of tetraphenylborate will give 1 mol of hydrogen gas. The hydrogen gas formed from the addition of deuteriated acetic acid was transferred immediately by vacuum and then analyzed through the gas inlet probe of a Varian CH-5 mass spectrometer. The ratio of H_2:HD:D_2 in the sample was calculated by comparison of the areas of the peaks with *m/e* 2, 3, and 4, respectively. In an independent experiment, the mass spectrometer and analytical method were calibrated with an authentic mixture of H_2 and D_2. The instrument response is 1:1 within experimental error.

Reaction of Borate 1 with Benzyl Chloride in the Presence of Pyridine. A DME solution of borate **1** as its potassium salt (15 mg, 1 mL) was prepared in a Vacuum Atmospherics drybox. A 2.5-mg (0.032-mmol) portion of pyridine was added to the solution. There was no consumption of the borate after 24 h. A 27.5-mg (0.22-mmol) portion of benzyl chloride was added to the pyridine-containing solution of borate 1. The red color of borate 1 was completely bleached 6 h after the addition of the benzyl chloride.

Acknowledgment. This work was supported by a grant from the National Science Foundation for which we are grateful. We wish to specially thank Michael Kropp of this Department for independently repeating the hydrogen isotope ratio experiment, Professor Larry Faulkner for assistance with the electrochemical measurements, Dr. Richard Milberg for his assistance with the mass spectroscopy, and Professor Peter Beak for his insightful comments on this paper.

[2+2] Photocycloaddition Reaction of Aryl-1,3-butadiynes with Some Olefins

Tae Suk Lee, Sang Jin Lee, and Sang Chul Shim*

Department of Chemistry, The Korea Advanced Institute of Science and Technology, P.O. Box 131, Chongryangni, Seoul 130-650, Korea

Received December 20, 1989

1-Aryl-1,3-butadiynes 1–6 were photolyzed in 2,3-dimethyl-2-butene (DMB) to obtain [2+2] type photocycloadducts 7–12, except for 5 which yields two primary photoadducts (11, 13) and a secondary photoadduct (14). Azulene quenching, fluorescence, and exciplex emission studies suggest the reaction to proceed from both singlet and triplet excited states in compounds 1–4 while only the triplet excited state is reactive in compounds 5 and 6.

Introduction

The [2+2] photocycloaddition reaction of olefins has been extensively studied, but only a few examples have been reported for alkynes.[1-3] In most cases cyclobutene rings are formed, but bicyclopropyl photoadducts as minor products were also observed.[3] When two alkene units are incorporated into a rigid molecule such as cyclohexa-1,4-diene, the major photoproduct was the bicyclopropyl adduct.[4,5]

Photochemistry of conjugated polyynes attracted some interest recently because of the phototoxicity of the compounds to various organisms. In particular, 1-phenyl-1,3,5-heptatriyne (PHT) has been studied extensively because of the strong phototoxicity to variety of substrates in aerobic or anaerobic conditions.[6-11] There are, however, only a few reports on the photochemistry of conjugated polyynes. We reported previously the photocycloaddition reaction of 1,6-diphenyl-1,3,5-hexatriyne (DPH) and PHT with 2,3-dimethyl-2-butene (DMB).[12-14] Little is known, however, of the photocycloaddition reaction of the conjugated aryl-1,3-butadiyne system, and the photocycloaddition reaction of the compounds with olefins was, therefore, investigated to give insight into the influence of C1 and C4 substituents on the photochemistry of aryl-1,3-butadiynes.

Results and Discussion

Photoreaction of 1–6 with DMB. Irradiation of 1-(1-naphthyl)-1,3-butadiyne (**1**), 1-(1-naphthyl)-4-phenyl-1,3-butadiyne (**2**), 1-(1-naphthyl)-5,5-dimethyl-1,3-hexadiyne (**3**), and 1-(1-naphthyl)-1,3-pentadiyne (**4**) in deaerated DMB solution with 350-nm UV light gave 1:1

---

(1) Arnold, D. R.; Chang, Y. C. *J. Heterocycl. Chem.* **1971**, *8*, 1097.
(2) Serve, M. P.; Rosenberg, H. M. *J. Org. Chem.* **1970**, *35*, 1237.
(3) Owsley, D. C.; Bloomfield, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 782.
(4) Askani, R. *Chem. Ber.* **1965**, *98*, 3618.
(5) Fujita, K.; Matsui, K.; Shono, T. *Chem. Abstr.* **1975**, *83*, 146784.
(6) McLachlan, D.; Arnason, T.; Lam, J. *Biochem. Syst. Ecol.* **1986**, *14* (1), 17.
(7) Weir, D.; Scaiano, J. C.; Arnason, J. T.; Evans, C. *Photochem. Photobiol.* **1985**, *42* (3), 223.
(8) Hudson, J. B.; Graham, E. A.; Towers, G. H. N. *Photochem. Photobiol.* **1986**, *43* (1), 27.
(9) Hudson, J. B.; Graham, E. A.; Towers, G. H. N. *Photochem. Photobiol.* **1982**, *36*, 181.
(10) McLachlan, D.; Arnason, T.; Lam, J. *Photochem. Photobiol.* **1984**, *39* (2), 177.
(11) Kagan, K.; Wielandt, K. T.; Chan, G.; Lhawan, S. N.; Jaworsky, J.; Prakash, I.; Arora, S. K. *Photochem. Photobiol.* **1984**, *39* (4), 465.
(12) Shim, S. C.; Lee, T. S. *Chem. Lett.* **1986**, 1075.
(13) Shim, S. C.; Lee, T. S. *Bull. Korean Chem. Soc.* **1986**, *7* (4), 304.
(14) Shim, S. C.; Lee, T. S. *J. Org. Chem.* **1988**, *53*, 2410.

0022-3263/90/1955-4544$02.50/0

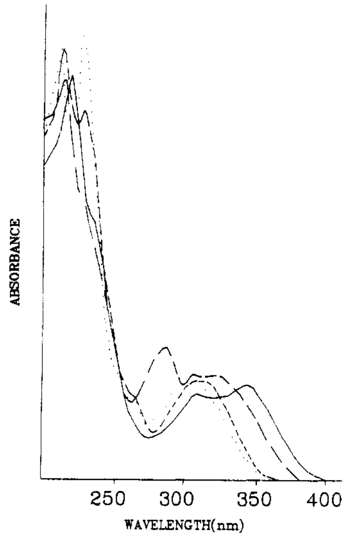
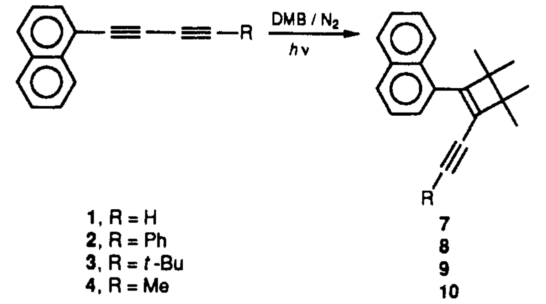


Figure 1. UV absorption spectra of 7 (—), 8 (– –), 9 (- - -), and 10 (···) in MeOH.

photoadducts 7–10. The C1–C2 triple bond underwent [2+2] photocycloaddition reaction as indicated by various spectral data.



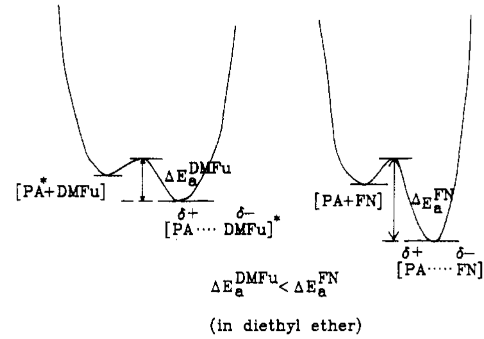
The UV spectra of the photoadducts (Figure 1) do not show the typical vibrational fine structure of conjugated polyacetylenes,[15] and absorption maxima are slightly red shifted compared with parent diynes, suggesting the loss of the conjugated diyne unit but maintaining the conjugated system. The ^{13}C NMR clearly show the existence of a triple bond as well as the position of the triple bond. All the photoadducts show two resonance peaks corresponding to sp-hybridized carbons and four methyl carbon peaks indicating the formation of 1:1 photoadducts. The site of the reaction could be determined from the chemical shift of the substituted aromatic carbon, which typically appears near 120–124 ppm for phenyl and 119–120 ppm for 1-naphthyl.[13-15] The peak at 122.37 ppm in 8, therefore, strongly supports the existence of an ethynylbenzene moiety. The peak at 5.38 ppm in 10 also indicates the remaining triple bond to be C3–C4 because the resonance line of terminal methyl group is very much upfield shifted due to the diamagnetic anisotropy of the triple bond. Mass spectra show the molecular ion peak (M^+) and M^+ – DMB peak in all the photoadducts, supporting the 1:1 photoadduct formation.

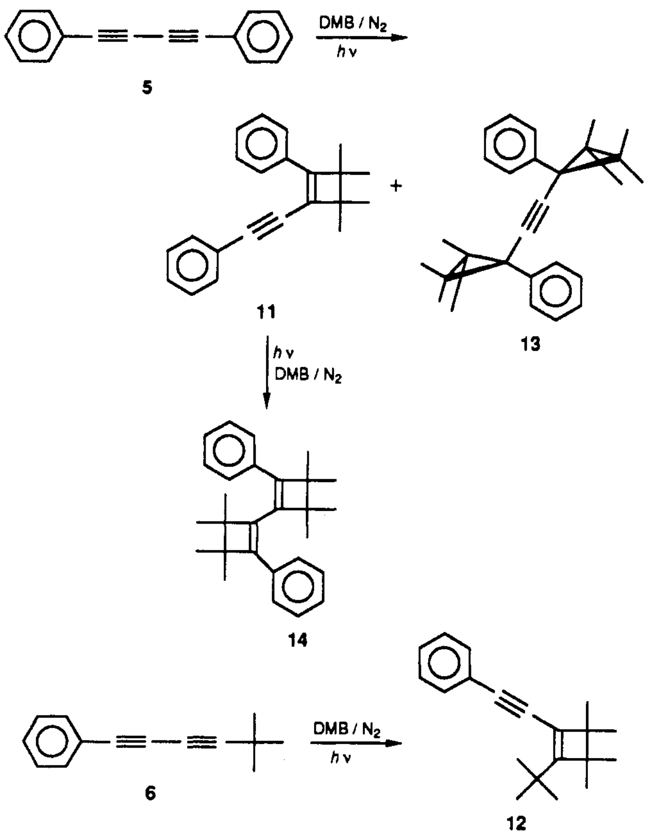
When 1,4-diphenyl-1,3-butadiyne (5) and 1-phenyl-5,5-dimethyl-1,3-hexadiyne (6) were irradiated in deaerated DMB with 300-nm UV light, photoadducts 11 and 13 from 5 and 12 from 6 were obtained as primary photoproducts. Polymers were obtained in all cases as major byproducts. Product 14 was obtained when 11 was further irradiated with DMB. Figure 2 shows the product formation against irradiation time.

Table I. Fluorescence Quantum Yields of 1-(1-Naphthyl)-1,3-butadiynes 1–4 in Various Solvents

	Φ_F			
solvent	1	2	3	4
acetonitrile	0.11	0.01	0.02	0.01
methanol	0.08	0.01	0.02	0.02
diethyl ether	0.20	0.02	0.03	0.02

Scheme I. Plausible Potential Energy Diagram of Exciplexes in Diethyl Ether (PA = Conjugated 1,3-Butadiynes)





The absorption maxima were red shifted except in 13, which shows a large blue shift as shown in Figure 3. The ^{13}C NMR spectrum of 11 shows two sp-hybridized carbon atoms, strongly supporting the formation of only one [2+2] monoadduct. The structure of 12 was identified as a 1:1 adduct by various spectral data, and the reaction site is determined to be a C3–C4 triple bond by the ^{13}C chemical shift of the aromatic center carbon substituted at 120.70 ppm. The structure of photoadduct 13 was determined to be a symmetrical 1:2 adduct by the presence of one sp-hybridized carbon peak at 84.37 ppm and by identifi-

---

[15] Dale, J. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969.

Table II. Fluorescence Quenching Constants ($k_q\tau$) of 1-(1-Naphthyl)-1,3-butadiynes 1-4 in Various Solvents with Some Olefins

	acetonitrile			methanol			diethyl ether		
	DMB	DMFU	FN	DMB	DMFU	FN	DMB	DMFU	FN[a]
1	0	14	5.4	0	16	0.99	0	14	1.7
2	0	9	6.9	0	14	3.7	0	9.8	2.3
3	20.14[a]	156	130	13.6	127	126	0	129	157
4	0	17	37	0	20	59	0	20	3.6

[a] Exiplex emissions were observed. Key: DMB, 2,3-dimethyl-2-butene; DMFU, dimethyl fumarate; FN, fumaronitrile.

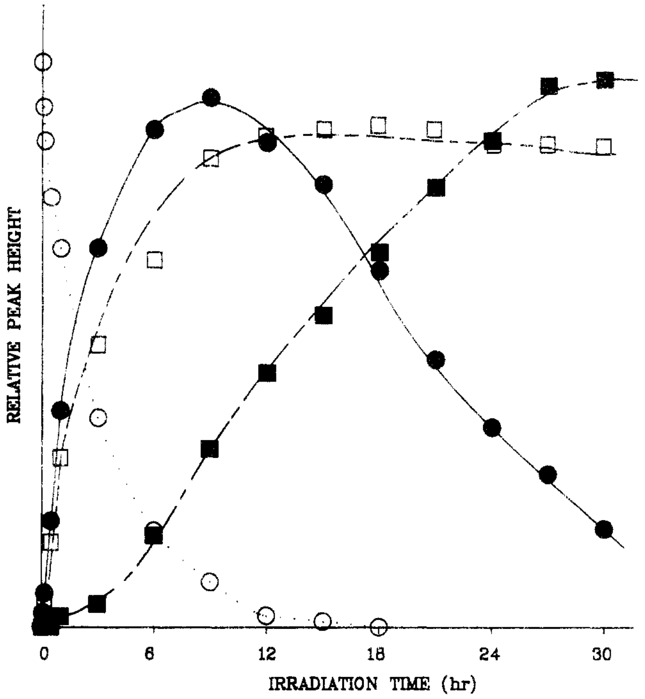


Figure 2. Product formation against irradiation time: DPB (···), **11** (—), **13** (- - -), **14** (–·–).

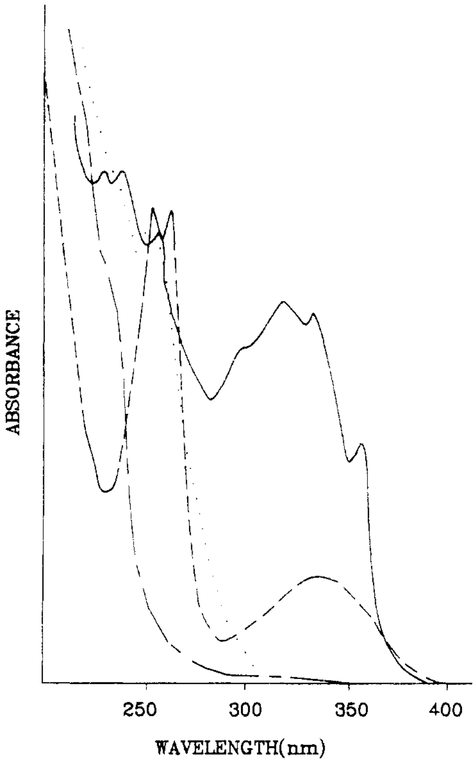


Figure 3. UV absorption spectra of **11** (—), **12** (···), **13** (–·–), and **14** (- - -) in MeOH.

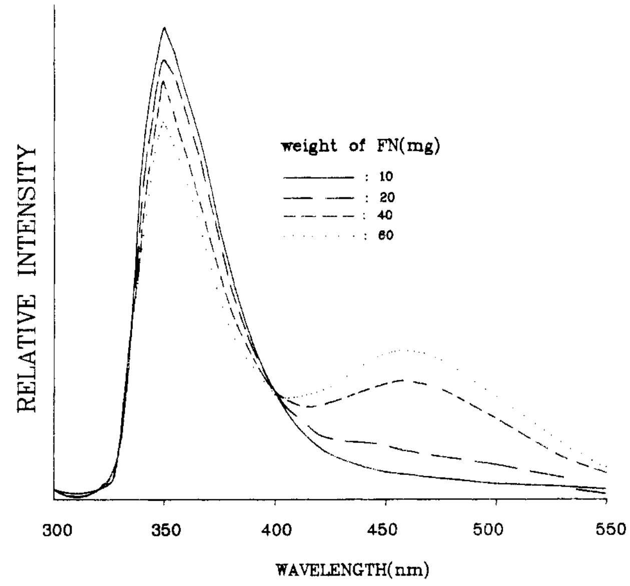


Figure 4. Exciplex emission spectra of 1-(naphthyl)-1,3-pentadiyne–fumaronitrile (FN) in diethyl ether.

cation of all nine remaining carbon peaks. The peak at 141.36 ppm strongly supports the existence of cyclopropyl-substituted benzene moeity.[14] The structure of **14** was determined to be a 1:2 adduct with two symmetric cyclobutene rings. Mass spectra of all the photoadducts show molecular ion (M^+), M^+ – DMB, and M^+ – 2 DMB (for **13** and **14**) peaks supporting the 1:1 and 1:2 adduct structures.

Fluorescence Quenching. The fluorescence quantum yields of **1–4** were measured in various solvents as shown in Table I. No fluorescence was observed from **5** and **6**.

The fluorescence quenching of **1–4** by olefins in various solvents is shown in Table II. Dimethyl fumarate (DMFu) shows the largest quenching constant. No fluorescence quenching was observed with DMB in acetonitrile, methanol, and diethyl ether except for **3**.

Fumaronitrile (FN) in diethyl ether exhibited an exciplex emission as shown in Figure 4. The results are explained by the excited-state potential energy diagram as shown in Scheme I. Exciplexes seem to be formed with FN ($E°_{1/2}$(red) = –1.36 eV) or DMFu ($E°_{1/2}$(red) = –1.54 eV) even though the exciplex emission was not observed with DMFu. Scheme I shows strong the possibility of a back-reaction (electron back-transfer) for the [diyne-DMFu]* exciplex because the interaction in the exciplex is relatively weak compared with that in [diyne-FN]* exciplex, which interaction energy is high and the back-reaction is unlikely to occur. In nonpolar solvents (such as Et_2O), therefore, the exciplex has a long enough lifetime to give the emission, but in polar solvents (such as CH_3CN and MeOH) the exciplex emission was not observed because the exciplex rapidly becomes a solvent-separated ion pair.[16]

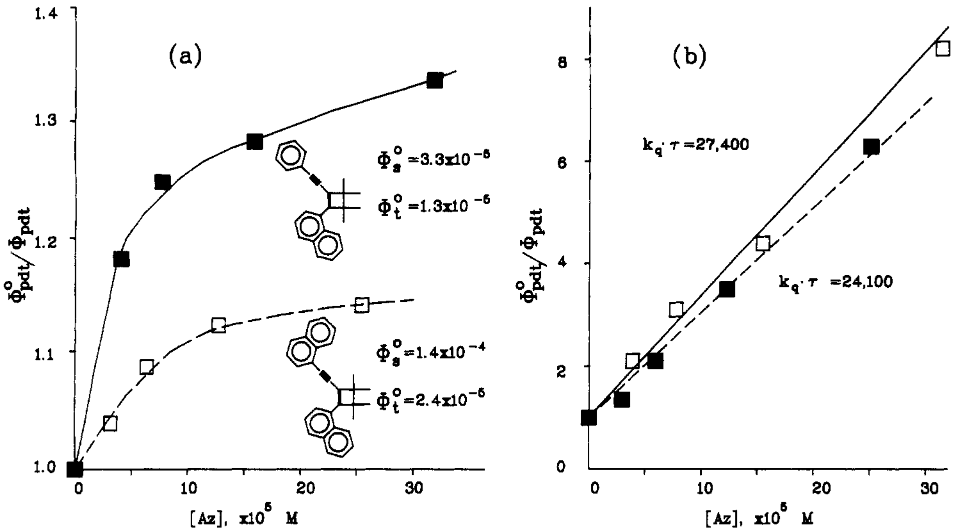


Figure 5. Azulene quenching: (a) direct photocycloaddition reaction of **1** (- - -) and **2** (—) with DMB at 366 nm; (b) triplet reaction to form **7** (- - -) and **8** (—).

Conjugated diynes **1**–**4** can be either electron donors or acceptors in the excited state, but they are more likely to be electron donors because no fluorescence quenching was observed with electron-rich olefins such as DMB in any solvent system. Exciplex emission of **3** with DMB in polar solvents (such as acetonitrile) was observed, suggesing that the exciplex with DMB has relatively weak charge separation. The results indicate the conjugated polyacetylenes to have poor electron-accepting ability.

Reaction Mechanism. The [2+2] photocycloaddition of **1** and **2** to DMB was efficiently quenched by azulene (E_T = 30 kcal/mol).[17] The Stern–Volmer plots of Φ^o_{pdt}/Φ_{pdt} vs. [Az] show the contribution of triplet excited state to the photocycloaddition reaction as shown in Figure 5.

The plots for **1** and **2** (Figure 5a) are curved, converging to about $\Phi^o_{pdt}/\Phi_{pdt} = 1.2$ and 1.4, respectively, strongly suggesting the contribution of both singlet and triplet excited states. Singlet and triplet excited-state contributions were calculated to be $\Phi^o_S = 1.4 \times 10^{-4}$ and $\Phi^o_T = 2.4 \times 10^{-5}$ for **1** and $\Phi^o_S = 3.3 \times 10^{-5}$ and $\Phi^o_T = 1.3 \times 10^{-5}$ for **2**. From Figure 5b, the pure triplet-state quenching constants ($k_q\tau$) were calculated to be very large (24 100 M^{-1} for **1** and 27 400 M^{-1} for **2**), indicating that **1** and **2** have long and about the same triplet lifetimes.

The azulene effect on the photocycloaddition reaction of **5** with DMB shows a linear relationship for the formation of **11** and **13** ($\Phi^o_{pdt}(11) = 3.2 \times 10^{-2}$, $\Phi^o_{pdt}(13) = 3.0 \times 10^{-2}$) with various concentrations of azulene. The quenching constants ($k_q\tau$) were obtained to be 4400 and 4800 M^{-1}, respectively, as shown in Figure 6, suggesting that **11** and **13** originated from the same excited state.

In the photocycloaddition reaction of conjugated polyacetylenes the terminal group of the conjugated system and the number of conjugated triple bonds will significantly influence their photochemical properties.[14]

The azulene quenching experiments show that the photocycloaddition reactions of 1-(1-naphthyl)-1,3-butadiynes proceed from both singlet and triplet excited states. Moreover, it is clear that the electron density (or diradical character) in the excited singlet and triplet states seems to be localized on the C1 and C2 because the cycloaddition occurs only on the C1–C2 triple bond in contrast to the photocycloaddition reaction of phenyl-1,3-butadiynes.

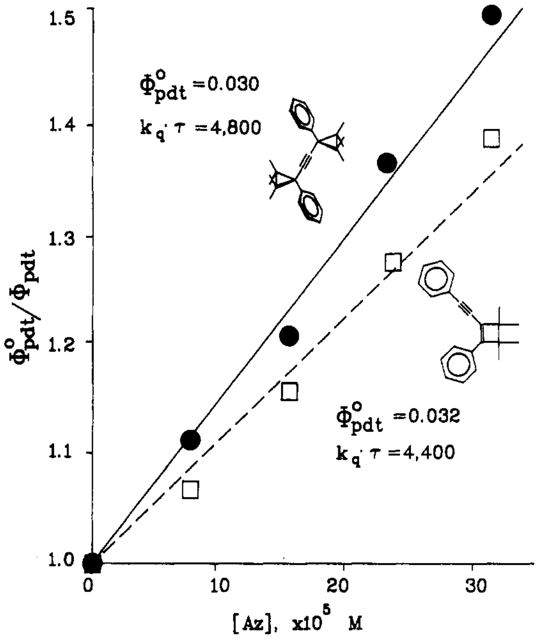
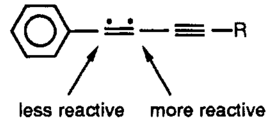


Figure 6. Azulene quenching of direct photocycloaddition reaction of **5** with DMB to give **11** (- - -) and **13** (—) at 313 nm.



The singlet excited-state reaction of 1-(1-naphthyl)-1,3-butadiynes should yield only a C1–C2 [2+2] cycloadduct in a concerted manner, but in the triplet excited state two reactive sites at C1 and C2 are expected to play a role for initial attack. The triplet-state reaction, however, gives only C1–C2 cycloadduct following the first attack of DMB molecule at the more reactive C2 carbon because the C1 radical is stabilized by the 1-naphthyl group as shown in Scheme II.

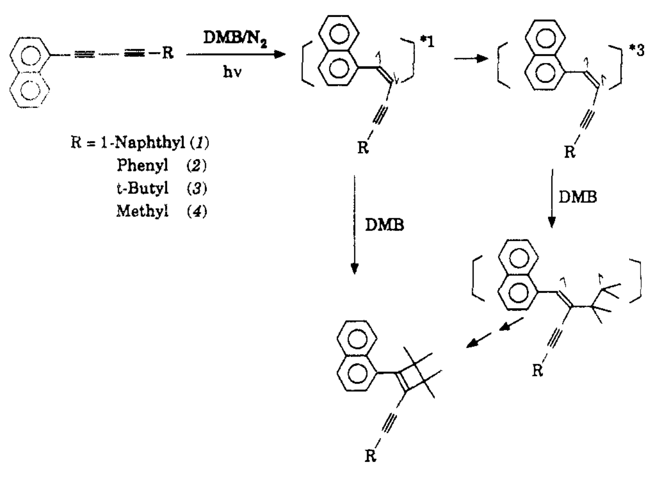
In contrast, in the excited state of phenyl-1,3-butadiynes, the electrons are delocalized throughout the conjugated

---

[16] Hercules, D. *Modern Analytical Chemistry*; Plenum Press: New York and London, 1976; p 319.

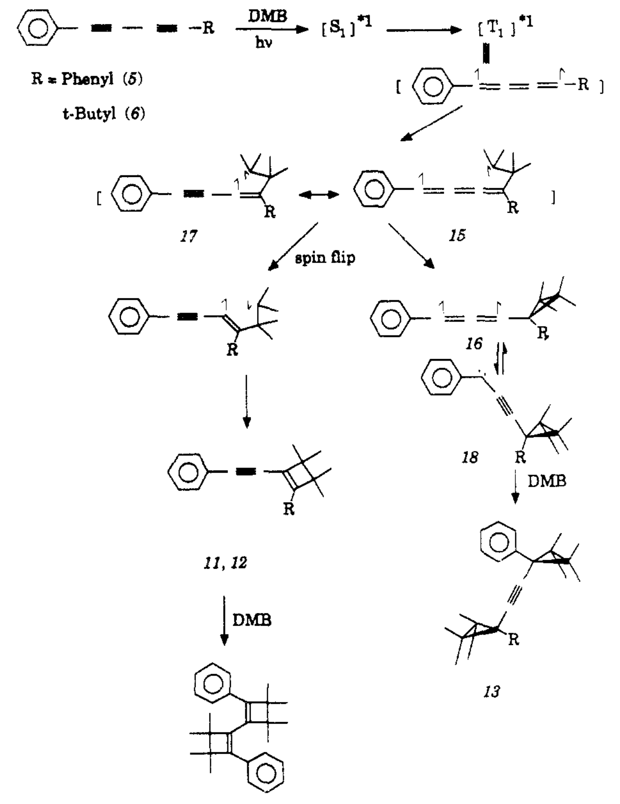
[17] Absorption by azulene at the wavelength of interest was corrected. A benzophenone sensitization experiment could not be carried out due to its strong reactivity toward DMB.

Scheme II. Plausible Photocycloaddition Reaction Mechanism of 1-(1-Naphthyl)-1,3-butadiynes with DMB

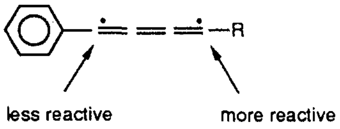


7, 8, 9, 10

Scheme III. Plausible Photocycloaddition Reaction Mechanism of Phenyl-Substituted 1,3-Butadiynes with DMB

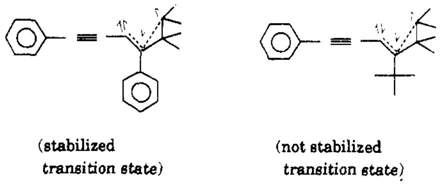


diyne system as in the phenyl-1,3,5-hexatriynes (PHT) and the reactive sites are C1 and C4. The delocalized triplet



state of the phenyl-substituted 1,3-butadiynes is directly related to the more reactive C4 radical because the C1 radical is stabilized by the phenyl group. Interesting results are, however, obtained from the irradiation of **5** and **6** with DMB. Photoadducts **11** and **13** were obtained from **5** as primary photoadducts, while only photoadduct **12** was obtained from **6**. A possible reaction mechanism is shown in Scheme III.

Scheme IV. Plausible Transition State That Is Stabilized by Groups on C4



In the triplet excited state, first attack on the C4 carbon by the DMB molecule gives a triplet diradical intermediate **15**. For **5**, the C1 and C4 positions are exactly the same, but for **6** the first addition should occur on C_4 due to its higher reactivity compared with C1. In **15** (or **17**), ring closure into **16** will compete against the spin flip, which leads to singlet diradical intermediate to form the cyclobutene ring. When R is the *tert*-butyl group, the spin flip is preferred to the ring closure. When R is phenyl, however, a significant portion of **15** undergoes ring closure, leading to the formation of **13** via a carbene intermediate **18**, which is in equilibrium with **16** via the transition state stabilized by the group on C4 as shown in Scheme IV. The phenyl group at C4 stabilizes the transition state more than the *tert*-butyl group, reducing the activation energy to form the cyclized intermediate **16** (or **18**). As a result, the spin-flip and the ring-closure processes compete against each other, and consequently photoadducts **11** and **13** were obtained from **5** but only photoadduct **12** was obtained from **6**.

The 1-naphthyl group on the C1 carbon, therefore, causes participation of singlet pathway and localization of electrons (or diradical character) on C1 and C2 carbons in the excited state, while the phenyl group on the C1 carbon causes the delocalization of electrons (or diradical character) throughout the conjugated system. It seems that the results were caused by the difference of the inductive effect of the naphthyl and phenyl groups. Thus, both groups on C1 and C4 can affect the photochemical behavior of 1-aryl-1,3-butadiynes, not only the reaction site but also the reaction mechanism.

Experimental Section

Instruments. ^1H NMR spectra were run on either a Varian T60A, FT80A, or Bruker AM-200-SY spectrometer, with TMS as an internal standard. ^{13}C NMR spectra were run on a Bruker AM-200-SY spectrometer with $CDCl_3$ as a solvent and as an internal standard. Mass spectra were measured on a Hewlett-Packard 5985A GC/MS system by the electron impact method (EI) at 70 eV. IR spectra were recorded on a Perkin-Elmer 283B spectrometer in NaCl cell or as a KBr pellet.

Elemental analyses were carried out on an F&M Scientific Corp. C, H, N analyzer, Model 180. A Cary 17 spectrophotometer was used for UV spectral data. Fluorescence spectra were recorded on an Aminco Bowman spectrophotofluorometer with an Aminco XY recorder at room temperature. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph equipped with Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 and 280 nm, and Model U6K Universal injector. μ-Bondapak C_{18} and Radialpak Si columns were used for quantitative analysis.

Materials. Compounds **1**–**6** were prepared by the literature method.[18] 2,3-Dimethyl-2-butene (Aldrich Chemical Co.) was used as received, and azulene (Aldrich) was vacuum sublimed. Dimethyl fumarate and fumaronitrile (Aldrich) were recrystallized from ethanol and quinine bisulfate (Aldrich) from water. Chromatographic and spectroscopic grade solvents (Merck) were

---

(18) Shim, S. C.; Lee, T. S. *Bull. Korean Chem. Soc.* **1986**, *7* (5), 357.

used for HPLC, absorption, and emission spectroscopy. Extrapure solvents for column chromatography and preparative thin-layer chromatography were used after purification by distillation or standard methods.[19] Column chromatography was performed by using Kiesel gel 60 (Merck, 70–230 and 230–400 mesh). Preparative thin-layer chromatography was conducted by using Kiesel gel 60 GF_{254} (Merck) containing a fluorescent indicator.

Quantum Yield Measurements. Sample solutions (3 mL) in Pyrex ampules were degassed by three freeze–pump–thaw cycles with cooling in liquid nitrogen and then sealed. These samples were irradiated in a merry-go-round apparatus with Hanovia 450-W medium-pressure mercury arc lamp (Type 679A36). To isolate the mercury emission line of 365 nm, CS 0-52 and 7-37 Corning glass filter were used. Corning glass filter CS 7-54 and a solution filter of 2.5×10^{-3} M potassium dichromate in 1% sodium carbonate aqueous solution were used to get 313-nm monochromatic light. Light intensities were measured by ferrioxalate actinometry, and the quantitative analysis for the quantum yield measurements was carried out by HPLC.

Irradiation of 1–4 with 2,3-Dimethyl-2-butene. Deaerated 4 mM DMB solutions of 1–4 were irradiated with 350-nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 3500-Å lamps. After irradiation for 24 h, the resulting photoreaction mixture was concentrated in vacuo and photoadducts **7–10** were isolated by column chromatography with *n*-hexane as an eluent in 5%, 10%, 43%, and 77% yields, respectively. **7**: ^{1}H NMR ($CDCl_3$) δ 8.50–7.18 (m, 20 H), 1.37 (s, 6 H), 1.33 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 152.57, 132.93, 132.02, 131.36, 130.88, 130.36, 129.16, 127.53, 127.24, 127.02, 125.92, 125.48, 125.37, 125.22, 125.00, 124.85, 124.08, 123.93, 123.67, 120.00, 93.13, 87.11, 49.10, 48.11, 22.15, 21.76; IR (NaCl) 3060, 2960, 2930, 2860, 1595, 1580, 1514, 1485, 1465, 1400, 1370, 1265, 1025, 861, 800, 771, 739, 700 cm^{-1}; UV (methanol) λ_{max} 340, 305, 212 nm; MS, *m/e* 386 (M^+, 33.3), 302 ($M^+ - DMB$), 165 ($C_{13}H_9^+$, 100). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.27; H, 6.80. **8**: ^{1}H NMR ($CDCl_3$) δ 8.40–7.11 (m, 12 H), 1.27 (s, 6 H), 1.26 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 152.41, 132.92, 131.28, 130.64, 130.44, 130.27, 127.20, 127.17, 127.09, 125.94, 124.80, 124.62, 124.05, 123.91, 123.69, 122.37, 94.95, 82.25, 48.97, 47.94, 21.61, 21.32; IR (NaCl) 3060, 2980, 2960, 2925, 1600, 1590, 1580, 1510, 1490, 1450, 1400, 1370, 794, 770, 750, 685 cm^{-1}; UV (methanol) λ_{max} 315, 283, 208 nm; MS, *m/e* 336 (M^+, 96.7), 252 ($M^+ - DMB$, 31.1), 165 ($C_{13}H_9^+$, 100). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.83; H, 7.18. **9**: ^{1}H NMR ($CDCl_3$) δ 8.35–7.25 (m, 7 H), 1.23 (s, 6 H), 1.21 (s, 6 H), 1.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) 149.51, 132.83, 131.45, 130.29, 126.95, 126.83, 126.40, 124.59, 124.15, 123.82, 123.45, 104.86, 71.82, 48.26, 47.41, 29.99, 27.12, 22.17, 21.39; IR (NaCl) 3050, 2980, 2960, 2928, 2210, 1600, 1580, 1518, 1485, 1460, 1370, 1260, 1027, 970, 930, 880, 864, 797, 786, 772, 736, 701, 635 cm^{-1}; UV (methanol) λ_{max} 309, 222, 209 nm; MS, *m/e* 316 (M^+, 90.9), 232 ($M^+ - DMB$, 13.4), 165 ($C_{13}H_9^+$, 100). Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.14; H, 8.89. **10**: ^{1}H NMR ($CDCl_3$) δ 8.50–7.25 (m, 7 H), 1.97 (s, 3 H), 1.37 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 152.44, 134.64, 133.37, 132.20, 132.19, 128.90, 128.65, 127.62, 126.48, 126.32, 125.72, 125.41, 93.11, 74.22, 50.42, 49.45, 23.74, 23.30, 5.38; IR (NaCl) 3060, 2980, 2960, 2930, 2220, 1595, 1580, 1510, 1485, 1455, 1370, 1020, 940, 880, 860, 840, 795, 774, 734, 700, 700, 636 cm^{-1}; UV (methanol) λ_{max} 298, 221, 207 nm; MS, *m/e* 274 (M^+, 14.8), 190 ($M^+ - DMB$, 42.1), 189 ($M^+ - DMB - H$, 70.8), 165 ($C_{13}H_9^+$, 100). Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.97; H, 8.90.

Irradiation of 5 and 6 with 2,3-Dimethyl-2-butene. DMB solutions (4 mM) in 20 mL of sample ampules were deaerated in three freeze–pump–thaw cycles. Deaerated DMB solutions were irradiated with 300-nm UV light in a Rayonet photochemical reactor equipped with RUL 3000-Å lamps. After the irradiation for 24 h, the reaction mixture was evaporated in vacuo and photoadducts **11–14** were separated by preparative thin-layer chromatography followed by column chromatography with *n*-hexane–diethyl ether (20:1, v/v) and *n*-hexane, respectively, in 14%, 22%, 20%, and 10% yields, respectively. **11**: ^{1}H NMR ($CDCl_3$) δ 7.85–7.00 (m, 10 H), 1.39 (s, 6 H), 1.25 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 153.83, 135.03, 132.41, 129.24, 129.15, 129.08, 128.93, 127.42, 127.37, 124.90, 96.80, 84.50, 49.44, 47.63, 23.75, 22.87; IR (NaCl) 3070, 3040, 2980, 2940, 1605, 1580, 1490, 1450, 1375, 1075, 910, 890, 840, 760, 690 cm^{-1}; UV (methanol) λ_{max} 323, 305, 245, 230, 225 nm; MS, *m/e* 286 (M^+, 21.2), 202 ($M^+ - DMB$, 28.2), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 7.75. **12**: ^{1}H NMR ($CDCl_3$) δ 7.35–7.00 (m, 5 H), 2.20 (s, 12 H), 0.96 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 159.25, 129.01, 127.09, 126.43, 125.81, 120.70, 102.03, 86.50, 45.50, 31.24, 30.65, 27.05; IR (NaCl) 3100, 3080, 3040, 2980, 2940, 2220, 1610, 1450, 1370, 1270, 1110, 895, 780, 715, 700 cm^{-1}; UV (methanol) λ_{max} 240 nm; MS, *m/e* 266 (M^+, 18.5), 251 ($M^+ - CH_3$, 14.2), 182 ($M^+ - DMB$, 3.9), 91 ($C_7H_7^+$, 39.0), 41 ($C_3H_5^+$, 100). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.22; H, 9.86. **13**: ^{1}H NMR ($CDCl_3$) δ 7.04 (s, 10 H), 1.05 (s, 12 H), 0.80 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 141.36, 131.69, 128.47, 126.34, 84.37, 33.67, 29.12, 21.23, 21.04; IR (KBr) 3090, 3000, 2960, 2930, 1625, 1475, 1404, 1385, 1370, 1115, 1020, 930, 775, 704 cm^{-1}; UV (methanol) λ_{max} 250 (sh) nm; MS, *m/e* 370 (M^+, 4.8), 286 ($M^+ - DMB$, 19.2), 202 ($M^+ - 2\ DMB$, 100), 91 ($C_7H_7^+$, 76.7). Anal. Calcd for $C_{28}H_{34}$: C, 90.75; H, 9.25. Found: C, 90.77; H, 9.25. **14**: ^{1}H NMR ($CDCl_3$) δ 7.60–7.00 (m, 10 H), 1.40 (s, 12 H), 1.21 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 147.39, 141.70, 135.42, 131.19, 127.97, 127.62, 126.64, 126.57, 48.93, 45.71, 23.38, 23.34; IR (NaCl) 3057, 2950, 2911, 1594, 1450, 1366, 1117, 910, 763, 693 cm^{-1}; UV (MeOH) λ_{max} 335, 262, 254 nm; MS, *m/e* 370 (M^+, 23.8), 286 ($M^+ - DMB$, 11.1), 202 ($M^+ - 2\ DMB$, 58.6), 91 ($C_7H_7^+$, 66.9). Anal. Calcd for $C_{28}H_{34}$: C, 90.75; H, 9.25. Found: C, 90.76; H, 9.25.

Fluorescence Quantum Yield Measurements. The emission spectra were corrected for the response characteristics of photomultiplier tube (IP21, s-4 spectral response) and monochromator of the instrument as a function of wavelength. The fluorescence quantum yields of 1–4 were determined in various solvents (acetonitrile, methanol, diethyl ether) relative to quinine bisulfate solution (low concentration, in 0.1 N H_2SO_4, 3130- or 3660-Å excitation, $\Phi_F^\circ = 0.55$) by the following relationship[20]

$$\Phi_F = \Phi_F{}^r (I_s/I_r)(A_r/A_s)(n_s/n_r)^2$$

where $\Phi_F{}^r$ represents fluorescence quantum yield of reference, I_s, I_r and A_s, A_r are fluorescence intensities and absorbances of sample and reference, respectively, and n_s and n_r are refractive indices of sample and reference. In quantum yield determinations, absorbance at excitation wavelength (or sample concentration) was kept as low as possible in order to minimize errors due to the front surface imprisonment and inner filter effects.

Fluorescence Quenching. Fluorescence spectra of 1–4 were obtained in the presence of various concentrations of DMB, FN, and DMFu in various solvents (acetonitrile, methanol, diethyl ether), respectively. The $k_q\tau$ values were obtained from the Stern–Volmer plot.

$$\Phi_F^\circ/\Phi_F = 1 + k_q\tau[\text{quencher}]$$

Azulene Effect. The product quantum yields were measured in the presence of various concentrations of azulene ($(0–3) \times 10^{-4}$ M), and absorption of azulene was corrected. The quantitative analyses were carried out by HPLC under following conditions. For **1**, and **2**: column, Radialpak Si; solvent, *n*-hexane. For **5**: column, μ-Bondapak C_{18}; solvent, methanol–water (10:1, v/v).

Acknowledgment. This investigation was supported by the Korea Science and Engineering Foundation and the Korea Advanced Institute of Science and Technology.

---

(19) Perrin, D. D.; Armarego, W. L. F.; Perrin, B. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980.

(20) Parker, C. A. *Photoluminescence of Solutions*; American Elsevier: New York, 1968; p 262.