

Photoreaction of 1,4-Diphenyl-1,3-butadiyne and 1,4-Di-*t*-butyl-1,3-butadiyne with Some Olefins

Sang Chul Shim[†] and Sung Sik Kim

Korea Advanced Institute of Science and Technology, P.O. Box 150 Chungyangni, Seoul 131, Korea
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A diacetylene compound, 1,4-diphenyl-1,3-butadiyne, was photolyzed with 2,3-dimethyl-2-butene, 1,4-cyclohexadiene, dimethyl fumarate, and methyl crotonate, as a model reaction of the phototoxic conjugated polyynes with DNA or RNA and [2+2] photocycloadducts were obtained except for 1,4-cyclohexadiene. In the photoreaction of 1,4-diphenyl-1,3-butadiyne with 2,3-dimethyl-2-butene, a [2+2+2] photoadduct was additionally obtained. The photolysis of 1,4-di-*t*-butyl-1,3-butadiyne with 2,3-dimethyl-2-butene also yielded a [2+2] photoadduct. Fluorescence was observed from all the photoadducts while the reactants did not show any fluorescence.

Introduction

Certain naturally occurring conjugated polyynes have been reported to be phototoxic to a variety of microorganisms, human skin fibroblasts, Syrian hamster cells, mosquito larvae and *Paramecium*¹⁻⁶. For example, 1-phenylhepta-1,3,5-triyne (PHT) which is a conjugated poly-yne occurring in high concentration in the leaves of the tropical weed *Bidens pilosa* L. is phototoxic toward various organisms containing membranes, including eukaryotic cells, fungi, bacteria, and viruses in the presence of long wave UV⁷. PHT, unlike the naturally occurring photoactive psoralens, does not form interstrand cross-links with calf thymus DNA^{8,9} while furocoumarins inactivate viruses by cross-linking the DNA¹⁰. Instead, PHT has been known to exert its phototoxic action via the viral membrane damage which inactivates DNA or RNA to replicate⁸. However, nothing is known about the photochemistry of polyynes even though it is essential to understand the molecular mechanism of phototoxicity of the compounds. This membrane damage may involve the modification of cellular DNA or RNA.

The conjugated di-ynes are reported to be less toxic than the conjugated tri-ynes¹ but the cross-addition products were isolated and characterized in the photochemical reaction of 1,4-diphenyl-1,3-butadiyne (DPB) and 1,4-di-*t*-butyl-1,3-butadiyne (DBB) with some olefins.

Experimental

Materials. Dichloromethane, diethyl ether, *n*-hexane, chloroform, and methanol were used with or without further purification. 1,4-Diphenyl-1,3-butadiyne (DPB), 2,3-dimethyl-2-butene (tetramethylethylene, TME), dimethyl fumarate (DMFU), 1,4-cyclohexadiene (CH), methyl crotonate (MCR), and 3,3-dimethyl-1-butyne were purchased from Aldrich Chemical Company and were used as received. 1,4-Di-*t*-butyl-1,3-butadiyne (DBB) was prepared by coupling of 3,3-dimethyl-1-butyne in pyridine using cupric acetate (recrystallization yield, 60%). The product exhibits the following spectral properties; ¹H NMR (60 MHz, CCl₄), δ 1.30 ppm (s, CH₃ of *t*-butyl); UV (methanol), λ_{max} 215, 226, 238 and 251 nm; IR, ν_{max}

2,880-2,980 (ν_{C-H} of *t*-butyl), 2,150 (ν_{C=C}).

Instruments. UV spectra were measured on a Cary 17 Spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 283B Grating Spectrophotometer. ¹H NMR spectra were obtained on a Varian FT-80A NMR Spectrometer at 79.542 MHz or a Varian T-60A NMR Spectrometer. Mass spectra were obtained on a Hewlett Packard 5985A GC/MS System using electron impact (EI) method. Elemental analyses were carried out on a F & M Scientific Cooperation-C.H.N. Analyzer Model 180. Fluorescence and phosphorescence spectra were recorded on an Aminco-Bowman Spectrofluorometer with Amino-XY recorder. Phosphorescence lifetime was measured on this instrument in conjunction with Tektronix 5115 storage oscilloscope. HPLC 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 nm, and 280 nm, and Model U6K Septumless Universal Injector. The bonded phase chromatographic column (μ-porasil) and Radial Pak columns operating in the Radial Compression Module (RCM 100) were used as received for the analytical purposes. Low pressure liquid chromatography was performed by the following assembled liquid chromatography system; Pumping system; Waters Associates Model 6000A, Detector; UV monitor (Bio-Rad, Model 1330 at 254 nm), Recorder; Linear (input voltage 10 mV, chart speed 3 cm/h), Column; LiChroprep Si 60(40-63 μm) (Lobar prepacked column, Merck), Solvent; diethyl ether-*n*-hexane (1:19 v/v), Flow rate; 5.0 ml/min.

Irradiation Apparatus. Irradiation was carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company) Model RPR-208 or RPR-100 equipped with 300 nm or 254 nm UV lamps.

Irradiation of Diacetylene Compounds with Some Olefins.

Irradiation of DPB with TME. Degassed *n*-hexane solution of DPB (2 mmol) and TME (20 mmol) was irradiated in a Rayonet Photochemical Reactor Model RPR-208 or RPR-100 equipped with 300 nm UV lamps. After the irradiation for 175 hours, the resulting photoreaction mixtures were concentrated in vacuo, and analyzed by HPLC (solvent; diethyl ether-*n*-hexane 1:19

v/v). The photoadducts were isolated by low pressure preparative liquid chromatography using diethyl ether-*n*-hexane (1:19 v/v) and LiChroprep Si 60(40-63 m) prepacked column. 1; UV (methanol), λ_{\max} 345, 323, 300, 282, 245, 235, 223, and 205 nm; IR (NaCl), 3,020-3,080 ($\nu_{\text{C-H}}$ in phenyl ring), 2,860-2,980 ($\nu_{\text{C-H}}$ of methyl groups), 1,573 cm^{-1} ($\nu_{\text{C-C}}$ of cyclobutene ring); $^1\text{H NMR}$ (80 MHz, CDCl_3), δ 7.33-8.27 (*m*, 2 C_6H_5), 1.73 (*s*, 4 CH_3) and 1.60 ppm (*s*, 4 CH_3); MS (70 eV), *m/e* 286 ($\text{C}_{22}\text{H}_{22}^+$, M-C $_6\text{H}_{12}$), 271 ($\text{C}_{21}\text{H}_{19}^+$, M-C $_6\text{H}_{12}$ -CH $_3$, 100 %) and 202 (M-2 C_6H_{12}); Elemental analysis, C/H 90.73/8.94 (calculated C/H 90.81/9.19); Fluorescence spectrum (methanol), λ_{em} 360, 380, and 400 nm (shoulder) (λ_{ex} = 300 nm). 2; UV (methanol), λ_{\max} 273 and 300 nm (shoulder); IR, 2,185 ($\nu_{\text{C=C}}$, very strong), 1,640 cm^{-1} ($\nu_{\text{C-C}}$ of cyclohexene ring); $^1\text{H NMR}$ (80 MHz, CDCl_3), δ 7.20-7.95 (*m*, 2 C_6H_5), 1.50 (*s*, 4 CH_3) and 1.10 ppm (*s*, 4 CH_3); MS (70 eV), *m/e* 301, 287, 259, 217, 202, 105 (100%), 91 and 77; Elemental analysis, C/H 90.79/9.09 (calculated, C/H 90.81/9.19).

Irradiation of DPB with 1,4-Cyclohexadiene. 33.4 mmol (100 mg) of DPB dissolved in 15 ml of 1,4-cyclohexadiene was deoxygenated for 30 min and irradiated with 300 nm UV light for 40 hours. The photoreaction mixtures were concentrated in vacuo. The photoadduct was isolated by preparative thin layer chromatography using *n*-hexane as an eluting solvent. 3; UV (methanol), λ_{\max} 333, 313 and 222 nm; IR, 3,030-3,090 ($\nu_{\text{C-H}}$ of phenyl ring), 2,860-2,965 ($\nu_{\text{C-H}}$ of aliphatic moiety), 1,030 (deformation mode of the cyclopropane ring) and 840 cm^{-1} ($\nu_{\text{C-H}}$ of the cyclopropane ring); $^1\text{H NMR}$ (80 MHz, CDCl_3), δ 7.22-7.95 (*m*, 2 C_6H_5), 7.03 (*d*, 2 \times 1H, *J* = 16 Hz), 6.35 (*d*, 2 \times 1H, *J* = 16 Hz), 6.68 (*d*, 2 \times 1H, *J* = 12 Hz), 5.90 (*d*, 2 \times 1H, *J* = 12 Hz), 1.53 (*s*, broad, 2 \times 2H), and 1.26 ppm (*s*, broad, 2 \times 2H); MS (70eV), *m/e* 362(M $^+$), 202 ($\text{C}_{16}\text{H}_{10}^+$, M-2 C_6H_6) and 204 ($\text{C}_{16}\text{H}_{12}^+$, 100 %); Fluorescence spectrum (methanol), λ_{em} 380, 400, and 420 nm (shoulder) (λ_{ex} = 355 nm).

Irradiation of DPB with Dimethyl Fumarate. 3.3 mmol (200 mg) of DPB and 27 mmol (1.2g) of dimethyl fumarate dissolved in 300 ml of dichloromethane was degassed for 3 hours by bubbling nitrogen gas. The resulting solution was irradiated with 300 nm UV light for 60 hours. The residue was concentrated in vacuo and was separated to obtain the photoadduct by preparative thin layer chromatography using chloroform as an eluting solvent. 4; UV (methanol), λ_{\max} 341, 321, and 232 nm; IR, 1,730, 1,735 cm^{-1} ($\nu_{\text{C=O}}$); $^1\text{H NMR}$ (80 MHz, CDCl_3), δ 7.25-7.80 (*m*, 2 \times C_6H_5), 4.17 (*d*, 2 \times 1H, *J* = 3 Hz), 4.03 (*d*, 2 \times 1H, *J* = 3 Hz), 3.81 (*s*, 2 CH_3), and 3.76 (*s*, 2 CH_3); Fluorescence spectrum (methanol), λ_{em} 355, 375 and 395 nm (shoulder) (λ_{ex} = 300 nm).

Irradiation of DBB with TME. A solution of 3.1 mmol (100 mg) of 1,4-di-*t*-butyl-1,3-butadiyne (DBB) and 208 mmol (5 ml) of TME in *n*-hexane was degassed for 30 min and was irradiated in a Rayonet Photochemical Reactor Model RPR-100 equipped with 254 nm UV lamps. After the irradiation for 15 hours, the resulting photoreaction mixtures were concentrated in vacuo, and subjected to preparative thin layer chromatography using *n*-hexane as an eluting solvent. 5; UV (methanol), λ_{\max} 219, 227, 236 (shoulder), and 260 (shoulder) nm; $^1\text{H NMR}$ (60 MHz, CCl_4), δ 1.20 (*s*, 2 \times 2 CH_3), 1.25 (*s*, 2 \times *t*-butyl), and

1.67 ppm (*s*, 2 \times 2 CH_3); Fluorescence spectrum (methanol), λ_{em} = 340 nm (λ_{ex} = 280 nm).

Results and Discussion

Photophysical properties of 1,4-Diphenyl-1,3-butadiyne. Conjugated poly-ynes exhibit characteristic absorption spectra with the most prominent feature being a very high intensity band with well-defined vibrational fine structures^{11, 12} which are attributed to the allowed $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ transition¹³. The UV absorption spectra show λ_{\max} at 325, 304, 285, 245, and 215 nm (ϵ_{\max} = ca. 10^4 / mol·cm) (Figure 1).

The molecules are parallel to each other in crystals and undoubtedly the index of refraction is greatest along the molecular axis and the absorption is polarized along the axis of the molecule¹⁴. The phosphorescence and its polarization of DPB were determined as shown in Figure 2.

No fluorescence was observed from DPB. According to beer,¹⁴ none of the poly-ynes with less than four triple bonds fluoresces except diphenylacetylene. The phosphorescence decay lifetime was 100 ms in *n*-hexane at 77°K, the same value that Beer has obtained in EPA (5 parts by volume of isopentane, 5 parts ether, 2 parts ethanol) at 103°K.

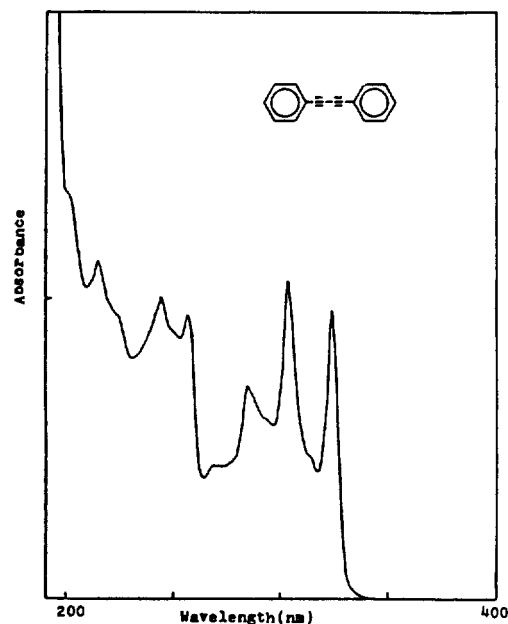


Figure 1. UV spectrum of 1,4-diphenyl-1,3-butadiyne in methanol.

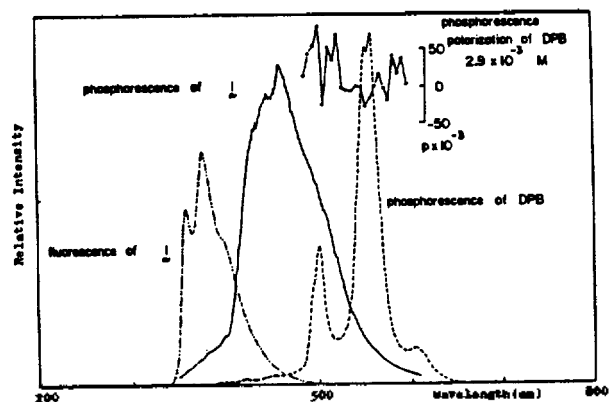


Figure 2. Fluorescence and phosphorescence of 1 in *n*-hexane and phosphorescence of DPB in *n*-hexane at 77 K.

Photoreaction of DPB with 2,3-Dimethyl-2-Butene. When a degassed *n*-hexane solution of DPB and 2,3-dimethyl-2-butene (TME), an electron rich olefin, is irradiated with 300 nm UV light for 175 hours, cross-cycloaddition products are obtained (Figure 3).

The reaction mixtures were analyzed by HPLC using diethyl ether-*n*-hexane (1:19 v/v) as an eluting solvent (Figure 4) and the products were isolated by low pressure preparative liquid chromatography using diethyl ether-*n*-hexane (1:19 v/v) and LiChroprep Si 60 (40-63 μm) prepacked column.

A new compound **1** does not show the typical polyacetylene vibrational bands^{11,12}. The new absorption band observed at 345 nm is due to the conjugation of the two phenyl rings at 1,4-position and a newly produced 1,3-diene moiety (see Sadtler UV 1088). The UV spectra of the compound **1**, 2,2'-diphenyl-1,1'-dicyclobutenyl, and 1,4-diphenyl-1,3-butadiene¹⁵ resembled each other. The infrared spectrum shows $\nu_{C=C}$ of cyclobutene at 1,573 cm^{-1} , ν_{C-H} and δ_{C-H} of methyl groups at 2,960-2,980 cm^{-1} and 1,360-1,400 cm^{-1} , respectively. The $\nu_{C=C}$ at 2,140 cm^{-1} of DPB disappeared. Cyclic compounds have various C=C stretching frequencies depending on the ring size and substituents. Cyclobutene, for example, has its C=C stretching mode at 1,565 cm^{-1} which is increased by substitution. Cyclopentene and cyclohexene have C=C stretching frequencies of 1,630 and 1,645 cm^{-1} , respectively. From the UV and IR spectral analyses, it is clear that a diene moiety is newly

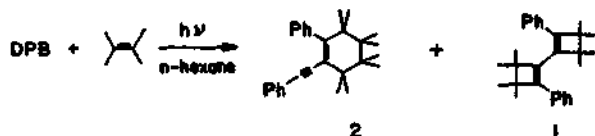


Figure 3. Photoreaction of DPB with TME in *n*-hexane.

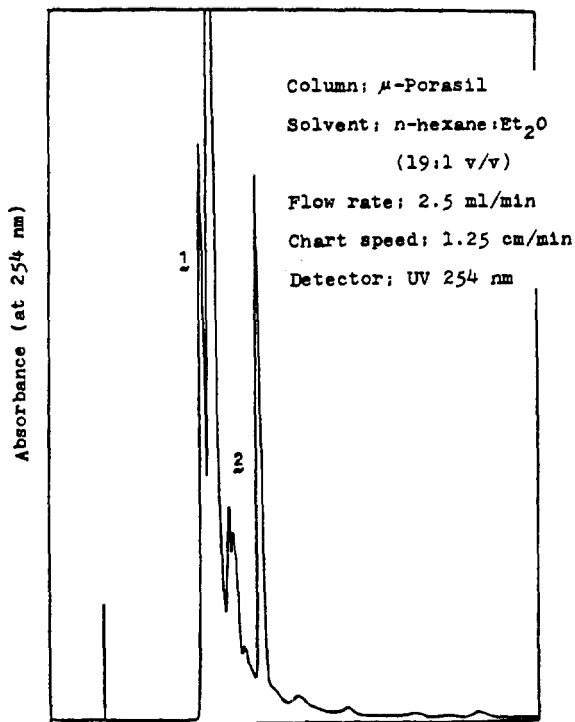
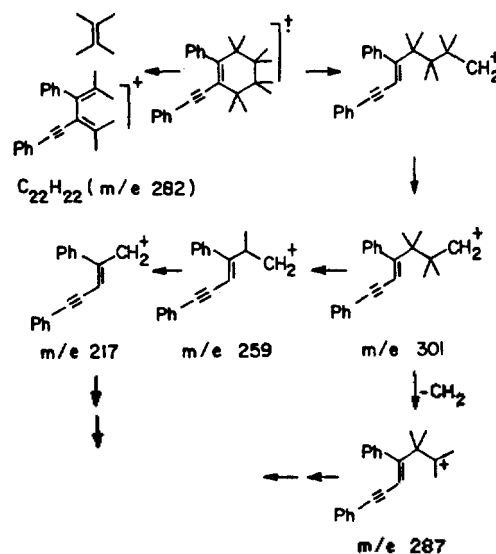


Figure 4. HPLC Analysis of the Photoreaction Mixtures of DPB and TME.

produced by addition of 2,3-dimethyl-2-butene to the triple bonds of DPB. The ¹H NMR spectra of **1** taken in chloroform-*d* show two kinds of methyl protons at 1.60 and 1.73 ppm, and phenyl protons at 8.27-7.33 ppm. The compound **1** fluoresces with fluorescence bands at 360 and 380 nm while the reactant DPB does not. The phosphorescence spectrum of **1** was taken at 77°K. The UV spectrum ($\lambda_{max} = 273$ and 300 (shoulder)) of the compound **2** is similar to those of *cis*-stilbene ($\lambda_{max} = 276$ nm in methanol)¹⁶ and 1,2-diphenyl-tetramethylcyclobutene ($\lambda_{max} = 277$ nm in *n*-hexane)¹⁷. The absorption bands of phenyl acetylene moiety are submerged in the absorption bands of *cis*-stilbene moiety. The IR spectrum shows the strong $\nu_{C=C}$ band at 2,185 cm^{-1} and $\nu_{C=C}$ cyclohexene at 1,640 cm^{-1} . The ¹H NMR spectrum taken in chloroform-*d* shows two groups of methyl protons at 1.50 ppm (3 and 6 position, α -position to the double bond) and 1.10 ppm (4 and 5 position, β -position to the double bond), and phenyl protons at 7.2-8.0 ppm(m). Because the difference between the chemical environment of the two groups of methyl protons in **2** is greater than that of **1**, the chemical shifts difference in **2** (0.4 ppm) is bigger than that of **1** (0.13 ppm). The chemical shifts of the two groups of methyl protons in **2** were also found at higher fields than that in **1**. The peak at *m/e* 286 in mass spectrum (EI, 70 eV), which can be produced by a retro-Diels-Alder reaction, is small (relative abundance 1.3). The steric strain of **2** containing a substituted cyclohexene ring moiety is smaller than that of **1** containing a substituted cyclobutene ring moiety. Hence, in the case of compound **2**, one single-bond cleavage of cyclic moiety prior to the cleavage of the highly branched carbon atom is possible. Peaks at 301, 287, and 217 may result from this kind of random rearrangement as hydrocarbons noted by the early spectrometrists in the petroleum industry (Scheme 1).

Base peak at *m/e* 105 can result from isobaric ions such as ethyl benzene ion and a random rearrangement product.

The excited singlet state of acetylene is known to be a *trans*-vinyl biradical¹⁸. The results obtained can be interpreted in terms of a biradical intermediate^{18,19} formed by biradical like excited alkyne attacking TME to form the vinyl biradicals which form the photoadducts on coupling.



Scheme 1. Random rearrangement of **2**.

Possibility of 1:1 photoadduct, 1-phenylacetylenyl-2-phenyl-tetramethylcyclobutene, is excluded on the basis of following observations; Fragmentation pattern below m/e 286 in mass spectra is quite different from that of 1 and the ratio of the number of the protons in ^1H NMR spectra is 10:12:12, not 10:6:6. The IR spectrum does not show $\nu_{\text{C}=\text{C}}$ of cyclobutene ring. 1,2-Diphenyl-tetramethylcyclobutene is in striking contrast of 2 which does not fluoresce.

The observation of only 2 kinds of methyl protons instead of 4 can be interpreted by means of the conformational isomerization of 2 at room temperature (Figure 5).

Photoreaction on DPB with 1,4-Cyclohexadiene. The photoreaction of DPB and 1,4-cyclohexadiene with 300 nm UV light produces a very interesting compound 3 (Figure 6)

The photoadduct was isolated by preparative thin layer chromatography using *n*-hexane as an eluting solvent. In the UV spectrum of the adduct, the longest wavelength vibrational band is observed at 333 nm (345 nm for DPB-TME photoadduct 1). This blue shift is attributed to the deviation of the chromophore from the planarity along the conjugated double bond. The IR spectrum shows the deformation mode of the cyclopropane ring at 1,030 and 840 cm^{-1} . The ^1H NMR spectrum of the photoadduct taken in chloroform-*d* proves the product to be a 1:2 photoadduct. The chemical shifts of methylene protons were deshielded to downfield due to the magnetic anisotropy of the benzene ring. The mass spectrum (EI, 70 eV) shows a molecular ion peak at m/e 362 which corresponds to the molecular weight of the photoadduct. The peaks at m/e 202 and 204 (100 %) prove the existence of DPB moiety.

Photoreaction of DPB with Dimethyl Fumarate. The degassed dichloromethane solution of DPB and dimethyl fumarate, an electron deficient olefin, was irradiated with 300 nm UV light. The analogous photoadduct to DPB-TME adduct was formed (Figure 7).

In the UV spectrum in methanol, the longest absorption band is found at 341 nm (345 nm for DPB-TME photoadduct 1). Small blue shift is attributed to the symmetry of the molecule which can counterbalance to a certain extent the electron-withdrawing

force of COOCH_3 groups. ^1H NMR spectrum in chloroform-*d* shows two kinds of cyclobutene ring protons at 4.03 ($d, J = 3$ Hz) and 4.17 ppm ($d, j = 3$ Hz). This coupling constant indicates that the two kinds of cyclobutene ring protons are located in the opposite direction to each other (about 90°C).

Fluorescence spectra were also observed for this adduct in methanol solvent. The fluorescence is a common property of the DPB-olefin photocycloadducts containing cyclobutene rings. Fluorescence emission spectrum in methanol at room temperature is shown along with those of DPB-TME, DPB-CH, and DPB-MCr photoadduct in Figure 8.

The fluorescence spectra are dependent upon the chemical structure of the fluorophore. From the fluorescence data in this study, the electron-withdrawing groups at the fluorophores give the blue-shifted fluorescence emission band (Figure 8).

The UV spectra of DPB-olefin photoadducts in methanol were measured at room temperature (Figure 9).

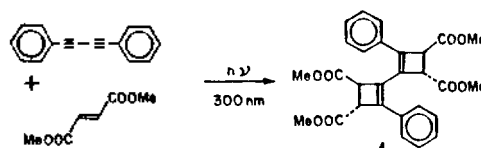


Figure 7. Photoreaction of DPB with dimethyl fumarate.

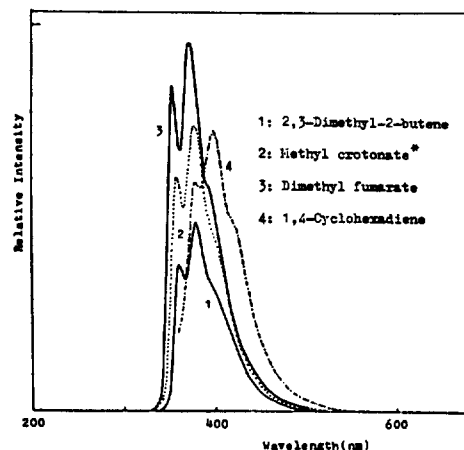


Figure 8. Fluorescence spectra of DPB-olefin Photoadducts.

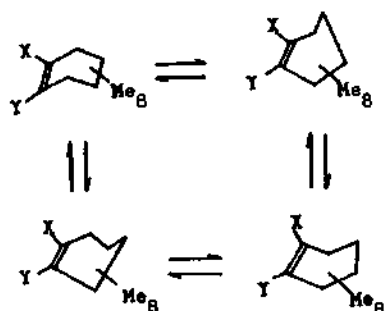


Figure 5. Suggested conformational isomerization of 2 at room temperature. X = Ph, Y = Ph-C \equiv C.

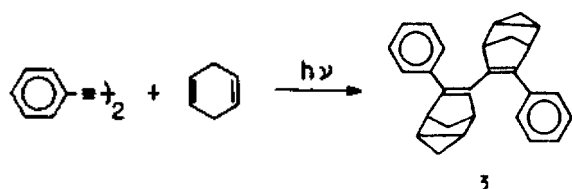


Figure 6. Photoreaction of DPB with 1,4-cyclohexadiene

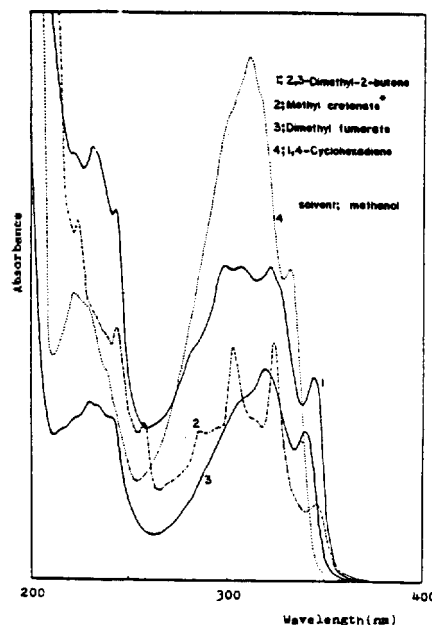


Figure 9. UV spectra of DPB-olefin photoadducts

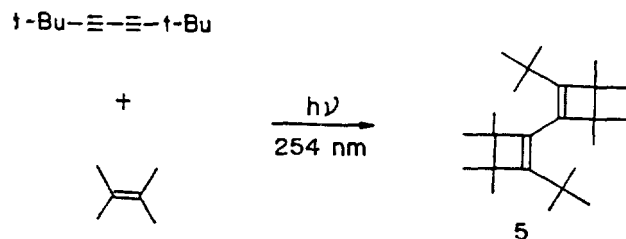


Figure 10. Photoreaction of DBB with TME in *n*-hexane.

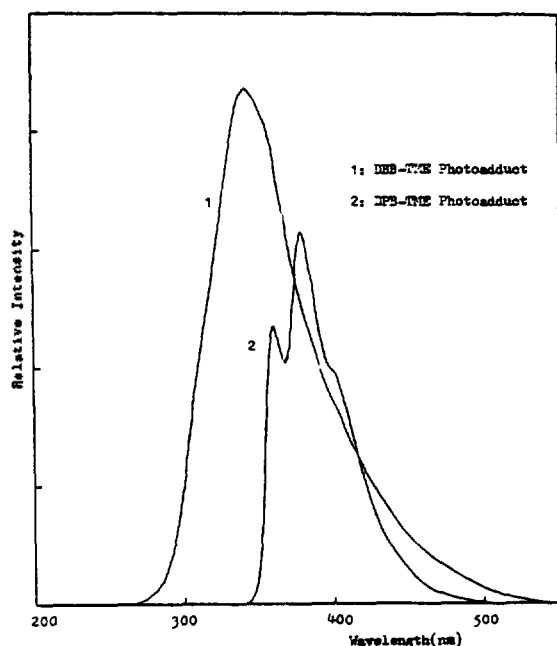


Figure 11. Fluorescence spectra of DBB-TME photoadduct and DPB-TME photoadduct in methanol. Each spectrum was measured in different concentration.

Photoreaction of DBB with TME. When a degassed *n*-hexane solution of DBB and TME is irradiated with 254 nm UV light for 15 hours, a cross-cycloaddition product 5 was obtained (Figure 10).

DBB, like DPB, shows the typical polyacetylene vibrational absorption bands at 215, 226, 238, and 251 nm in methanol. No fluorescence was found. Exposure for 15 hours using 254 nm UV light gave the fluorescence which was observed on the silica gel TLC plates. The fluorescence emission band for the photoadduct was observed at 340 nm (λ_{ex} 280 nm) (Figure 11).

All the [2+2] photocycloadduct of DPB and DBB with olefins gave fluorescence indicating that the [2+2] photoadducts containing cyclobutene rings are formed.

The fluorescence emission is a common property of the [2+2] photocycloadducts of DPB, and DBB, with some olefins.

These results suggest that the membrane damage may involve the modification of cellular DNA or RNA, possibly through the cycloaddition of polyacetylenes to pyrimidine bases of DNA or RNA.

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