PHOTOCHEMISTRY OF 1-(PHENYL)-4-(2-PYRIDYL)-1,3-BUTADIYNE : PHOTOREACTION WITH SOME OLEFINS

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Abstract—Irradiation of 1-phenyl-4-(2-pyridyl)-1,3-butadiyne (**2-PPB**) with dimethyl fumarate (DMFu) and 2,3-dimethyl-2-butene (DMB) yields photoadducts, **1-12**. The mechanism of the photoreaction of **2-PPB** with olefins is similar to that of 1,4-diphenyl-1,3-butadiyne with olefins.

INTRODUCTION

1-Phenyl-1,3,5-heptatriyne (PHT) has been reported to be phototoxic to biological systems in the presence of UV-A radiation (320−400 nm). The action mechanism via membrane damage of PHT, however, has not yet been established on the molecular level.[1,2] The photoreactions of PHT with some olefins such as 2,3-dimethyl-2-butene (DMB)[3], acrylonitrile (AN),[4,5] etc. have been studied as a model reaction for PHT

Scheme 1. Photoreaction of 1,4-diphenyl-1,3-butadiyne with dimethyl fumarate.

phototoxicity. Photolysis of PHT generated 1:2 dicyclopropyl photoadducts in neat DMB and 1:1 [2+2] type photocycloadducts in dichloromethane of unsymmetrical olefins.

1,4-Diphenyl-1,3-butadiyne (DPB) has been reported to yield similar products.[6] The same photoreaction with electron deficient dimethyl fumarate (DM Fu), however, yields very interesting 1:1-(**A**) and 1:2-photoadducts (**B** and **C**). The 1:1 photoadduct is initially formed and extended irradiation results in decrease of **A** and the formation of 1:2 photoadducts. The quenching studies on the photocycloaddition reaction indicate that the primary reaction leading to **A** to proceed from the triplet excited state of DPB and **C** is produced from the triplet excited state of **A**, while **B** is produced via the singlet excited state of **A** (Scheme 1).

In this investigation, we report a photocycloaddition reaction of 1-phenyl-4-(2-pyridyl)-1,3-butadiyne (**2-PPB**) with DMFu and DMB to give an insight into the influence of heteroaromatic terminal groups on the photochemistry of 1-aryl-1,3-butadiynes.

MATERIALS AND METHODS

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 and a Bruker AC-200 spectrometer. Absorption spectra were recorded on a Shimadzu 3100 S spectrophotometers. Mass spectra were determined at 70eV with a Hewlett-Packard 5985 A GC/MS interface by electron impact (EI) method. Reverse phase high performance liquid chromatography (HPLC) was performed on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000 A solvent delivery system, Model 440 UV absorbance detector fixed at 254 m, and Model U6K universal injector. Lichrosorb RP-18 column was used for preparative analyses. Normal phase HPLC was performed on Waters 510 HPLC pump, Waters 712 WISP and Waters 486 Tunable Absorbance Detector at 254 nm using Lichrosorb Si-60 column. Rayonet Photochemical Reactor was used for the photoreaction. Melting points were taken
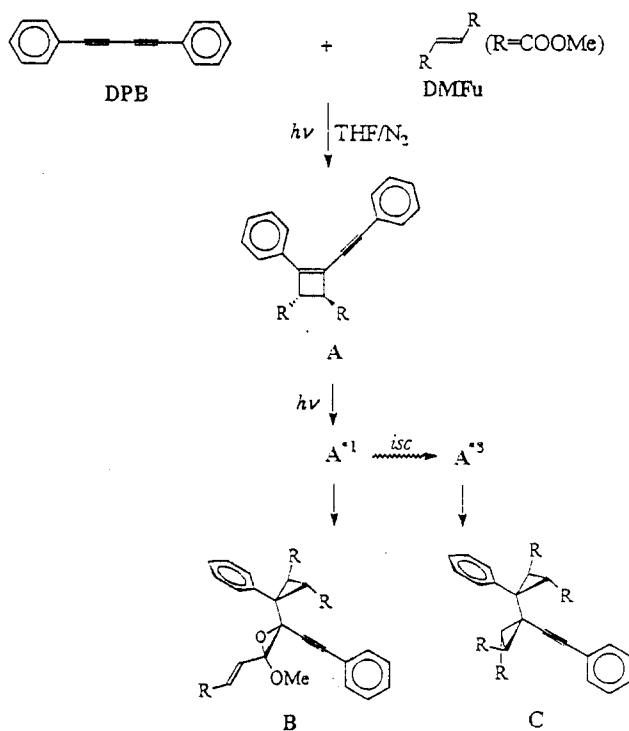
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on a Thomas Hoover hot-stage capillary melting point apparatus.

Materials. 2-Bromopyridine, phenylacetylene, copper(I) iodide, copper(I) chloride, triphenylphosphine, bromine, and ethylamine were purchased from Aldrich Chemical Co. and used without further purification. Bis(triphenylphosphine)palladium dichloride and bromophenylacetylene were prepared by the reported methods.[7,8] Solvents of reagent grade for chromatography were used without further purification. Solvents for chemical reactions were used after distillation by standard methods.[9] HPLC (Tedia) and spectroscopic grade solvents (Merck) were used for HPLC and absoption spectra, respectively.

Synthesis of 1-phenyl-4-(2-pyridyl)-1,3-butadiyne. 2-Methyl-4-(2-pyridyl)-3-butyn-1-ol : 2-Methyl-3-butyn-1-ol (4.85 mL, 50 mmol) was added to a solution of bis(triphenylphosphine)palladium dichloride (420 mg, 0.6 mmol), copper(I) iodide (114 mg, 0.6 mmol), and 2-bromopyridine (2.86 mL, 30 mmol) in triethylamine (100 mL) under nitrogen atmosphere. The mixture was heated to 40°C and maintained at the temperature for 1 h. After evaporation of solvents, the reaction mixture was extracted with diethyl ether and separated by column chromatography on a silica gel column using 1/1 n-hexane/ethyl acetate as eluent to give 2-methyl-4-(2-pyridyl)-3-butyn-1-ol in 98% yield. ^{1}H NMR (CDCl₃, 300 MHz) δ 8.51 (d, 1H), 7.58 (m, 1H), 7.35 (d, 1H), 7.17 (m, 1H), 3.78 (s, 1H), 1.61 (s, 6 H) ppm.

2-Ethynylpyridine : The mixture of 2-methyl-4-(2-pyridyl)-3-butyn-1-ol (4.185 g, 25.96 mmol) and sodium hydroxide (2.5 g, 62.5 mmol) in benzene (100 mL) was refluxed for 2 h. The mixture was filtered through a silica gel column using 1/1 n-hexane/diethyl ether and then the solvent was removed under reduced pressure to give 2-ethynyl-pyridine in 80% yield. ^{1}H NMR (CDCl₃, 300MHz) δ 8.49 (d, 1H), 7.57 (m, 1H), 7.38 (d, 1H), 7.17 (m, 1H), 3.10 (s, 1H) ppm; ^{13}C NMR (CDCl₃, 50MHz) δ 149.8, 142.1, 136.0, 127.3, 123.2, 82.5, 77.0 ppm.

1-Phenyl-4-(2-pyridyl)-1,3-butadiyne : 2-Ethynylpyridine (1.031 g, 10 mmol) was added to the solution of copper (I) chloride (0.1 g, 1 mmol), hydroxylamine hydrochloride (0.1 g, 1.5 mmol) in methanol (50 mL) under nitrogen atmosphere. A solution of bromophenylacetylene (1.809 g, 10 mmol) in methanol (50 mL) was added dropwise in 30 min and then the mixture was stirred at 25°C for 1 h under nitrogen atmosphere. The reaction mixture was evaporated and extracted with diethyl ether. The product was isolated by silica gel column chromatography with 3/2 n-hexane/diethyl ether as eluents and recrystallized from n-hexane in 60% yield. mp 74.0°C; ^{1}H NMR (CDCl₃, 300MHz) δ 8.57(d, 1H), 7.65 (m, 1H), 7.50 (m, 3H), 7.34 (m, 3H), 7.25 (m, 1H) ppm; ^{13}C NMR (CDCl₃, 50MHz) δ 150.1, 142.0, 136.0, 132.4, 129.4, 128.3, 127.9, 123.3, 121.0, 82.3, 80.1, 73.5, 73.4 ppm; UV (Acetonitrile) λ_{max}(logε) 327.5 (4.31), 307.1 (4.37), 290.5 (4.26), 239.4 (4.37), 227.5 (4.38), 215.0 (4.40)nm; MS (70eV) m/e 203 (M⁺).

Photoreaction of 1-phenyl-4-(2-pyridyl)-1,3-butadiyne (2-PPB). Photoreaction of 2-PPB with Dimethyl fumarate (DMFu) : A solution of 2-PPB (4 mM) and DMFu (100 mM) in dichloromethane was deaerated by nitrogen purging for 3 h and irradiated with 300 nm UV light in a Rayonet Photochemical Reactor equipped with RUL-300 nm lamps. After the irradiation for 8 h, the resulting photoreaction mixture was concentrated under reduced

pressure. The remaining reactants, 2-PPB and DMFu, were removed by column chromatography using 3/2 n-hexane/ethyl acetate as eluents. The photoadducts were isolated from the reaction mixture by a normal phase HPLC using a Hibar Lichrosorb Si-60 column (mean particle size 7nm, E. Merck) and n-hexane/ethyl acetate /dichloromethane = 6/2/1 elution system. Compound 1:^{1}H NMR (CDCl₃, 200 MHz) δ 8.56 (d, 1H), 7.68 (m, 1H), 7.49 (d, 1H), 7.17 (m, 6H), 4.39 (d, J=9.2Hz, 1H), 4.39 (d, J=9.6Hz, 1H), 4.03 (d, J=9.2Hz, 9.6Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 3.33 (s, 3H)ppm; ^{13}C NMR (CDCl₃, 50 MHz) δ 170.8, 170.7, 170.6, 170.3, 156.5, 148.8, 136.2, 131.7, 128.3, 128.1, 122.5, 122.0, 121.7, 89.0, 84.3, 55.6, 52.5, 52.4, 52.3, 51.9, 47.7, 43.8, 43.7, 43.6, 43.3 ppm; UV (methanol) λ_{max} 320.8, 250.5 nm; MS (70eV) m/e 491 (M⁺, 1.5), 432 (M⁺-CH₃O₂C, 12.2), 372 (M⁺-2CH₃O₂C and H, 20.2), 288 (100). Compound 2: ^{1}H NMR (CDCl₃, 200 MHz) δ 8.57 (q, 1H), 7.95 (d, 1H), 7.69 (m, 1H), 7.51 (m, 2H), 7.35 (t, 3H), 7.19 (m, 1H), 4.18 (d, J=2.2Hz, 1H), 3.91 (d, J=2.2Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H)ppm; ^{13}C NMR (CDCl₃, 50 MHz) δ 171.6, 170.4, 150.2, 149.7, 148.0, 136.0, 131.9, 129.2, 128.4, 123.3, 122.4, 122.1, 121.9, 98.7, 82.9, 52.4, 52.3, 48.6, 45.8 ppm; UV (methanol) λ_{max} 340.6, 322.6, 240.8, 234.7 nm; MS (70eV) m/e 347 (M⁺ 31.7), 346 (M⁺-H, 100). Compound 3: ^{1}H NMR (CDCl₃, 200 MHz) δ 8.61 (q, 1H), 7.71 (m, 3H), 7.50 (d, 1H), 7.36 (m, 3H), 7.25 (m, 1H), 4.13 (d, J=2.0 Hz, 1H), 4.01 (d, J=2.0 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H)ppm; ^{13}C NMR (CDCl₃, 50 MHz) δ 171.9, 170.5, 150.1, 149.9, 142.6, 136.1, 132.1, 129.7, 128.5, 127.6, 126.2, 123.2, 117.8, 96.1, 82.6, 52.4, 52.4, 47.8, 46.5 ppm; UV (methanol) λ_{max} 348.0(sh), 325.0, 232.2 nm; MS (70eV) m/e 347 (M⁺, 37.6), 287 (100). Compound 4: ^{1}H NMR (CDCl₃, 300 MHz) δ 8.57 (d, 1H), 8.01 (d, 1H), 7.71 (m, 1H), 7.54 (m, 2H), 7.32 (m, 3H), 7.17 (m, 1H), 4.34 (d, J=5.6 Hz, 1H), 4.10 (d, J=5.6 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H)ppm; ^{13}C NMR (CDCl₃, 50 MHz) δ 170.6, 169.6, 150.7, 150.2, 149.5, 135.9, 131.7, 129.0, 128.3, 123.2, 122.2, 121.8, 121.8, 103.8, 83.1, 52.1, 52.0, 47.7, 46.3 ppm; UV (methanol) λ_{max} 349.8, 321.6, 240.9, 233.7 nm; MS (70eV) m/e 347 (M⁺, 43.3), 346 (M⁺-H, 68.8), 288 (92.6), 228 (48.2). Compound 5: ^{1}H NMR (CDCl₃, 300 MHz) δ 8.56 (d, 1H), 7.71 (m, 3H), 7.56 (q, 1H), 7.34 (m, 3H), 7.27 (q, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 4.26 (d, J=5.6 Hz, 1H), 4.10 (d, J=5.6 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H)ppm; ^{13}C NMR (CDCl₃, 50 MHz) δ 174.2, 170.5, 150.2, 149.1, 142.5, 136.1, 132.3, 129.7, 128.6, 127.7, 126.3, 123.2, 117.5, 95.9, 83.1, 52.3, 52.2, 47.5, 46.9ppm; UV (methanol) λ_{max} 324.4, 236.2 nm; MS (70eV) m/e 348 (M⁺+H, 24.1), 347 (M⁺, 30.6), 288 (46.3), 228 (48.2). Compound 6: ^{1}H NMR (CDCl₃, 300 MHz) δ 8.49 (d, 1H), 7.40 (m, 1H), 7.33 (m, 2H), 7.20 (m, 4H), 7.07 (q, 1H), 4.11 (d, J=1.8 Hz, 2H), 4.02 (d, J=1.8 Hz, 2H), 3.88 (s, 6H), 3.68 (s, 3H), 3.57 (s, 3H)ppm; ^{13}C NMR (CDCl₃, 50 MHz) δ 177.7, 171.7, 171.7, 171.0, 150.5, 149.2, 144.1, 141.9, 135.8, 134.9, 133.2, 132.1, 129.0, 128.4, 122.7, 122.7, 122.5, 52.4, 52.3, 52.1, 52.1, 47.9, 47.4, 47.3, 46.1 ppm; UV (methanol) λ_{max} 328.0, 283.5, 253.5, 246.4 nm; MS (70eV) m/e 491 (M⁺, 12.8), 432 (M⁺-CH₃O₂C, 100.0), 372 (M⁺-2CH₃ O₂C and H, 15.3). Compound 7: ^{1}H NMR (CDCl₃, 200 MHz) δ 8.53 (d, 1H), 7.54 (m, 4H), 7.17 (m, 4H), 4.40 (d, J=9.0 Hz, 1H), 4.37 (d, J=9.4 Hz, 1H), 4.08 (d, J=9.4 Hz, 1H), 4.07

(d, J=9.0 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 3.17 (s, 3H)ppm; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 171.0, 170.3, 170.2, 169.8, 150.0, 142.7, 137.1, 136.0, 128.0, 127.6, 127.5, 126.8, 123.0, 90.1, 84.4, 55.1, 52.7, 52.5, 52.4, 51.9, 46.7, 45.9, 45.7, 44.0, 43.3ppm; UV (methanol) λ_{max} 279.4, 242.4nm; MS (70eV) m/e 491 (M$^+$, 8.3), 476 (M$^+$-CH$_3$, 41.0), 432 (M$^+$-CH$_3$O$_2$C, 26.8), 372 (M$^+$-2CH$_3$O$_2$C and H, 33.8), 254 (27.3).

Relative concentration profile of the photoreaction 2-PPB/DMFu, 2/DMFu, and 3/DMFu Against irradiation time : The relative photocycloaddition quantum yields were determined under the conditions in which all the incident light was absorbed by 2-PPB, 2, and 3 at initial stage of photolysis ([2-PPB], [2], and [3]=4 mM, [DMFu] =100 mM), respectively. The solutions deaerated by nitrogen purging were irradiated with a Hanovia 450 W medium pressure mercury arc lamp (Type 679A36) in a merry-go-round apparatus. Actinometry was not carried out and relative quantum yields were determined by HPLC peak areas under the following analytical conditions: Hibar Lichrosorb Si-60 column (mean particle size 5 nm, E. Merck), eluents; n-hexane/ethyl acetate/dichloromethane=6/2/1, flow rate=1.5 mL/min.

Oxygen Effects on the Photoreaction of 2-PPB/DMFu : The relative quantum yields of the photoreactions of 2-PPB (4 mM) with DMFu (100 mM) to give 2 and 3 were measured in the presence of oxygen (purged with dry oxygen) with respect to each deaerated solution. Merry-go-round apparatus was used with a Hanovia 450 W medium mercury arc lamp. The quantitative analysis was carried out by HPLC using the following conditions: Hibar Lichrosorb Si-60 column (mean particle size 5 nm, E. Merck), eluents; n-hexane/ethyl acetate/dichloromethane =6/2/1, flow rate=1.5 mL/min.

Photoreaction of 2-PPB with 2,3-Dimethyl-2-butene (DMB) in Dichloromethane : A solution of 2-PPB (4 mM) and DMB (200 mM) in dichloromethane was deaerated by nitrogen purging for 3 hours and irradiated with 300 nm UV light in a Rayonet Photochemical Reactor equipped with RUL-300 nm lamps. After the irradiation for 8 h, the resulting photoreaction mixture was concentrated under reduced pressure. The remaining reactant, 2-PPB, was removed by column chromatography using 3/1 n-hexane/diethyl ether as eluents. The photoadducts were isolated from the reaction mixture by a normal phase HPLC using a Hibar Lichrosorb Si-60 column (mean particle size 7 nm, E. Merck) and n-hexane/ethyl acetate/dichloromethane = 12/1/1 or n-hexane/ethyl acetate/dichloromethane = 6/2/1 elution system. Compound 8: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.58 (d, 1H), 7.92 (d, 1H), 7.67 (m, 1H), 7.53 (m, 2H), 7.35 (m, 3H), 7.09 (m, 1H), 1.41 (s, 6H), 1.25 (s, 6H)ppm; ^{13}C NMR, (CDCl$_3$, 50 MHz) δ 153.3, 153.0, 149.3, 135.7, 131.8, 130.6, 128.4, 128.3, 123.3, 122.2, 121.9, 97.4, 83.2, 49.1, 47.3, 22.4, 22.0 ppm; UV (methanol) λ_{max} 344.7, 326.0, 243.7 nm; MS (70eV) m/e 287 (M$^+$, 7.8), 286 (M$^+$-H, 40.4), 272 (100), 257 (75.5), 181(41.5). Compound 9: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.46 (d, 1H), 7.47 (m, 1H), 7.35 (m, 3H), 7.20 (m, 2H), 7.07 (m, 1H), 6.82 (d, 1H), 5.94 (s, 1H), 4.93 (s, 1H), 4.84 (s, 1H), 1.85 (s, 3H), 1.23 (s, 6H)ppm; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 163.1, 149.7, 149.5, 143.8, 139.7, 135.7, 128.9, 127.4, 127.1, 127.1, 122.1, 111.8, 107.3, 91.9, 88.5, 46.0, 27.0, 20.2 ppm; UV (methanol) λ_{max} 305.3 nm; MS (70eV) m/e

287 (M$^+$, 23.9), 272 (100), 257 (62.8), 230 (29.6), 204 (28.8). Compound 10: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.64 (d, 1H), 7.76 (m, 2H), 7.66 (m, 1H), 7.50 (2, 1H), 7.31 (m, 4H), 1.37 (s, 6H), 1.25 (s, 6H)ppm; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 155.3, 150.0, 143.6, 135.9, 133.8, 128.4, 128.1, 127.4, 126.6, 125.5, 122.5, 95.2, 83.5, 48.7, 47.0, 22.8, 20.0 ppm; UV (methanol) λ_{max} 331.3, 233.3 nm; MS (70eV) m/e 287 (M$^+$, 9.4), 286 (M$^+$-H, 40.4), 272 (100), 257 (38.7), 178 (17.1).

Photolysis of 2-PPB in 2,3-Dimethyl-2-butene(DMB) : A solution of 2-PPB (4mM) in DMB (200 mM) was deaerated by nitrogen purging for 3 h and irradiated with 300 nm UV light in a Rayonet Photochemical Reactor equipped with RUL-300 nm lamps. After the irradiation for 8 h, the resulting photoreaction mixture was concentrated under reduced pressure. The remaining reactant, 2-PPB, was removed by column chromatography using 3/1 n-hexane/diethyl ether as eluents. The photoadducts were isolated from the reaction mixture by a normal phase HPLC using a Hibar Lichrosorb Si-60 column (mean particle size 7 nm, E. Merck) and n-hexane/ethyl acetate/dichloromethane = 12/1/1 or n-hexane/ethyl acetate/dichloromethane = 6/2/1 elution system. Compound 8: same spectra above experiment. Compound 10: same spectra above experiment. Compound 11: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.49 (d, 1H), 7.51(m, 1H), 7.15 (m, 7H), 1.18 (s, 12H), 0.96 (s, 6H), 0.91 (s, 6H)ppm; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 159.9, 148.6, 140.4, 135.9, 131.0, 127.8, 125.9, 125.7, 120.9, 84.9, 82.8, 34.7, 33.0, 29.1, 28.5, 20.5, 20.4, 20.2, 20.2 ppm; UV (methanol) λ_{max} 264.0 nm; MS (70eV) m/e 371 (M$^+$, 9.4), 272 (M$^+$-CH3, 46.0), 256 (M$^+$-2CH$_3$ and H, 11.9), 204 (100), 160 (26.8). Compound 12: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.57 (d, 1H), 7.60 (m, 1H), 7.43 (m, 2H), 7.26 (m, 4H), 7.11 (m, 1H), 5.58 (s, 1H), 4.87 (s, 1H), 4.79 (s, 1H), 1.71 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H), 1.25 (s, 6H), 1.05 (s, 6H)ppm; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 158.6, 149.2, 148.8, 137.2, 136.0, 129.3, 128.4, 128.3, 128.0, 126.1, 121.3, 110.9, 90.1, 83.4, 78.3, 76.0, 34.4, 30.0, 24.4, 24.2, 20.6, 20.3, 20.3, 20.2, 18.6 ppm; UV (methanol) λ_{max} 264.7 nm.

RESULTS AND DISCUSSION

Photoreaction

Irradiation of 2-PPB with DMFu in deaerated dichloromethane solution at 300 nm yields 1:1 (2, 3, 4, and 5) and 1:2 photoadducts (1, 6, and 7). Photoadducts 1-7 were isolated by column chromatography and refined by HPLC. The structure of these photoadducts was determined by various physical methods, including ^{13}C-NMR spectroscopy which is vital for the determination of the reaction sites.

The photoadducts 1-7 do not show the characteristic vibrational fine structure of conjugated polyacetylenes in UV absorption spectra as shown in Figure 1. The absorption maxima were red shifted in 2-6, while blue shifted in 1 and 7. Mass spectra of all the photoadducts show M$^+$ peaks, indicating that the photoadducts 2-5 are formed by addition of

one molecule of DMFu, while **1**, **6**, and **7** are formed by addition of two molecules of DMFu to one 2-PPB.

Typically, ^{13}C NMR peaks of ethynyl and cyclobutenyl substituted carbons in pyridine ring are observed at the 142 ppm and 150 ppm while cyclopropyl substituted pyridyl carbon appears near 156 ppm. Ethynyl substituted and cyclobutenyl substituted phenyl carbons are shown at the 122 and 132 ppm, while cyclopropyl substituted phenyl carbon appears near 137 ppm, respectively, by the additive rule of ^{13}C chemical shift. The appearance of resonance signal at 142-149 ppm (cyclobutene ring sp^2 carbon, deshielded by phenyl or pyridyl) is the strong evidence of the existence of pyridyl or phenyl substituted cyclobutene groups.
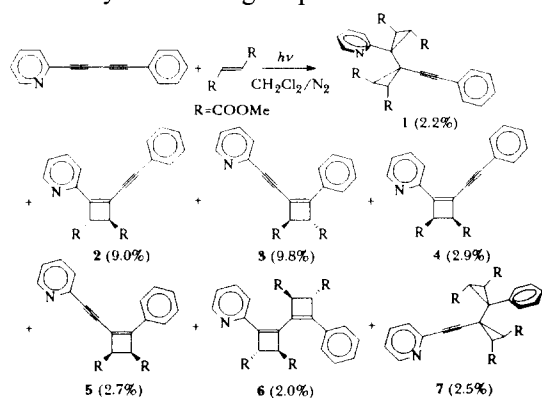
^1H NMR spectroscopy is also a powerful tool to determine the structure of 1:1 photocycloadducts. In ^1H NMR spectra of **2** and **4**, the proton of pyridyl 3-position was shifted downfield and in those of **3** and **5**, the protons of phenyl 2- and 6-positions, were shifted downfield due to the anisotropic effect of remaining acetylene group. In addition, the appearance of two resonance peaks with coupling patterns of cyclobutene ring is eminent to prove that two methoxycarbonyl groups are attached to *cis* or *trans* position with respect to each other ($J_{cis} \sim 5.6$ Hz; $J_{trans} \sim 2.0$ Hz). ^1H NMR spectra of **1** and **7** show four protons of cyclopropane with large coupling constants ($J \sim 9.2$ Hz).

Dichloromethane solution of **2-PPB** and **DMB** was deaerated by N_2 purging and irradiated with 300 nm to obtain 1:1 photoadducts (**8**, **9**, and **10**).
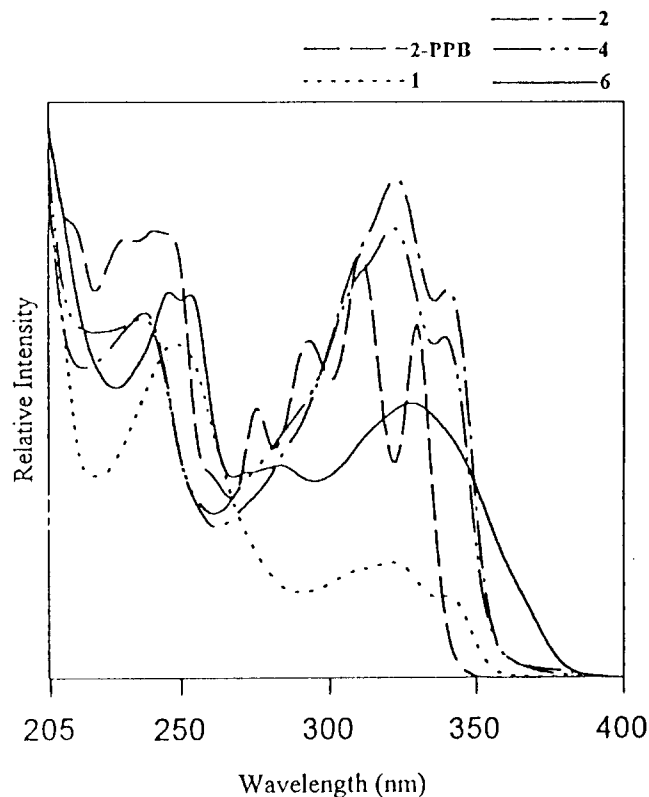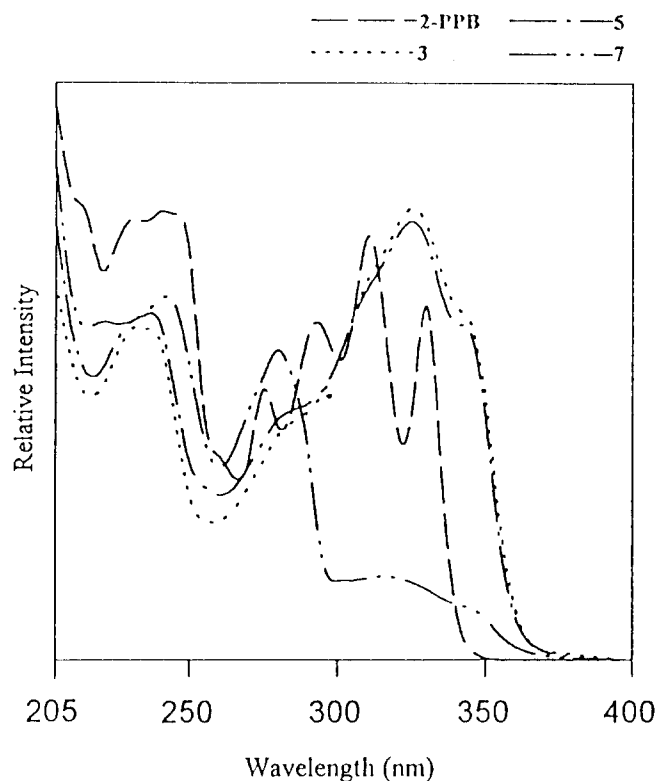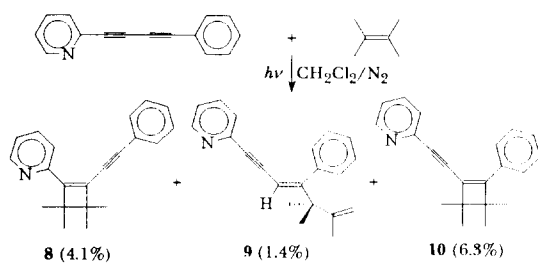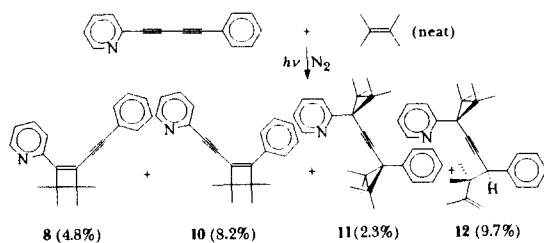

Figure 1. UV absorption spectra of **2-PPB** and its photoadducts with DMFu (**1-7**).

Deaerated DMB solution of 2-PPB was irradiated with 300 nm to obtain 1:1 photoadducts (8 and 10) and 1:2 photoadducts (11 and 12).

8 (4.8%)   10 (8.2%)   11 (2.3%)   12 (9.7%)

As shown in Figure 2, 8-12 do not show the characteristic vibrational fine structure of conjugated polyacetylenes in the UV absorption spectra. The absorption maxima were blue shifted in 11 and 12, while red shifted in 8 and 10. Mass spectra of all the photoadducts show M^+ peaks, indicating that the products 8, 9, and 10 is formed by addition of one molecule of DMB, while 11 and 12 are formed by addition of two molecules of DMB to one 2-PPB.

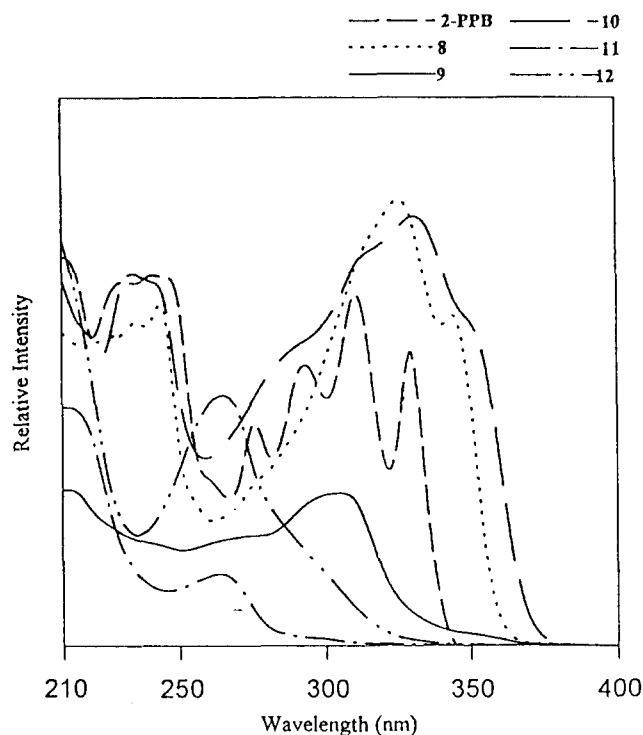Figure 2. UV absorption spectra of 2-PPB and its photoadducts with DMB (8-12).

Since ^1H NMR and ^{13}C NMR spectra of 8 and 10 are analogous to those of 2 and 3, the position of cyclobutene ring can be clarified. For adduct 11, cyclopropyl substituted pyridine carbon (159.9 ppm) and benzene carbon (140.4 ppm) were identified. The regiochemistry of 1:1 photoadduct, 9, and 1:2 photoadduct, 12, was assigned by nuclear Overhauser effects. In 9, saturation of H_a enhances the intensity

of two methyl proton peaks (H_b; 1.56%) and irradiation of methyl protons (H_b) results in the enhancement of H_a (1.85%) and ortho protons of phenyl ring (1.11%). When H_a is saturated, no proton of phenyl ring or pyridyl ring is influenced. In 12, when H_c is irradiated, ortho proton of phenyl ring is enhanced (2.5%). Mass spectrum of 12 shows substantial evidence for the structure determination. The fragment corresponding to the loss of C_6H_{11} appears at m/e 288.

9   12
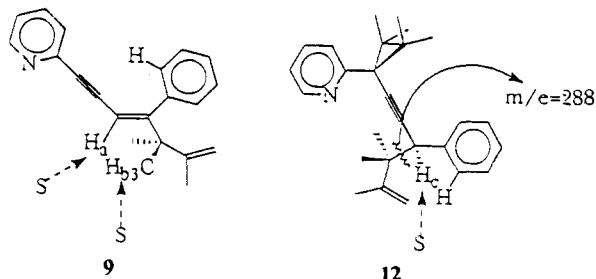
Reaction Mechanism

Two major photoadducts with longer retention times than the parent 2-PPB and DMFu were obtained on the HPLC chromatogram when dichloromethane solution of 2-PPB and DMFu was exposed to 300 nm light. No such product was detected when 2-PPB or DMFu were irradiated individually or when they were mixed in the dark. The photooxidation reaction is not possible since a great care was taken to deoxygenate the solutions by purging with highly pure nitrogen.

As shown in Figure 3, the 1:1 photoadducts (2 and 3) are initially formed and prolonged irradiation of the solution results in the formation of 1:2 photoadducts (1, 6, and 7) indicating that 2 and 3 are the primary and 1, 6, and 7 are the secondary photoadducts. Photolysis of pure 2 with DMFu in dichloromethane yields 1 and 6. Photolysis of pure 3 with DMFu in dichloromethane yields 7. When oxygen is present, 2 and 3 are efficiently quenched supporting the triplet reaction mechanism ($\Phi_{N_2}/\Phi_{O_2}=0.3$).

From these results, a plausible photoreaction mechanism is proposed as shown in Scheme 2. Triplet excited state of 2-PPB reacts with DMFu initially to give the primary product (2 and 3). 2 absorbs the second photon and reacts with another molecule of DMFu to produce 1 and 6, while 3 reacts with another molecule of DMFu to produce 7.

The structural form of photoadduct 6 is formed in the photoreaction of 2-PPB with DMFu, not in the photoreaction of DPB with DMFu. More interestingly, extended irradiation of 2 with DMFu only results in the formation of 6, but extended
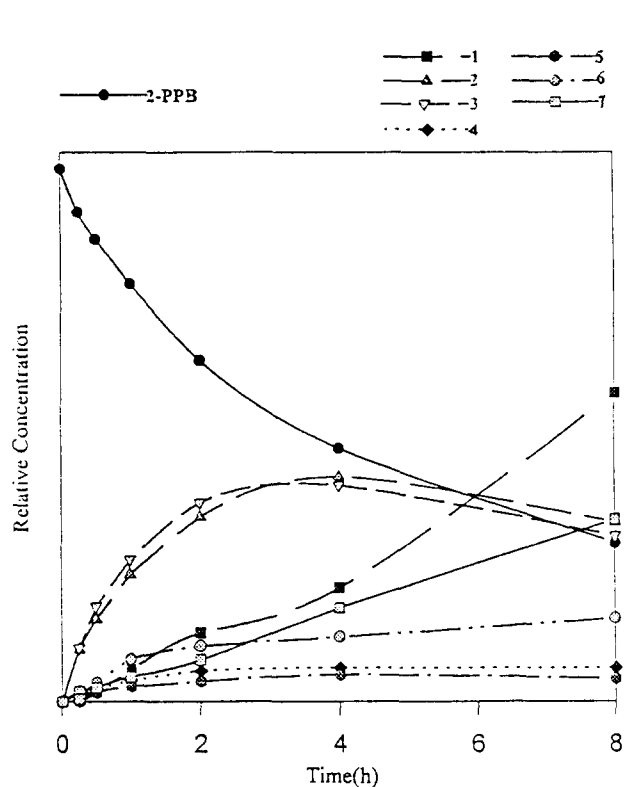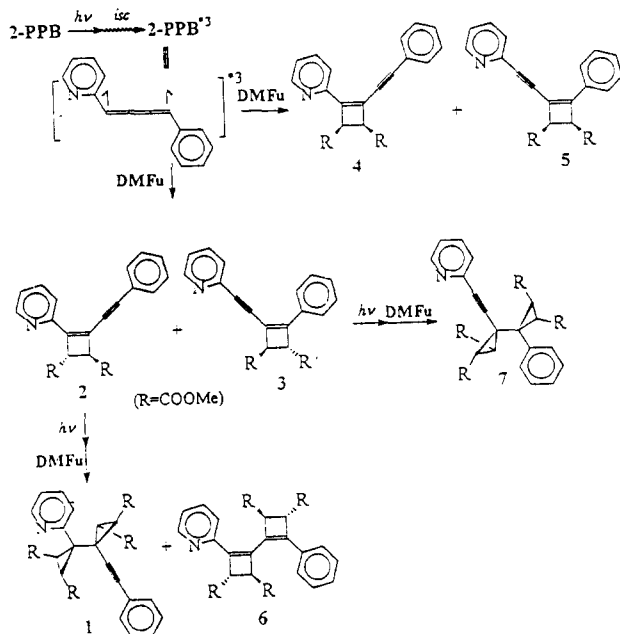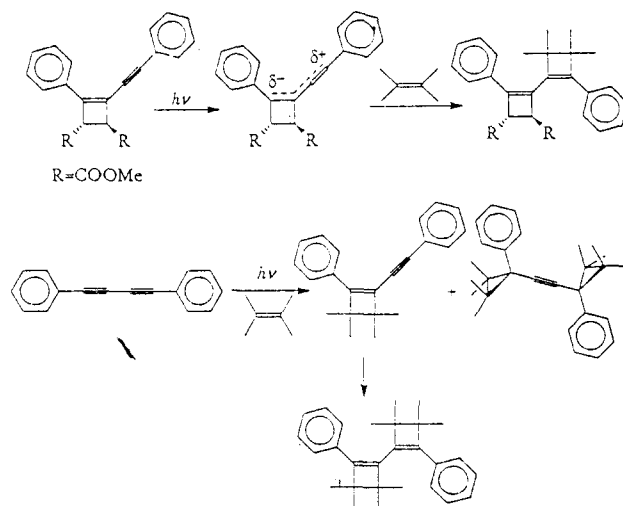
Figure 3. Relative concentration profile of photoreaction
2-PPB/DMFu against irradiation time.

Scheme 2. Plausible photoreaction mechanism of 2-PPB
with DMFu.

irradation of **3** with DMFu does not. When the
primary photoadduct in the photoreaction of DPB
with DMFu was irradiated in electron-rich olefin
solution such as DMB, the remaining triple bond

reacts with electron-rich olefin.[11] The attack site of
1:1 adduct by DMB to give 1:2 adduct is dependent
on the electron density of olefins, suggesting that the
triplet excited state of 1:1 photoadduct has a polar
character.

The same analogy can be applied to **2** and **3**, *i.e.*,
the negative charge character is developed in the
cyclobutene ring. However, the polar character will
be diminished if 2'-pyridyl substituent is present in
the cyclobutene ring as in **2**. If **2** has a perfect
diradical character in excited state, the remaining
acetylene of **2** will react with DMFu to give **7**.

Photoreaction of **2-PPB** with DMB in dichloro-
methane yields three 1:1 photoadducts (**8, 9,** and
10), while DPB does not react with DMB in the
same condition. In photoreaction of **2-PPB** in neat
DMB solution, two 1:1 and two 1:2 photoadducts
were generated. It was reported in the previous
investigation that DPB photoreacts with DMB in
the triplet excited state to give 1:1 and 1:2
photoadduct(s).[12]

The reactive excited state of **2-PPB** to give
photoadducts is probably cummulene type of triplet
excited state, similar to that of DPB. The reaction
pathway for these adducts is proposed as shown in
Scheme 3.

Interesting results are obtained in these reactions.
Hydrogen abstraction adducts such as **9** and **12** are
generated instead of secondary photoadducts analogous
to secondary hotoadduct of DPB-DMB system. This
is probably due to the pyridyl group. As shown in
Scheme 3, reactive species are **8a↔8b** and **10a↔10b**.
8a↔8b has shorter lifetime than **10a↔10b** because
photoreaction in dichloromethane yields **10** more
than **8** and because **11** and **12** are formed in neat
DMB solution. Due to the pyridyl group, triplet
biradical (**10b**) is very much stablized so that the
rate of the hydrogen abstraction competes favorably
with the rate of spin flip and consequently photo-
adduct **9** is formed.
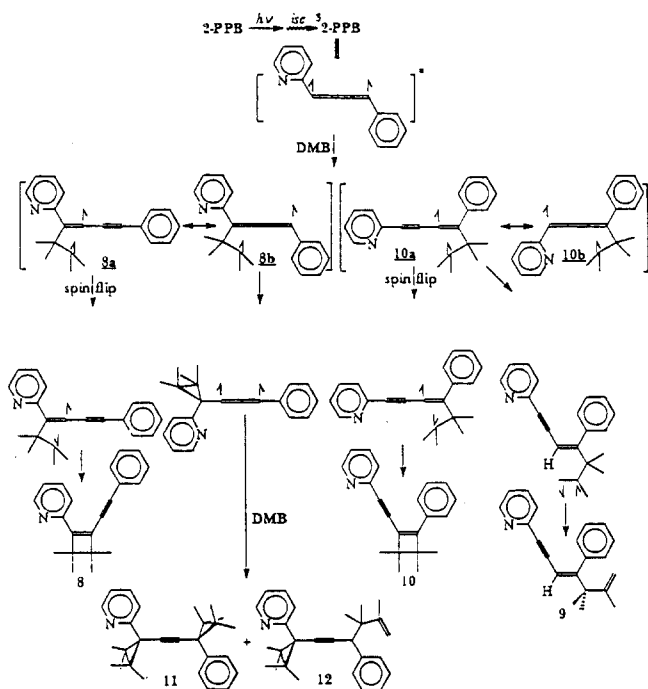
Scheme 3. Plausible photoreaction mechanism of 2-PPB with DMB

CONCLUSION

2-PPB shows strong phosphorescence and triplet energy lies around 241kJ/mol. 2-PPB was more reactive than DPB in the photoreaction with olefins such as DMFu and DMB because intersystem crossing is enhanced by introducing n-π^* state.

Photoreaction of 2-PPB with DMFu in deaerated dichloromethane solution yields 1-7. Mechanistic investigation shows that 2 and 3 are primary photoadducts and 1, 6, and 7 are secondary photoad ducts. Oxygen quenching shows that 2 and 3 are produced from the triplet excited state of 2-PPB. 1 and 6 are generated from extended irradiation of 2 and 7 is formed from 3. The formation of 6 may be affected by electron withdrawing pyridyl group in the excited state of 2.

Photoreaction of 2-PPB with DMB in dichloromethane yields 8-10, and photoreaction in neat DMB yields 8, 10, 11 and 12. The triplet state lifetime of 2-PPB-DMB seems to be longer than that of DPB-DMB because of the presence of pyridyl

group.

Further mechanistic investigations are in progress in this laboratory.

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