mixed micelles, dyes may not be solubilized randomly, but prefer to occupy a position adjacent to another dye. This preferance is determined by the dye-dye interaction energy, which is larger in AO than in MB.

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Photoreaction of 1,4-Disubstituted-1,3-Butadiyne with Alcohol

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Irradiation of 1,4-diphenyl-1,3-butadiyne and 5,5-dimethyl-1-phenyl-1,3-hexadiyne with methanol yields 1:1 polar addition products, [E]- and [Z]-1,4-diphenyl-1-methoxy-1-buten-3-yne and [E]- and [Z]-5,5-dimethyl-1-methoxy-1-phenyl-1-hexen-3-yne, respectively. These geometrical isomers were converted into each other reaching the photostationary state on irradiation with 300 nm UV light. The photoaddition reaction of 1,4-diphenyl-1,3-butadiyne and 5,5-dimethyl-1-phenyl-1,3-hexadiyne with methanol seems to proceed from the zwitterionic lowest excited state.

Introduction

Certain naturally occurring conjugated polyacetylenes have been reported to be phototoxic to a variety of microorganisms, human skin fibroblasts, mosquito larvae, and Paramecium.[1-5] The examples are shown in Figure 1. In particular, 1-phenyl-1,3,5-heptatriyne(PHT), a polyacetylenic compouond isolated from Bidens pilosa L, does not induce cross-links in calf thymus DNA in the presence of UVA in contrast to 8-methoxypsoralen phototoxicity which involves cross-link in DNA.[1,6,7] Instead, phototoxic poly-ynes such as PHT exert their phototoxic action via the viral membrane damage and as a consequence the viral genome, DNA or RNA, is unable to replicate.[8] A mechanism involving free radical of PHT has been proposed.[9]
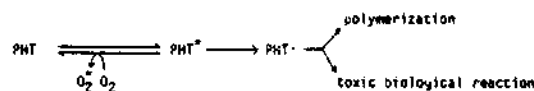
PHT by the absorption of photon leads to the formation of the excited state, PHT*, and the subsequent formation of free radical species PHT·. The toxic reaction and the polymerization reaction compete for the species and the excited state of PHT is also quenched by O_2 leading to the lower toxicity of PHT. But this mechanism does not show phototoxic sites and photoadducts of PHT with substrates. Nothing is definitely known yet about the photochemistry of conjugated polyynes except 1,4-dialkylsubstituted diynes which abstract hydrogen atom when they were irradiated in hydrogen donor solvents (pentane, cyclohexane, methylene dichloride, meth-

anol, isopropyl alcohol). One of the triple bonds of diyne is reduced to double bond.[10] This photoreduction reaction was reported to undergo via triplet state of conjugated diacetylene. The photoaddition reaction of 1,4-diphenyl-1,3-butadiyne(**1**) and 5,5-dimethyl-1-phenyl-1,3-hexadiyne(**2**) with methanol as a model reaction of PHT is investigated to give an insight into the mechanism of PHT phototoxicity.

A:

(1-Phenyl-1,3,5-heptatriyne : PHT)

B:

(trans-7-Phenyl-2-hepten-4,6-diyn-1-ol)

C: CH₃-CH=CH-(C≡C)₃-CH=CH-CHOH-CH₂OH

(3,11-Tridecadien-5,7,9-triyn-1,2-diol)

Figure 1. Natural phototoxic conjugated polyacetylenes.

Results and Discussion

Several 1,4-disubstituted-1,3-butadiynes were photolyzed in degassed methanol. Photoproducts were isolated and their structure was determined by various spectral data which are summarized in Table 1.

When a degassed methanol solution of 1,4-diphenyl-1,3-butadiyne(**1**) is irradiated with 300 nm UV light, photoadducts [Z]-1,4-diphenyl-1-methoxy-1-buten-3-yne(**3**) and [E]-1,4-diphenyl-1-methoxy-1-buten-3-yne(**4**) are obtained, **3** being the major product. The UV spectra of **1** and photoadducts are shown in Figure 2. Conjugated poly-ynes exhibit

characteristic electronic absorption spectra with the most prominent feature being a very high intensity band with well-defined vibrational fine structure. The photoadducts **3** and **4** do not exhibit these typical poly-yne bands. The major product **3** indicates that the preferred geometry of the lowest (π,π^*) singlet state of **1** is not linear but transoid zwitterionic species with ∠HCC angle of about 120°.[11] No photoadduct with 1:2 ratio of **1** to methanol indicates more efficient secondary photoreaction of the adduct than the methanol addition reaction. When **3** and **4** were irradiated with 300 nm UV light respectively, both **3** and **4** photoisomerized reaching the photostationary state with 54% of **3**. This result suggests the possibility of formation of **4** from **3** which is produced via more favorable zwitterionic lowest excited state of **1** through *trans-cis* photoisomerization. This mechanism of the photoaddition reaction of **1** with methanol is shown in Scheme 1. **1** is excited to give zwitterionic lowest excited state and subsequently zwitterionic species is protonated to give stable vinylium ion followed by addition of methoxy group to give **3** and **4**. The formation of vinylium ion was supported by the structure of photoadducts which is consistent with the structure formed by polar or Markownikoff addition of methanol to acetylene bond and the biradical type lowest excited state of **1** which will abstract hydrogen atom was excluded.

Irradiation of methanol solution of 5,5-dimethyl-1-phenyl-1,3-hexadiyne(**2**), an unsymmetrical diyne like PHT, leads to the formation of photoadducts like in **1**. The photoadducts are identified as [Z]-5,5-dimethyl-1-methoxy-1-phenyl-1-hexen-3-yne (**5**) and [E]-5,5-dimethyl-1-methoxy-1-phenyl-1-hexen-3-yne (**6**) on the basis of spectral analyses. The UV spectra of **2** and photoadducts are shown in Figure 3. In this reaction, **5**, was obtained as a major photoadduct supporting the transoid zwitterionic lowest excited state. The fact that methanol adds to the 1,2-position of **2** implies the contribution of phenyl substituent. The mechanism for the photoaddition reaction of **2** with methanol is shown in Scheme 2.

Since aryls containing α,β-unsaturated groups increase the basicity of the unsaturated groups markedly on excitation,[12]

Table 1. Spectral Data of 1, 2 and Their Photoadducts

no	¹H NMR(CDCl₃,δ)	IR(cm⁻¹)	UV(λmax,nm)	MS(m/e)
1	7.4(m,10H)	3065,2160,760,690ᵃ	326,304,286,257,244	202(M⁺)
3	7.2-7.8(m,10H),6(s,1H),3.9(s,3H)	3050,2950,2200,750,690ᵃ	325,314,286,258,245	234(M⁺),202 (M⁺-CH₂OH)
4	7.2-7.8(m,10H),6.3(s,1H),3.8(s,3H)	3050,2950,2220,760,690ᵃ	315,235	234(M⁺),202 (M⁺-CH₃OH)
2	7(m,5H),1.1(s,9H)	3080,2980,2250,750,690ᵇ	287,270,257,243,232,220	182(M⁺),167 (M⁺-CH₃),152 (M⁺-CH₂H₄)
5	7.2-7.8(m,5H),5.8(s,1H),3.9(s,3H), 1.4(s,9H)	3060,3000,2240,760,700ᵇ	290,230,224	214(M⁺),199 (M⁺-CH₃),184 (M⁺C₂H₄),167 (M⁺-CH₂H₇O)
6	7.2-7.8(m,5H),6.13(s,1H),3.8(s,3H), 1.4(s,9H)	3060,3000,2240,760,700ᵇ	285	214(M⁺),199 (M⁺-CH₃),184 (M⁺-C₂H₄),167 (M⁺-C₂H₇O)

ᵃ KBr pellet. ᵇ NaCl cell.

Table 2. Substituent Effect on the Photoaddition Reaction of 1,4-Disubstituted Diacetylenes(R-C≡C-C≡C≡R') with MeOH

no	R	R'	solvent	excitation wavelength(nm)	irradiation time(hr)	photoadducts
1	phenyl	phenyl	MeOH	300	120	**3 , 4**
2	phenyl	t-butyl	MeOH	300*	10	**5 , 6**
7	t-butyl	t-butyl	MeOH	254	120	no reaction
8	methyl	trimethylsilyl	MeOH	254	120	no reaction
9	trimethylsilyl	trimethylsilyl	MeOH	254	120	no reaction

* 450-w Hanovia medium pressure mercury arc lamp.
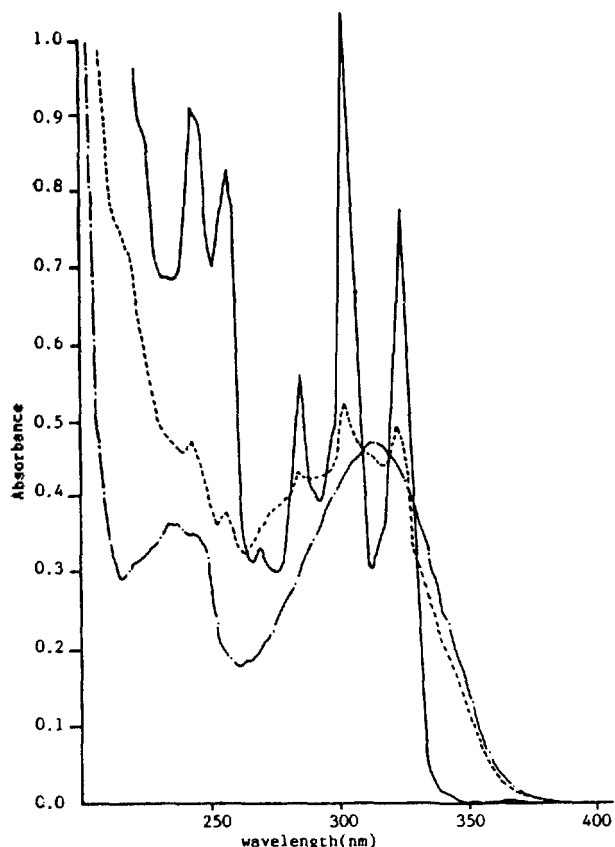
Figure 2. Ultraviolet absorption spectra of 1,4-diphenyl-1,3-butadiyne(1)(—), [Z]-1,4-diphenyl-1-methoxy-1-buten-3-yne(3)(---), and [E]-1,4-diphenyl-1-methoxy-1-buten-3-yne(4)(---) in methanol.

phenylsubstituted triple bond should be protonated more readily in the excited state than in the ground state and also more readily than the alkyl substituted triple bonds. Irradiation of 1,4-di-t-butyl-1,3-butadiyne, 1-methyl-4-trimethylsilyl-1,3-butadiyne, or 1,4-bis(trimethylsilyl)-1,3-butadiyne, with methanol does not give any methanol addition photoproducts. Table 2 suggests that the photoaddition reaction of 1,3-butadiyne with methanol require one or two phenyl substituents at the ends of conjugated diynes.

Experimental

Instruments. ¹H-Nuclear magnetic resonance spectra were run in CDCl₃ on a Varian T-60A spectrometer and Varian FT-80A spectrometer. Infrared spectra were obtained on a Perkin-Elmer 283B spectrophotometer in KBr pellets and NaCl cell. UV-VIS spectra were recorded on a Cary-17
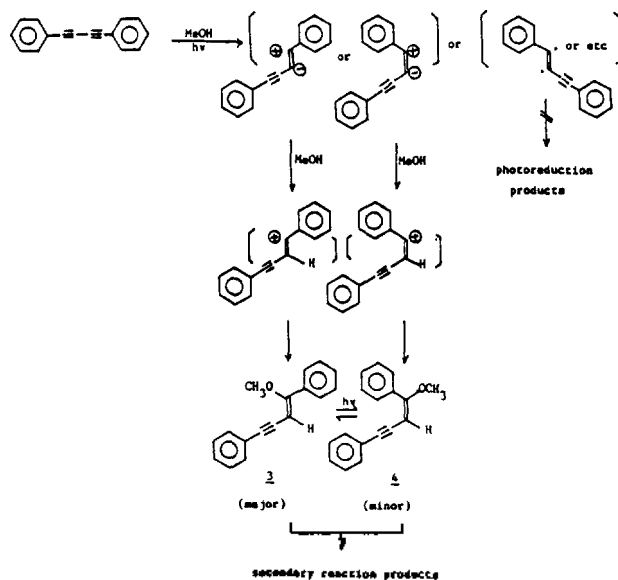
Scheme 1.

spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett Packard 5985A GC/MS system by electron impact method.

Materials. 1,4-Dimethyl-2-butyne, methyliodide, 3,3-dimethyl-1-butyne, phenylacetylene, trimethylsilylchloride, n-butyllithium (1.6M hexane solution), N,N,N',N'-tetramethylethylenediamine were purchased from Aldrich Chemical Co. and were used without further purification. [Z]-1-Methoxybut-1-en-3-yne was purchased from Fluka and was purified according to the literature procedure prior to use.[13]

Extra pure solvents were used as received or after purification by distillation or standard method.[14] The column chromatography was performed by using Kieselgel 60(Merck, 70-230 mesh). Preparative thin layer chromatography was conducted by using Kieselgel 60 GF₂₅₄(Merck) containing a fluorescent indicator.

Bromophenylacetylene(10) and 1,3-butadiyne(11) were prepared by the reported methods.[15,16]

5,5-Dimethyl-1-phenyl-1,3-hexadiyne(2) was prepared by Cadiot-Chodkiewicz coupling method from bromophenylacetylene and 3,3-dimethyl-1-butyne. Yield: 45%.

2,2,7,7-Tetramethyl-1,3-octadiyne(7) was prepared by reported Hay coupling method. Yield: 85%.

1-Trimethylsilyl-1,3-pentadiyne(8) – (a) A solution of (11)(30 mmol) in THF(60 ml) was treated with n-BuLi(30 mmol) at -78°C. After 5 min Me₃SiCl(32 mmol) was added slowly, and the mixture was warmed to room temperature and set aside for 20 min. The mixture was cooled down to -78°C

Scheme 2.

Figure 3. Ultraviolet absorption spectra of 5,5-dimethyl-1-phenyl-1.3-hexadiyne(**2**)(—), [Z]-5,5-dimethyl-1-methoxy-1-phenyl-1-hexen-3-yne(**5**)(---), and [E]-5,5-dimethyl-1-methoxy-1-phenyl-1-hexen-3-yne(**6**)(---) in methanol.
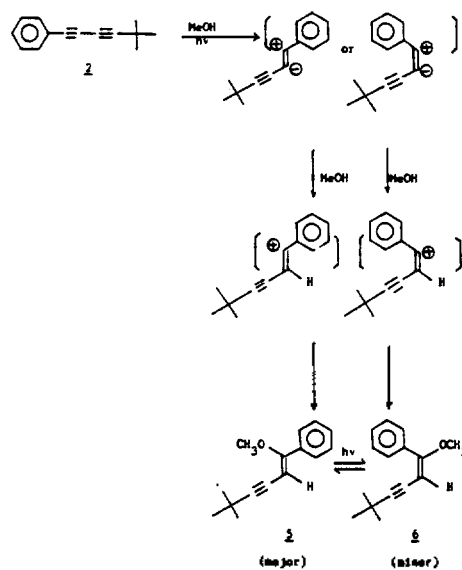
again and n-BuLi(30 mmol) was added slowly with stirring. After 5 min CH_3I(32 mmol) was added and the mixture was warmed to room temperature and stirred for 2 hr before being worked up. Crude product was purified by vacuum distillation. bp. 35°C(5 torr) Yield: 80%. (b) A solution of [Z]-1-methoxybut-1-en-3-yne (30 mmol) which was purified according to the literature procedure in THF(60 m*l*) was sequentially treated with n-BuLi(30 mmol) at -78°C followed by Me_3SiCl (32 mmol). The mixture was warmed to 0°C and stirred for 2 hr. **8** was prepared by sequential treatment of mixture at -40∿ -45°C with n-BuLi (60 mmol) during 30 min followed by CH_3I(62 mmol) the resulting reaction mixture was warmed to room temperature and stirred for 2 hr before worked up. Yield: 80%.

1,4-Bis(trimethylsilyl)-1,3-butadiyne(9) was prepared by reported method[18] similar to the preparation of **8**.

Irradiation of 1 with methanol. Degassed 2 mM methanol solution of **1**(200 mg) was irradiated with 300 nm UV light in a Rayonet Photochemical Reactor Model RPR-208 equipped with RUL-3000Å lamps. After the irradiation for 120 hr, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, **3** and **4**, were isolated by preparative thin-layer chromatography using n-hexane as an eluting solvent followed by column chromatography using diethylether-n-hexane (1:20) as an eluting solvent. Their spectral data were shown in Table 1.

Irradiation of 2 with methanol. Degassed 4 mM methanol solution of **2**(290 mg) was irradiated with 450-w Hanovia medium pressure mercury arc lamp fitted into a quartz immersion probe for 10 hr, distilled in vacuo and the distillate was separated by preparative thin-layer chromatography three times using n-hexane as an eluting solvent. The resulting photoadducts, **5** and **6**, were further purified by column chromatography using diethylether-n-hexane(1:20) as an eluting solvent. Their spectral data are summarized in Table 1.

Irradiation of 7,8,9. Degassed 2 mM methanol solutions of **7,8,9** were irradiated with 254 nm UV light in a Rayonet Photochemical Reactor Model RPR-208 equipped with RUL-2537Å lamps for 120 hr. These reaction mixtures give no photoproduct.
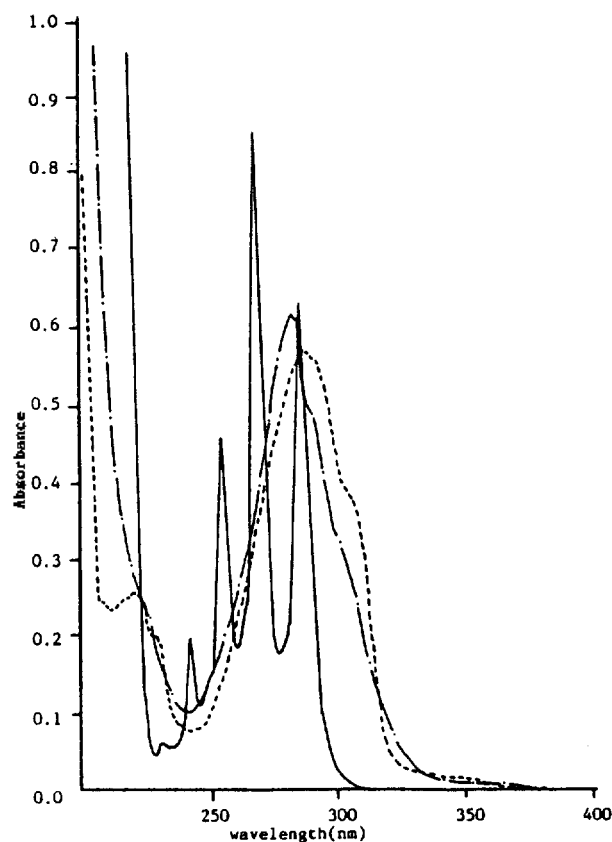
Photoisomerization of 3 and 4. Deuterated chloroform ($CDCl_3$) solutions of **3** and **4** in NMR tube were irradiated with 300 nm UV light, respectively. In this experiment the changes of NMR peak ratio of **3** and **4** versus time were detected.

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Photoelectron Transport Across Phospholipid Liposomes Pigmented by Anthracene and Naphthalene Derivatives

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In order to investigate effective solar energy conversion system, the light-induced electron transfer reactions have been examined across single-lamellar liposomes incorporated organic photosensitizers such as anthracene and naphthalene derivatives. We have observed photosensitized reduction of methyl viologen (1,1'-dimethyl-4,4'-bipyridinium^{2+}) dissolved in the exterior aqueous phase of the pigmented phospholipid liposomes when EDTA, as electron donor, is dissolved in the enclosed aqueous phase of the liposomes. The anthroyl stearic acid incorporated in the hydrophobic bilayer of liposomes leads to much less quantum yield for the photosensitized reduction of MV^{2+} than the anthracene carboxylate incorporated in the outer hydrophilic layer. However, β-carotene with anthroyl stearic acid incorporated into the bilayer enhances the quantum yield significantly (Φ=0.2-0.3), preventing the reverse reaction of electron transfer (MV: $\rightarrow MV^{2+}$) so that it might be useful for solar energy conversion into chemical energy. A naphthalene derivative, octadecyl naphthylamine sulfonic acid incorporated into the outer layer of liposomes results in less efficiency of MV^{2+} reduction than anthroyl stearic acid. These results have been also tested with respect to lipid components of liposomes.

Introduction

Scientists have focussed their attention to photobiological solar energy conversion to estimate the possibility of obtaining electrical and chemical energy from sunshine. The green plant is the typical photobiological system which converts quanta into chemical energy with high degree of efficiency and store them long enough to do some chemistry.[1-8] The photosynthetic systems(PS) I and II of green plant reside in the green chloroplast which is a membranous structure consisted of lipid bilayer. The green pigment absorbs the sunlight and separates the positive and negative across the thylakoidal membrane during the process of electron transport. The separated charges can be used for oxidizing water in the PS I or reducing carbon dioxide in the PS II through Calvin cycle.[2,5]

The natural photosynthesis has been stimulated in several laboratories by using pigmented artificial lipid membranes such as lipid vesicles (liposomes) and black lipid membranes (BLM).[9-13] Recent works have shown that BLM or liposomes containing photosensitizers(PHS) such as chlorophyll or ruthenium bipyridine(Ru(bpy)$_3^{2+}$) exhibit interesting photoelectron transfer across the bilayer of membrane from electron donor (D) site to electron acceptor site(A), and subsequently generates D* and A⁻(see scheme I).
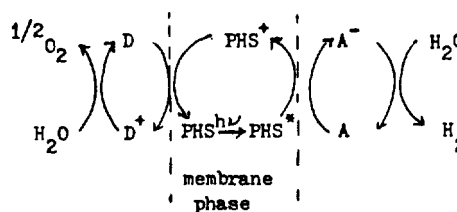
Scheme I.

This system has been expected to show that the forward photoelectron transfer (PHS* + A → PHS⁺ + A⁻) is efficient and the back reaction is obviated to be useful for reduction of H$_2$O in the presence of a certain catalyst.[14] However, there are still some obstacles to be overcome to use that system for practical purpose. First, the efficiency of the forward reaction is relatively lower than in homogeneous solution. Even if the efficiency is increased, the back reaction is also enhanced. Thus, the artificial photosystem should be optimized by better combination of a proper photosensitizer and lipid component. Secondly, the artificial lipid membranes are not so stable, and it is necessary to develop more stable synthetic lipid-like polymer.

Hopefully to solve these problems, we have tried to develop ever more improved models for light-sensitized electron