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Photoaddition Reactions of *p*-Quinones to Conjugated Diyne

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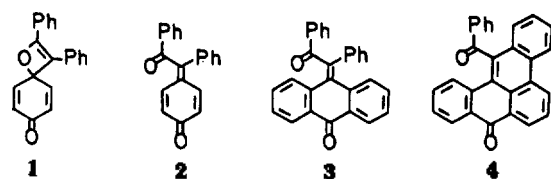
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Irradiation of solutions of *p*-quinones and conjugated diyne, 1,4-diphenylbutadiyne, with 350 nm UV light gave the photoproducts such as quinomethane in good yields (70-85%).

Introduction

The photochemical addition of *p*-quinones to compounds containing olefinic or acetylenic linkages has been the subject of a number of publications.¹⁻¹¹ Photodimerization of *p*-benzoquinone and some of its methyl derivatives gives either cyclobutanes or spiro-oxetanes depending on the nature of the quinone.^{1,4} The photoaddition of diphenylacetylene to *p*-benzoquinone forms a quinomethane (**2**), through an unstable intermediate, spiro-oxetene(**1**). Tetrachloro-*p*-benzoquinone (chloranil) readily forms a novel photorearrangement product by the photoreaction with some cyclic olefins.¹² Irradiation of the quinonoid compounds and diphenylacetylene in dichloromethane gives the photoproducts, such as **2,3**, or **4**.^{1,3,13,15}



Scheme 1

Irradiation of the anthraquinone methide(**3**) causes dehydrocyclization to give the corresponding benzanthrone (**4**).¹⁴

In our previous studies, the photoaddition of diphenyl-

acetylene to anthraquinone forms (**4**) besides (**3**) (ca. 1:1, molar ratio).¹³ Irradiation of a solution of anthraquinone, diphenylacetylene and iodine in dichloromethane gave (**4**) as a major product, and (**3**) as a minor product.¹³ The photoproduct (**3**) readily undergoes dehydrocyclization to (**4**) during the purification by the column chromatography (silica gel).¹³ The photoreaction of anthrone and diphenylacetylene in dichloromethane afforded the photooxidation products such as (**3**), (**4**) and the dimer in air.¹³ We now report that irradiation of conjugated diyne, such as diphenylbutadiyne, and *p*-quinones gives 1:1 photoadducts as the major products.

Experimental

Materials. Dichloromethane, acetonitrile, *n*-hexane, benzene, diethyl ether, ethyl acetate and methanol were purified before use. *p*-Benzoquinone, chloranil, anthraquinone, dicyclopentadiene and diphenylbutadiyne were purchased from Aldrich Chemical Company. The column chromatography was performed by using Kiesel gel (Merck Co., 70-230 mesh). Kiesel gel 60 F254 (Merck Co., silica gel) was used for the thin layer chromatography.

Instruments. Infrared spectra were recorded on a Perkin-Elmer 283B Grating Spectrophotometer in KBr pellets. ¹H-NMR spectra were obtained on a Bruker AC-100 Spectrometer. Mass spectra were obtained on a Jeol GC/MS

system (JMS-DX 300) using electron impact(EI) method. UV spectra were recorded on a Hitachi 556 Spectrophotometer. Fluorescence spectra were obtained on a JASCO Spectrofluorometer (FP 770).

Irradiation Apparatus. Irradiation was carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company, Model RPR 208) equipped with 350 nm UV lamps. The progress of the photoreactions was monitored by the precoated TLC (silica gel, Kiesel gel 60 F254, Merck Co.; UV visualization).

Photoreactions of *p*-Quinones with Diphenylbutadiyne

Irradiation of *p*-Benzoquinone with Diphenylbutadiyne. 648 mg(6.0 mmol) of *p*-benzoquinone and 404 mg(2.0 mmol) of diphenylbutadiyne dissolved in 100 ml of acetonitrile was degassed with nitrogen gas for 30 min and irradiated with 350 nm UV light for 24 hours. The progress of the photoreaction was monitored by pre-coated TLC plates (silica gel, Kiesel gel HF-254, Merck Co.) using *n*-hexane-ethyl acetate (4:1, v/v) as an eluting solvent. Removal of the solvent in vacuo left a yellow oil, which was chromatographed on silica gel using *n*-hexane-ethyl acetate (4:1, v/v) as an eluting solvent (isolation yield, 85%). **5:** UV(MeOH), mp 117°C; λ_{max} = 380 and 232 nm; IR(KBr), 3080-3020(ν_{CH} , aromatic), 2140($\nu_{C\equiv C}$), 1670 and 1630 cm^{-1} ($\nu_{C=O}$); 1H -NMR(100 MHz, $CDCl_3$), δ = 8.25-7.20(m, aromatic), 6.78-6.35 ppm(vinyl); Mass (EI), m/e = 310(M, $C_{22}H_{14}O_2$), 282(M-CO), 205(M- C_6H_5CO) 105(100%, C_6H_5CO) and 77(C_6H_5).

Irradiation of Chloranil with Diphenylbutadiyne. 738 mg(3.0 mmol) of chloranil and 404 mg(2.0 mmol) of diphenylbutadiyne dissolved in 400 ml of dichloromethane was degassed with nitrogen gas for 30 min and irradiated with 350 nm UV light for 17 hours. The photoproduct (**6**) was isolated by the column chromatography using *n*-hexane-diethyl ether (8:1, v/v) as an eluting solvent (isolation yield, 80%). **6:** UV(MeOH), mp 176°C; λ_{max} = 315, 290 and 245 nm; IR(KBr), 3060-3020 (ν_{CH} , aromatic), 2140($\nu_{C\equiv C}$), 1694 and 1683 cm^{-1} ($\nu_{C=O}$); 1H -NMR(100 MHz, $CDCl_3$), δ = 8.40-7.35 ppm (m, 10H); Mass(EI), m/e = 446(M), 105(100%, C_6H_5CO) and 77(C_6H_5).

Irradiation of Cyclopentadienbenzoquinone with Diphenylbutadiyne. 500 mg(3.5 mmol) of cyclopentadienebenzoquinone was synthesized as following; 3.48 ml of cyclopentadiene, which was obtained from distillation of dicyclopentadiene, was added to a solution of 5.0g of *p*-benzoquinone in 300 ml of benzene. The solution was stirred at 40°C for 4 hours. After the reaction was completed, the solvent was concentrated with a rotary evaporator and the crude product was obtained in 98% yields and was recrystallized from *n*-hexane in 90% yields. The structure of the product was identified by the following spectral data: UV(MeOH), λ_{max} = 225 nm; IR(KBr), 3060(ν_{CH} , vinylic), 2980-2880(ν_{CH} , aliphatic), and 1670($\nu_{C=O}$); 1H -NMR($CDCl_3$), δ = 6.53(2H), 6.05(2H), 3.55(2H), 3.25(2H) and 1.60 ppm(2H); Mass (EI), m/e = 174(M), 146(M-CO) and 66(100%, C_5H_6). 500 mg(3.5 mmol) of cyclopentadienebenzoquinone and 517 mg(2.6 mmol) of diphenylbutadiyne dissolved in 150 ml of acetonitrile was degassed with nitrogen gas for 30 min and irradiated with 350 nm uv light for 24 hours. The photoproduct (**7**) was isolated by the column chromatography(silica gel) using *n*-hexane-diethyl ether-dichloromethane(4:1:1, v/v/v) as

an eluting solvent(isolation yield, 76%).

7: UV(MeOH), mp 102°C; λ_{max} = 340 and 265 nm; IR(KBr), 3060(ν_{CH} , vinylic), 2980-2880 (ν_{CH} , aliphatic), 1675 and 1670 cm^{-1} ($\nu_{C=O}$); 1H -NMR($CDCl_3$), δ = 8.07-7.24(aromatic), 6.67-6.30(2H), 6.03(2H), 3.60(2H), 3.27(2H) and 1.52 ppm(2H); Mass(EI), m/e = 310(M-66(C_5H_6)), 282(310-CO), 205(310- C_6H_5CO), 105(100%, C_6H_5CO) and 77(C_6H_5).

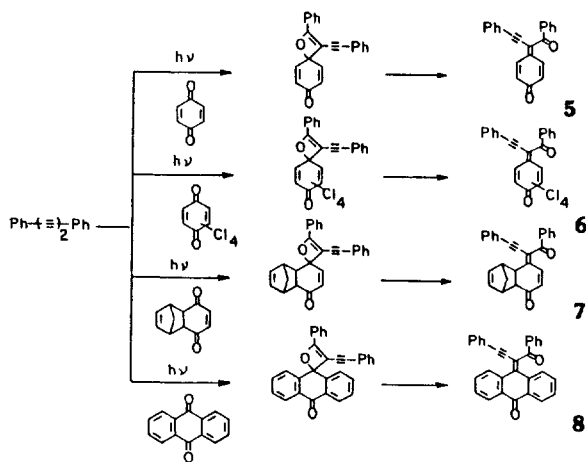
Irradiation of Anthraquinone with Diphenylbutadiyne.

1.0g(4.8 mmol) of anthraquinone and 855 mg(4.0 mmol) of diphenylbutadiyne dissolved in 300 ml of benzene was degassed with nitrogen gas for 30 min and irradiated with 350 nm UV light for 48 hours. The photoproduct (**8**) was isolated by the column chromatography (silica gel) using *n*-hexane-diethyl ether-ethyl acetate (8:1:1, v/v/v) as an eluting solvent(isolation yield, 72%).

8: UV(MeOH), mp 360°C; λ_{max} = 385, 314 and 240 nm; IR(KBr), 2180($\nu_{C\equiv C}$) and 1672-1670 cm^{-1} ($\nu_{C=O}$); 1H -NMR ($CDCl_3$), δ = 8.84-7.14 ppm(m, aromatic); Mass(EI), m/e = 410(M), 382(M-CO), 305(M- C_6H_5CO), 105(100%, C_6H_5CO) and 77(C_6H_5).

Results and Discussion

The photoaddition of *p*-quinones to olefins or alkynes has been reported as a widely-applicable reaction.¹⁻¹² The photoaddition of diphenylacetylene to *p*-benzoquinone forms a quinomethane(**2**), through an unstable intermediate, spiro-oxetene(**1**). Certain 1,3-diene undergoes 1,4-addition of *p*-benzoquinone to give spiro-pyrans.¹⁶



Scheme 2

Although photocycloadditions of alkynes with *p*-quinones have been extensively investigated, any example of the reactions involving the photoaddition of *p*-quinones to conjugated diene has not been described in the literature. Irradiation of a degassed acetonitrile solution of *p*-benzoquinones and diphenylbutadiyne with 350 nm UV light gave a photoproduct (**5**), not (**10**). It can be seen that the 1:1 photoadduct is formed via a more stable intermediate. The absorption band at longer wavelength (380 nm) of the product (**5**) is due to the extended conjugation. The IR spectrum of the 1:1 adduct shows two C=O stretching bands at 1670 cm^{-1} and 1630 cm^{-1} , and C≡C stretching band at 2140 cm^{-1} . The mass spectrum of (**5**) exhibited, in addition to the parent system at m/e 310, peaks at m/e 282(M-CO), 205(M- C_6H_5CO), 105(100%, C_6H_5CO) and 77(C_6H_5).

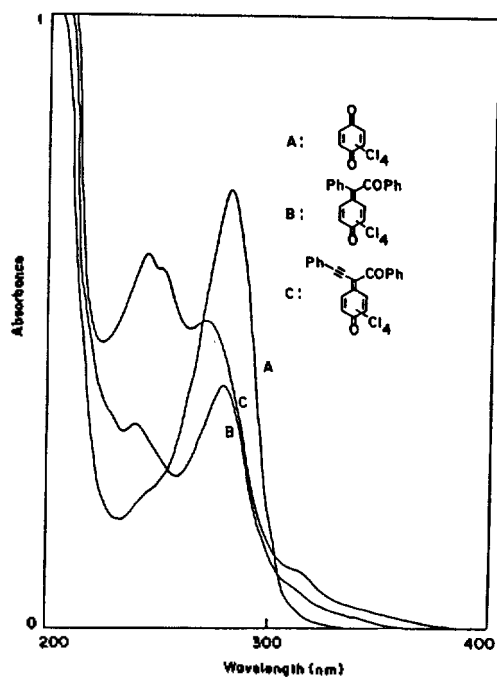


Figure 1. UV spectra of chloranil(A), chloranil-diphenylacetylene adduct(B), and chloranil-diphenylbutadiyne adduct(C) in methanol.

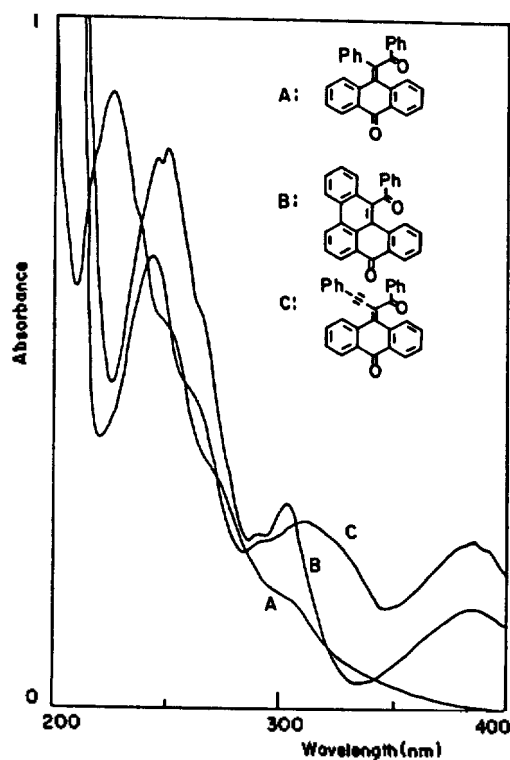
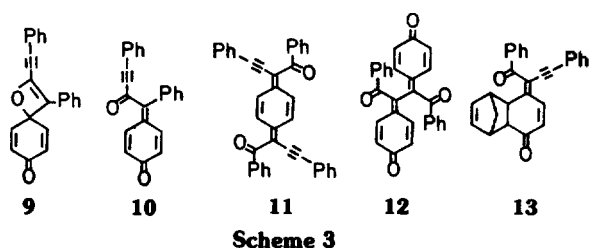


Figure 2. UV spectra of 3(A), 4(B), and 8(C) in methanol.



An alternative structure (10), which can be formed via an intermediate (9), or 1:2 adducts (11 or 12) were not shown in this reaction. Irradiation of a dichloromethane solution of chloranil and diphenylbutadiyne with 350 nm UV light gave a photoproduct (6). The IR spectrum of (6) exhibited two C=O stretching bands at 1694 cm^{-1} and 1683 cm^{-1} . The inductive effect by the electronegative chlorine atoms moves the absorption bands to the short wavelength. A strong C \equiv C stretching band of the 1:1 adduct (6) is observed at 2141 cm^{-1} in the IR spectrum. The peaks at m/e 105 and m/e 77 prove the existence of benzoyl group. The UV spectra of chloranil, the photoproduct of chloranil and diphenylacetylene, and the photoproduct of chloranil and diphenylbutadiyne are shown in Figure 1.

Cyclopentadienebenzoquinone was obtained in Diels-Alder reaction of *p*-benzoquinone with cyclopentadiene. When a degassed acetonitrile solution of cyclopentadienebenzoquinone and diphenylbutadiyne is irradiated with 350 nm light, a quinomethane product (7) is obtained as a major product. The absorption band at the longer wavelength (340 nm) of the product (7) is also due to the extended conjugation. The IR spectrum shows two C=O stretching bands at 1675 cm^{-1} and 1670 cm^{-1} , and C \equiv C stretching band at 2190 cm^{-1} . The $^1\text{H-NMR}$ spectrum of (7) shows two kinds of vinyl protons at 6.54 ppm (d, of d., 2H) and 6.03 ppm (s, broad, 2H). The two kinds of vinyl protons of cyclopentadienebenzoquinone appear at 6.53 ppm (s, enone moiety)

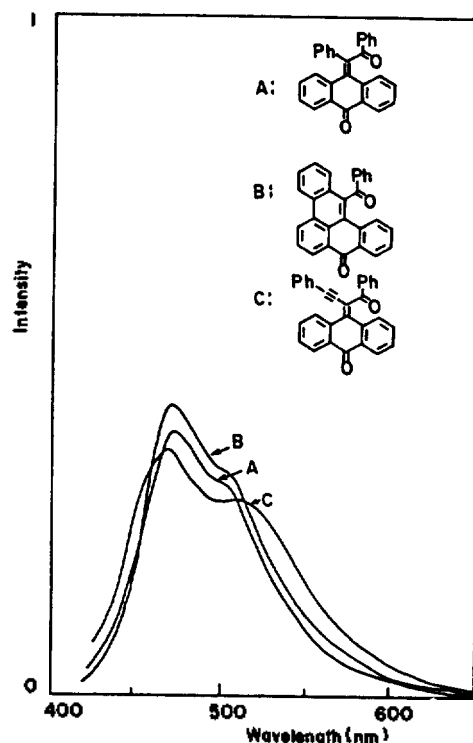


Figure 3. Fluorescence spectra of 3(A), 4(B), and 8(C) in methanol.

ty) and 6.05 ppm (s). The splitting situation (d, of d., two vinyl protons of enone moiety) of the photoproduct (7) shows the disappearance of plane of symmetry. From the above results, an alternative structure (13) was excluded, in which the two vinyl protons of enone moiety will be appeared as a broad singlet peak at ca. 6.5 ppm.

When irradiated with 350 nm UV light, diphenylbuta-

diyne reacted with anthraquinone to give the same type of 1:1 adduct (**8**). The UV spectra and fluorescence spectra of the photoproducts (**3**, **4**, and **8** are shown in Figure 2 and Figure 3, respectively.

The IR spectrum of (**8**) shows the two C=O stretching bands at 1672 cm⁻¹ and 1670 cm⁻¹, and C≡C stretching band at 2180 cm⁻¹. The mass spectrum of (**8**) showed the molecular ion peak at *m/e* 410. The peaks at *m/e* 105 and *m/e* 77 prove the existence of benzoyl group.

From the above results, conjugated diene, such as diphenylbutadiyne, reacts with *p*-quinones to give 1:1 photoadducts. No 1:2 adduct, such as (**11**) and (**12**), was found in these reactions. The fluorescence of *p*-benzoquinone was quenched by diphenylbutadiyne. A plot of ϕ_f/ϕ_F versus [diphenylbutadiyne] is linear with intercept equal to 1.0 and slope ($k_q\tau$) equal to 265 M⁻¹. The values of the slope were 107, 20 and 0.85 M⁻¹ for chloranil, anthraquinone and thioxanthone, respectively. In fact, the reactivity of thioxanthone toward diphenylbutadiyne was very low.

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Effects of SDS and Temperature on the Structural Changes of Bacteriorhodopsin

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Effects of SDS and temperature on the conformational changes of bacteriorhodopsin were studied using a, b, c bands of bacteriorhodopsin. In the SDS denaturation, bacteriorhodopsin in purple membrane was more labile than bacteriorhodopsin reconstituted into PC vesicles. These rather interesting results may be understood by effective SDS concentration in lipid layer.

Introduction

Bacteriorhodopsin (BR), a photoactive protein in purple membrane of *Halobacterium halobium*, has three absorption bands in the visible and near-UV: a band ($\epsilon = 63000 \text{ M cm}^{-1}$) at 570 nm, b band which lacks a clear maximum between 450 nm and intense band at 280 nm¹. Both a and b bands are due to the retinyl chromophore and band to the aromatic protein residue, tyrosine and tryptophan².

BR has "inside-out" structure of which the hydrophobic amino acid residues are located in the outside of protein³. The hydrophobic interaction of those nonpolar residue and ionic interactions among inside polar amino acid residue con-

tribute to the stability of BR⁴. As the environment around BR is perturbed, the stability of BR is altered via the change in above interaction. In extreme condition the denaturation of BR occurred. Sodium dodecyl sulfate (SDS) is often used as a means of denaturation of protein^{5,6}.

In present investigation, BR was incorporated into the phosphatidyl choline vesicle and change in stability of BR was observed using SDS and temperature.

Materials and Methods

Halobacterium halobium R1 was obtained from American type Collection, Rockford, MD, U.S.A.. L- α -phosphatidyl