PHOTOADDITION REACTIONS OF 1,4-DIPHENYLBUT-1-EN-3-YNE TO QUINONES

Sung Sik Kim[1]*, Ae Rhan Kim[1], Ji Ae Chang[1], Yoon Jung Mah[1], Jin Sun Lim,[1]
Dong Jin Yoo[2] and Il Cheol Jeon[1]
[1]Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea
[2]Department of Chemistry, Seonam University, Namwon 590-170, Korea

Abstract − Irradiation of 1,4-diphenylbut-1-en-3-yne 1 and some *p*-quinones in dichloromethane with 300 nm UV light yielded two types of adducts, *i.e.*, *p*-quinomethanes and cyclobutanes, in which the former were produced via the rearrangement of the initially formed spiro-oxetene intermediates. On the other hand 1 added to *o*-quinones to give three types of adducts, *i.e.*, 1,3-dienes, 1,4-dioxenes, or spiro-oxetanes, in which the former were found to be applied to synthesize phenanthrene derivatives. A methoxy derivative of enyne 39 was synthesized to investigate the type of the photoaddition to *o*-quinones, in which 1,4-dioxenes were obtained.

INTRODUCTION

Quinones are an important class of compounds as quinone dye-stuffs in industry or dehydrating agents in organic synthesis in addition to a vital role in biological systems.[1,2] 1,4-Quinones are a special example of cross-conjugated enediones, whereas 1,2-quinones can be compared dienediones. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas. *p*-Quinones are known to add photochemically to olefins to give spiro-oxetanes (*type* A adducts) and/or cyclobutanes (*type* B adducts), as shown in Scheme 1.[1-3] Various alkynes are also known to add to *p*-quinones to give spiro-oxetenes or cyclobutenes, which undergo rearrangement to give *p*-quinomethanes and the electrocyclic reactions, respectively.[1,2,4-7] Interestingly, some *p*-quinomethanes were found to be produced from the photoaddition reactions of *o*-quinones to diphenylacetylene in dichloromethane.[8]

o-Quinones are known to add to olefins to give 1,3-cyclo-
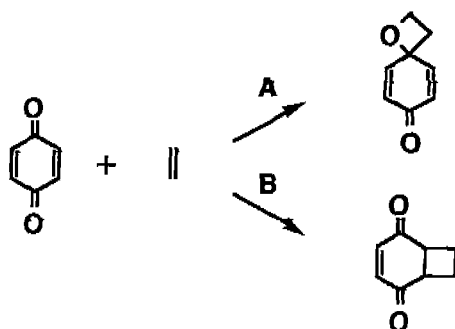
Scheme 1. Two representative types of photoadducts of *p*-quinones to olefins.

hexadienes (type C adducts), 1,4-dioxenes (type D adducts), and spiro-oxetanes (type E adducts), as shown in Scheme 2.[1,2,9] Alkynes generally add to *o*-quinones to give types D and E adducts, in which the latter undergo rearrangement to give *o*-quinomethanes.[1,2,8,10] The formation of *o*-quinomethanes was applied to a novel oxidative phototetramerization reactions of 1,4-diethynylbenzene.[10]

Our interest in the diverse reactivities of excited quinones has promoted us to investigate the type of the photoadducts of some quinones to enyne systems, such as 1,4-diphenyl-but-1-en-3-yne 1 and a methoxy derivative of the enyne 39, having one carbon-carbon double bond and one carbon-carbon triple bond conjugated with each other.
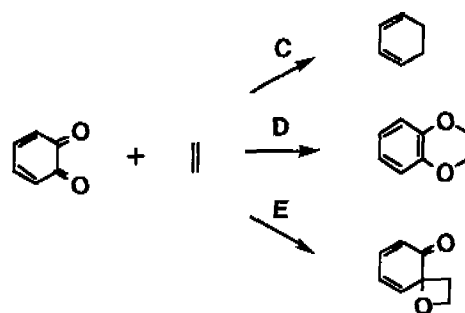
Scheme 2. Three representative types of photoadducts of *o*-quinones to olefins.

MATERIALS AND METHODS

Materials. The following quinones were purchased from Aldrich Chemical Company and used as received or recrystallized prior to use: tetrachloro-1,4-benzoquinone, tetrabromo-1,4-benzoquinone, 1,4-naphthoquinone, anthraquinone, tetrachloro-

---

*To whom correspondence should be addressed.

1,2-benzoquinone, tetrabromo-1,2-benzoquinone, 9,10-phenan-threnequinone, and acenaphthenequinone. 1,4-Diphenylbut-1-en-3-yne was synthesized from β-bromostyrene and phenylacety-lene.[11] Dichloromethane, n-hexane, ethyl acetate, and benzene were distilled prior to use. Silica gel (Kieselgel 60, 230-400 mesh, Merck Company) was used for column chromatography. Analytical thin layer chromatography (TLC) plates were purchased from Merck Company as aluminum sheets (20 × 20 cm) precoated with 0.25 mm silica gel together with fluorescent indicator.

Instruments. ^{1}H NMR spectra were recorded on a Jeol JMN EX NMR spectrometer. Chemical shifts δ were reported as ppm downfield from internal tetramethylsilane (TMS) standard. Infrared (IR) spectra were recorded on a Nicolet 5-DX 13 Fourier Transform spectrophotometer in KBr pellets or NaCl cells. Ultraviolet (UV) spectra were obtained on a Beckman DU 7500 spectrophotometer. Mass spectra were determined on a Hewlett Packard 5985 GC/MS system using electron impact method.

General procedure for the photocycloaddition Reactions. Preparative photoreactions were conducted in a photoreactor composed of a water-cooled inner condenser and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging with nitrogen gas (purity; 99.9%) for 30 min. The reaction was followed by TLC for disappearance of the starting materials. After irradiation with UV light, the reaction mixture was concentrated in vacuo and chromatographed over silica gel with n-hexane and ethyl acetate as the eluent.

Irradiation of 1,4-diphenylbut-1-en-3-yne and duroquinone. 1,4-Diphenylbut-1-en-3-yne (408 mg, 2.0 mmol) and duroquinone (164 mg, 1.0 mmol) in dichloromethane (100 mL) were irradiated with 300 nm UV light for 60 h. The photoadduct was obtained as a mixture of two isomers, *i.e.*, trans and cis isomer, with a ratio of 2.7 : 1.0, as revealed by ^{1}H NMR (Yields of the two: 80%). Spectral data of **14**(trans): UV(MeOH) λmax 393, 250, 247 nm; IR(KBr), 3064, 3036, 2980, 2931, 2207, 1960, 1883, 1658, 1447, 1264, 871 cm⁻¹; ^{1}H-NMR(CDCl₃) δ 7.07-7.92 (m, 10H), 3.93 (d, 1H), 3.72 (d, 1H), 2.08 (s, CH₃), 1.82 (s, CH₃), 1.62 (s, CH₃), 1.49 (s, CH₃); ^{13}C-NMR(CDCl₃) δ 199.5 and 198.0 (C=O), 131.7, 128.4, 127.3, 87.00, 86.50, 54.80, 49.93, 36.91, 20.93 (CH₃), 14.16 (CH₃), 13.76 (CH₃), 13.07 (CH₃); Mass(EI) m/e 368 (M⁺). Spectral data of **14**(cis): UV(MeOH) λmax 393, 250, 247 nm; IR(KBr), 3064, 3036, 2980, 2931, 2207, 1960, 1883, 1658, 1447, 1264, 871 cm⁻¹; ^{1}H-NMR(CDCl₃) δ 7.07-7.92 (m, 10H), 3.90 (d, 1H), 3.61 (d, 1H), 2.14 (s, CH₃), 1.62 (s, CH₃), 1.43 (s, CH₃), 1.00 (s, CH₃); ^{13}C-NMR(CDCl₃) δ 200.0 (C=O), 131.7, 128.0, 127.9, 127.4, 127.1, 88.00, 86.50, 54.85, 51.95, 51.90, 36.90, 20.93, 14.16, 13.76, 13.07; Mass(EI) m/e 368 (M⁺).

Irradiation of 9,10-Phenanthrenequinone and Phenanthrene. A solution of 9,10-phenanthrenequinone (104 mg, 0.5 mmol) and phenanthrene (89 mg, 0.5 mmol) in dichloromethane (200 mL) was irradiated with 300 nm UV light for 74 h to yield 1,4-dioxene **31** and its oxidation product **32** in 15% and 20% yield, respectively. Spectral data of

31: UV(MeOH) λmax 315, 297, 286, 271, 260, 252, 225, 221, 213 nm; ^{1}H-NMR(CDCl₃) δ 8.39-7.34 (m, 16H), 3.71 (s, 2H); Mass(EI) m/e 387 (M⁺). Spectral data of **32**: UV(MeOH) λmax 315, 297, 286, 271, 260, 254 nm; ^{1}H-NMR(CDCl₃) δ 8.07 (d, 4H), 7.68 (t, 4H), 7.61 (t, 4H), 7.36 (d, 4H); Mass(EI) m/e 385 (M₊).

Irradiation of Acenaphthenequinone and Acenaphthylene. A solution of acenaphthenequinone (91 mg, 0.5 mmol) and acenaphthylene (76 mg, 0.5 mmol) in dichloromethane (200 mL) was irradiated for 74 h to give 1,4-dioxene **34** and its oxidation product **35** in 23% and 20% yield, respectively. Spectral data of **34**: UV(MeOH) λmax 340, 320, 253, 243, 215 nm; ^{1}H-NMR(CDCl₃) δ 8.10-7.48 (m, 12H), 3.81 (s, 2H); 13C-NMR(CDCl₃) δ 131.5, 128.3, 128.0, 123.9, 121.4, 121.0, 42.0. Spectral data of **35**: UV(MeOH) λmax 340, 320, 250, 221, 215 nm; ^{1}H-NMR(CDCl₃) δ 8.30 (d, 4H), 8.14 (d, 4H), 7.88 (dd, 4H); ^{13}C-NMR(CDCl₃) δ 131.5, 128.3, 128.0, 123.9, 121.4, 121.0.

Irradiation of 9,10-Phenanthrenequinone and Acenaph-thylene. A solution of 9,10-phenanthrenequinone (104 mg) and acenaphthylene (76 mg) in dichloromethane (200 mL) was irradiated for 74 h to yield 1,4-dioxene **36** and its oxidation product **37** in 15% and 13% yield, respectively. Spectral data of **36**: UV(MeOH) λmax 315, 297, 287, 271, 252, 245, 230, 220 nm; ^{1}H-NMR(CDCl₃) δ 8.08-7.23 (m, 14H), 3.82 (s, 2H). Spectral data of **37**: UV(MeOH) λmax 315, 297, 287, 271, 260, 252, 225, 221, 213 nm; ^{1}H-NMR(CDCl₃) δ 8.42 (d, 2H), 8.15 (d, 2H), 8.09 (d, 2H), 7.84 (t, 2H), 7.60 (t, 2H), 7.48 (t, 2H), 7.36 (dd, 2H); ^{13}C-NMR(CDCl₃) δ 161.2, 151.3, 134.8, 130.6, 128.9, 124.6, 122.8, 121.7, 117.8.

Irradiation of Acenaphthenequinone and Phenanthrene. A solution of acenaphthenequinone (91 mg, 0.5 mmol) and phenanthrene (89 mg, 0.5 mmol) was irradiated in dichloromethene (200 mL) for 75 h to give 1,4-dioxenes **38** and its oxidation product **37** in 18% and 25% yield, respectively. Spectral data of **38**: UV(MeOH) λmax 315, 297, 287, 271, 252, 245, 230, 220, 218, 213 nm; ^{1}H-NMR(CDCl₃) δ 8.09-7.23 (m, 14H), 3.82 (s, 2H).

Irradiation of Methoxy Derivative of E-yne and o-Quinones. 4-Methoxy derivative **39** (117 mg, 0.5 mmol) and tetrachloro-1,2-benzoquinone **15a** (123 mg, 0.5 mmol) were irradiated in dichloromethane (50 mL) with 300 nm UV light for 24 h to give 1,4-dioxenes **40a** as a mixture of trans- and cis-adduct (58%, two isomers - 1.9 : 1.0). Spectral data of **40a**(trans): 400 MHz ^{1}H-NMR(CDCl₃), δ 7.47 (d, 2H), 7.26-7.23 (m, 5H), 6.94 (d, 2H), 5.40 (bs, 1H), 5.25 (bs, 1H), 3.79 (s, 3H); Mass (EI), m/e 478 (M⁺). Spectral data of **40a**(cis): 400 MHz ^{1}H-NMR(CDCl₃), δ 7.38 (d, 2H), 7.30-7.25 (m, 5H), 6.92 (d, 2H), 5.04 (d, 1H), 4.94 (d, 1H), 3.78 (s, 3H).

4-Methoxy derivative **39** (117 mg, 0.5 mmol) and 9,10-phenanthrenequinone **22** (104 mg, 0.5 mmol) were irradiated in dichloromethane (50 mL) with 300 nm UV light for 24 h to give 1,4-dioxenes **41** as a mixture of trans- and cis-adduct (42%, two isomers - 4.3 : 1.0). Spectral data of **41**(trans): 400 MHz ^{1}H-NMR(CDCl₃), d 8.65-7.01 (m, 17H), 5.59 (bs, 1H), 5.48 (bs, 1H), 3.86 (s, 3H); Mass (EI), m/e 442 (M⁺). Spectral data of **41**(cis): 400 MHz ^{1}H-NMR(CDCl₃),

δ 8.65-7.01 (m, 17H), 5.23 (d, 1H), 5.10 (d, 1H), 3.86 (s, 3H).

Photoaddition reactions of the methoxy derivative of enyne **39** with tetrabromo-1,2-benzoquinone **15b** or acenaphthenequinone **24** were investigated in the similar condition, however, no adducts could be isolated.

RESULTS AND DISCUSSION

Quinones are an important class of compounds in organic synthesis, in industry, and in nature.[1,2] p-Quinones are known to add to olefins to give spiro-oxetanes (type A adducts) and/or cyclobutanes (type B adducts).[1-3] Alkynes add photochemically to p-quinones to give spiro-oxetenes and cyclobutenes, in which the former undergo rearrangement to yield p-quinomethanes and the latter electrocyclic reaction to the corresponding dienes. In order to compare the relative reactivity of the carbon-carbon double bond and triple bond in conjugated enyne system, 1,4-diphenylbut-1-en-3-yne 1 was synthesized from b-bromostyrene and phenylacetylene and then irradiated with quinones.[11]

As for the photoaddition of **1** to some p-quinones, the reactive sites were found to be the carbon-oxygen double bond of p-quinones, such as 1,4-benzoquinones **2** (R=H, Cl, Br), 1,4-naphthoquinone **5** and anthraquinone **9**, and the carbon-carbon triple bond of **1**, as shown in Scheme 3.[12] When irradiated **1** and p-benzoquinone **2a** (R=H) in dichloromethane with 300 nm UV light, p-quinomethane **4** was obtained via unstable spiro-oxetene intermediate **3**. Irradiation (300 nm) of **1** ($10^{-2}M$) and 1,4-benzoquinone **2a** (10^{-2} M) in dichloromethane (100 mL) for 24 h gave p-quinomethane **4a** in 38% yield. ^{1}H-^{1}H correlation spectrum of **4a** showed that the peaks (d, 2H, overlapped) at δ 6.91 were correlated with the peaks (d'd, 2H, overlapped) at δ 7.34. Vinyl protons of ethynylbenzene moiety appeared at δ 7.64 (d'd, overlapped). Oxidative photocyclization reaction of **4a** was attempted in vain, in the presence of molecular oxygen. Irradiation of **1** (10^{-2} M) and tetrachloro-1,4-benzoquinone **2b** (R=Cl, 10^{-2} M) in dichloromethane (100 mL) also yielded the

same type of p-quinomethane **4b**.

Irradiation (300 nm) of **1** (10^{-2} M) and naphthoquinone **5** (10^{-2} M) in dichloromethane (100 mL) for 24 h gave a p-quinomethane **8** in 43% yield, which was thought to be formed via the formation of unstable spiro-oxetene **6**, followed by the rearrangement to give p-quinomethane **7** and finally the oxidative photocyclization.

Interestingly, irradiation (300 nm) of **1** (10^{-2} M) and anthraquinone **9** (10^{-2} M) in dichloromethane (100 mL) for 24 h yielded **12** in 47% yield, via the formation of spiro-oxetene **10**, followed by a rearrangement to p-quinomethane **11** and oxidative photocyclization reaction.

In contrast, the carbon-carbon double bond of the enyne **1** added to the carbon-carbon double bond of duroquinone, i.e., tetramethyl-1,4-benzoquinone **13**, as shown in Scheme 4. A dichloromethane solution of **1** and duroquinone **13** was irradiated with 300 nm UV light to give cyclobutanes **14** as a mixture of trans- and cis-adduct with a ratio of 2.7 : 1.0, as revealed by the nuclear Overhauser effect in ^{1}H NMR (Yields of the two: 80%). ^{1}H NMR spectrum of the trans-adduct **14**(trans) showed methine protons at δ 3.93 (d), 3.72 (d) in chloroform-d. In the case of cis-adduct **14**(cis), the methine protons were found at δ 3.90 (d) and 3.61 (d). The mass spectrum (EI) showed a molecular ion peak at m/e 368. A peak at m/e 204 proved the existence of **1** in the photoproduct **14**. Interestingly, a double photocycloaddition product of an alkyne to two mol of duroquinone **13** was isolated, in which 1:2 adduct was found to undergo intramolecular [2+2] cycloaddition reaction to give a cage molecule.[7]
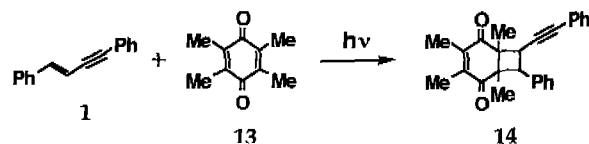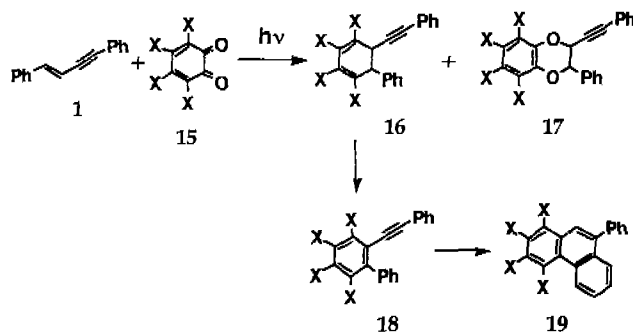
Scheme 4.

On the other hand, o-quinones are known to add to olefins to give 1,3-cyclohexadienes (type C adduct), 1,4-dioxenes (type D adduct), spiro-oxetanes (type E adduct), etc., as shown in Scheme 2. A conjugated olefin, 1,4-diphenyl-1,3-butadiene, was found to add to o-quinones to give type C adduct which can be utilized to synthesize phenanthrenes.[9] Irradiation (300 nm) of **1** (204 mg, 1.0 mmol) and tetrachloro-1,2-benzoquinone **15a** (X=Cl, 246 mg, 1.0 mmol) in
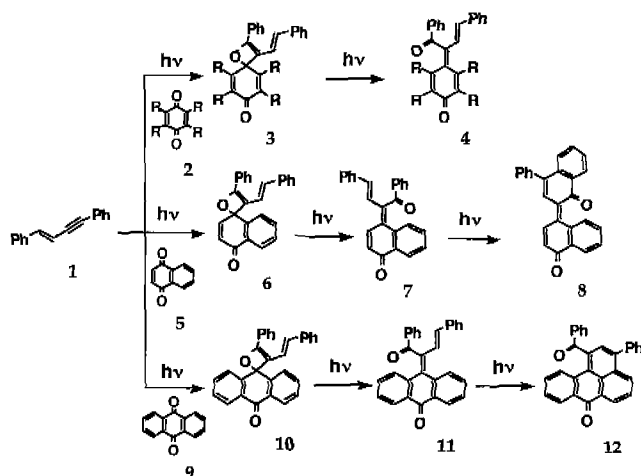
Scheme 3.

Scheme 5.

dichloromethane (100 mL) for 24 h also afforded type C adduct as 1,3-cyclohexadiene **16a** and its oxidized product **18a** (X=Cl, 5%), as well as dihydrodioxene **17a** (X=Cl, 55%), as shown in Scheme 5.[13]

The 1,3-dienes **16** (X=Cl, Br) are thought to be formed *via* photobisdecarbonylation of unstable intermediates **20** (Figure 1). The dioxenes **17a** were obtained as a mixture of two isomers *(cis/trans)* with a ratio of 1.0 : 1.4, as revealed by ^{1}H NMR. Two methine protons of cis isomer **17a***(cis)* were observed at δ 5.15 (d, J=7.3Hz) and 5.02 (d, J=7.3Hz), whereas those of trans isomer **4a***(trans)* were found at δ 5.50 (bs) and 5.36 (bs). Phenanthrenes **19** is thought to be formed through: the excitation of the carbon-carbon triple bond of tolan derivatives which generates transoid diradical intermediates **21** (Fig. 1), and its abstraction of hydrogen in benzene ring.
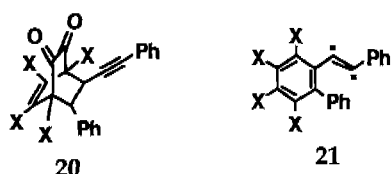

Figure 1.

Irradiation (300 nm) of **1** (204 mg, 1.0 mmol) and tetrabromo-1,2-benzoquinone **15b** (X=Br, 424 mg, 1.0 mmol) in dichloromethane (100 mL) for 24 h yielded dihydrodioxene **17b** (X=Br), a diphenylacetylene **18b** (X=Br), and 9-phenylphenanthrene **19b** (X=Br) in 45%, 7%, and 13% yields, respectively. 1,3-Cyclohexadiene derivative, like **16a**, was not found in this reaction. Dihydrodioxenes **17b** were obtained as isomeric mixture, *i.e.*, cis and *trans* isomer, with a ratio of 1.0 : 1.2, as revealed by ^{1}H NMR. Two methine protons of cis isomer **17b***(cis)* were observed at δ 5.16 (d, J=7.3Hz) and 5.01 (d, H=7.3 Hz), whereas those of *trans* isomer **17b***(trans)* were found at δ 5.45 (bs) and 5.35 (bs). The product could also be further recrystallized from *n*-hexane to yield **17b***(cis)* in pure form (15%). In order to confirm the exact structure, [1]H-^{13}C correlation spectrum of **19b** was also obtained in chloroform-d. A carbon peak (δ 107.7) of C-10 in phenanthrene ring was correlated with a proton peak at δ 7.06 (s, 1H, aromatic).

A study on the photoaddition reactions of **1** and *o*-benzoquinones **15** shows that initially formed 1,3-cyclohexadienes **16** can be oxidized to tolan derivatives **18** and then on irradiation in the presence of molecular oxygen to 9-phenanthrenes **19**. Prolonged irradiation of diphenylacetylene **18a** (X=Cl) gives rise to 9-phenylphenanthrene **19a**, which may be produced *via* the initial formation of transoid excited intermediate **21a**, cyclization, and [1,5] hydrogen shift to yield the phenanthrene. Interestingly, it was found that irradiation of **1** and **15a** in benzene, instead of dichloromethane, gave rise to **19a** in 48% yield as the major product. In this case, 1,3-cyclohexadienes **16a** and dihydrodioxenes **17a** were obtained in 11% and 2% yield, respectively. Irradiation of **1** and tetrabromo-1,2-benzoquinone **15b** in benzene yielded

19b (37%) as the major product in one-pot photoreaction. This result makes an interesting contrast with our previous result that 1-phenylphenanthrenes were obtained when irradiated substituted stilbenes in the presence of molecular oxygen.

It was found that 1,4-diphenyl-1,3-butadiene added to 9,10-phenanthrenequinone **22** to give keto oxetane as 1:1 adduct (type E adduct).[14] In contrast, **1** added to 9,10-phenanthrenequinone **22** to yield 1,4-dioxene **23** (type D adduct), as shown in Scheme 6. In the meantime the enyne **1** added to acenaphthenequinone **24** to yield keto oxetanes **25** (type E adducts) as shown in Scheme 2.[14] With 1,4-diphenyl-1,3-butadiene, the photoproduct was also found to be keto oxetanes.[14]
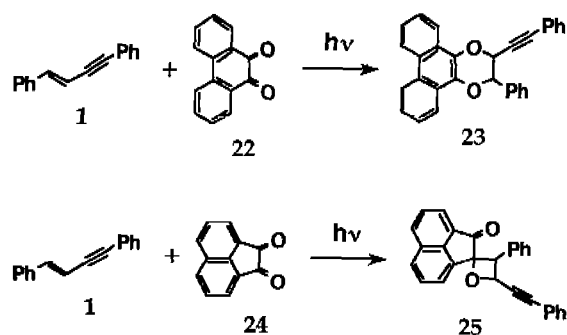
Scheme 6.

Irradiation of **1** (204 mg, 1.0 mmol) and 9,10-phenanthrenequinone **22** (208 mg, 1.0 mmol) in dichloromethane (100 mL) with 300 nm UV light for 48 h yielded 1,4-dioxene **23** in 65% yield. This fact implies that **23** is produced by the formation of 1,4-diradical intermediate **26** and then 1,6-diradical intermediate followed by coupling to give the final product. The lifetime of the more stable 1,4-diradical **26** is sufficiently long to give 1,6-diradical intermediate prior to cyclization to yield 6-membered ring compound **23**. Although the alternative radical intermediate **27** have stable benzyl radical, the evidence for the involvement of these radicals was not observed. Ethynylbenzene moiety reduces the steric factor occurring in **26**, in comparison with phenyl group in **27**. Mass spectrum (EI) of **23** showed a molecular ion peak at m/e 412. ^{1}H NMR analysis of **23** revealed a 2.3 : 1.0 ratio of *cis*-adduct and *trans*-adduct. Two methine protons of **23***(cis)* were observed at δ 5.63 (d, J = 2.9 Hz) and 5.54 (d, J = 2.9 Hz) in ^{1}H NMR spectra (CDCl₃), whereas those of **23***(trans)* were found at δ 5.30 (d, J = 7.3 Hz) and 5.15 (d, J = 7.3 Hz). The H-C-C-H dihedral angles ϕ of the two isomers were obtained by using Chem 3D Plus program, in which ϕ values of **23***(cis)* and **23***(trans)* were 62.7° and 173.1°, respectively. The magnitude of the splitting between the two H's, *i.e.*, $^3J_{H-C-C-H}$ is the largest when ϕ= 0° or 180°, and is the smallest when ϕ= 90°.[10] Thus, it can be considered that $^3J_{trans}$ is larger than $^3J_{cis}$.

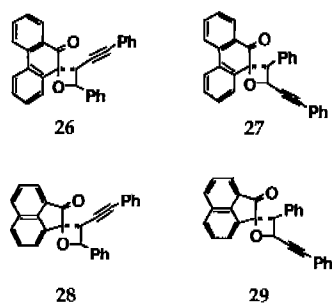In contrast, photoaddition of **1** to acenaphthenequinone **24**,

Figure 2.

gives only type E adduct, *i.e.*, keto oxetane, **25**, as shown in Scheme 6.[14] With **1** (204 mg, 1.0 mmol), acenaphthenequinone **24** (182 mg, 1.0 mmol) afforded keto oxetane **25** in 39% yield.[14] 1,4-Diphenyl-1,3-butadiene was also added to **24** to give keto oxetane.[13,14] H-C-C-H dihedral angles of **25**(*cis*) and **25**(*trans*) were 5.62° and 106.8°, respectively. Actually, $^3J_{cis}$ and $^3J_{trans}$ were 8.1 Hz and 6.6 Hz, respectively.[10]
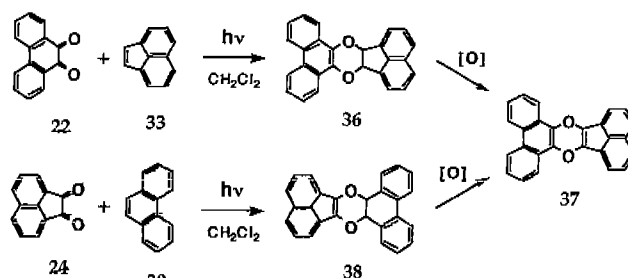
In order to elucidate the difference between the reaction types of **22** and **24**, bond angles of 9,10-dihydroxyphenanthrene and 1,2-dihydroxyacenaphthylene were calculated by using Chem 3D Plus program. The O-C-C bond angles of O-C-C-O moiety in 9,10-dihydroxyphenanthrene and 1,2-dihydroxyacenaphthylene were 120.2° and 125.6°, respectively. Thus, it can be thought that larger deviation of O-C-C bond angles from 120° prevent from the formation of 6-membered ring compounds. Consequently, larger O-C-C bond angles may reduce steric factor, as in the case of **29**. The electronic factors are considered to be more important in the formation of **29** than in that of **26**. On the basis of the electronic factors, **29** is more stable than **28**, because benzyl radical moiety in **29** is resonance-stabilized by four canonical forms.

This studies show that there are many factors, such as steric factor, electronic factor, bond angles, etc., governing the reaction pathways in the photoaddition reactions of *o*-quinones to some conjugated molecules. In the case of enyne system, it was found that carbon-carbon double bond is much more reactive toward *o*-quinones than carbon-carbon triple bond.

9,10-Phenanthrenequinone **22** and acenaphthenequinone **24** also added to aromatic compounds, such as phenanthrene **30** and acenaphthylene **33**, to yield type D adduct as 1,4-dioxenes. When irradiated 9,10-phenanthrenequinone **22** (104 mg, 0.5 mmol) and phenanthrene **30** (89 mg, 0.5 mmol) in

dichloromethane (100 mL) with 300 nm UV light for 74 h, 1,4-dioxene **31** (15%) and its oxidation product **32** (20%) were obtained, as shown in Scheme 7. On irradiation of acenaphthenequinone **24** (91 mg, 0.5 mmol) and acenaphthylene **33** (76 mg, 0.5 mmol) in dichloromethane (100 mL) with 300 nm UV light for 74 h give the same type of adducts, **34** (23%) and **35** (20%).

The cross-photoaddition reactions were also investigated to get 1,4-dioxenes, **36** or **38**, and their oxidation product **37**, as shown in Scheme 8. Irradiation of 9,10-phenanthrenequinone **22** (104 mg, 0.5 mmol) and acenaphthylene **33** (76 mg, 0.5 mmol) in dichloromethane (200 mL) with 300 nm UV light for 74 h yielded **36** (15%) and **37** (13%). The photoproducts **38** and **37** were also obtained in 18% and 25% yield, respectively, when irradiated acenaphthenequinone **24** (91mg, 0.5 mmol) and phenanthrene **30** (89 mg, o.5 mmol) in dichloromethane (200 mL) with 300 nm UV light for 74 h.
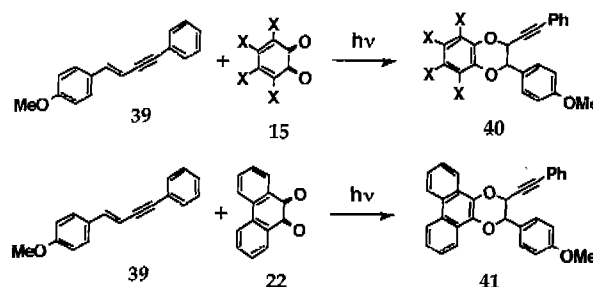

Scheme 8.

As described above, **1** was found to add to *o*-quinones at its carbon-carbon double bond. Further studies are in progress to explore mechanistic factors responsible for the differences of the reaction pathways. Ethoxy derivative **39** of the enyne was synthesized to investigate its photoreactivity toward o-quinones. Irradiation of **39** and tetrahalo-1,2-benzoquinones **15a** (X=Cl) in dichloromethane with 300 nm UV light yielded type D adducts **40**, as a mixture of *trans*- and *cis*-adduct with a ratio of 1.9 : 1.0, as revealed by ^{1}H NMR (Yields of the two: 58%). 9,10-Phenanthrenequinone **22** also added to the methoxy derivative **39** to give type D adducts **41** as 1,4-dioxenes, as a mixture of *trans*- and *cis*-adduct with a ratio of 4.3 : 1.0, as revealed by ^{1}H NMR (Yields of the two: 42%). Such adducts could not be isolated from the photoreactions of **1** with tetrabromo-1,2-benzoquinone **15b** or acenaphthenequinone **24** in the similar conditions.
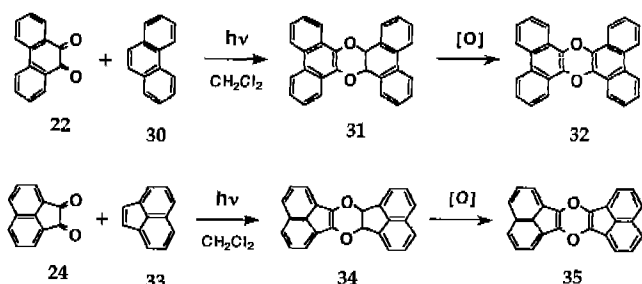
Scheme 7.

Scheme 9.

In summary, **1** was found to add to *p*-quinones to give spiro-oxetenes or cyclobutanes, in which the reactive sites were dependent upon the starting materials. **1** also added to *o*-quinones to yield three types of adducts, *i.e.*, 1,3-dienes, 1,4-dioxenes, or spiro-oxetanes, in which the reactive site of **1** was the carbon-carbon double bond. The types of photoaddition were dependent upon the *o*-quinones.

Some conjugated enynes containing electron-donating methyl or electron-withdrawing chlorine, nitro, and cyano groups will be synthesized to investigate whether the reactive sites of the enynes are inversed or not, when irradiated with quinones.

REFERENCES

1. Laird, T. (1979) In *Comprehensive Organic Chemistry*, ed. by Stoddart, J. F., Pergamon Press, Vol. 1, pp. 1213.

2. Maruyama, K. and A. Osuka, 1988. In *The Chemistry of the Quinonoid Compounds*; ed. by Patai, S. Rappoport, Z., John Wiley & Sons, Inc. New York, Part 1, pp. 759.

3. Kim, A. R., S. S. Kim, D. J. Yoo and S. C. Shim (1997) Photoaddition Reactions of Duroquinone to Phenyl Substituted Ethylenes. *Bull. Korean Chem. Soc.* **18(6)**, 665-667.

4. Bosch, E., S. M. Hubig, S. V. Lindeman and J. K. Kochi (1998) Photoinduced Coupling of Acetylenes and Quinone in the Solid State as Preorganized Donor-Acceptor Pairs. *J. Org. Chem.* **63**, 592-601.

5. Kim, S. S., D. Y. Yoo, A. R. Kim, I. H. Cho and S. C. Shim

6. Bosch, E., S. M. Hubig and J. K. Kochi (1998) Paterno-Buchi Coupling of (Diaryl)acetylenes and Quinone *via* Photoinduced Electron Transfer. *J. Am. Chem. Soc.* **120**, 386-395.

7. Kim, S. S., A. R. Kim, K. J. O, D. J. Yoo and S. C. Shim (1995) Photoaddition Reactions of 1,4-Diethynylbenzene to tetramethyl-1,4-benzoquinone and Photochemical Transformation of the Photoadducts. *Chemistry Lett.* 787-788.

8. Kim, A. R., Y. J. Mah and S. S. Kim (1998) Formation of *o-/p*-Quinomethanes and *p*-Quinodimethanes from the Photoaddition of Diphenylacetylene to *o*-Quinones. *Bull. Korean Chem. Soc.* **19(12)**, 1295-1297.

9. Kim, S. S., Y. H. Yu, S. C. Shim and I. H. Cho (1994) Formation and Oxidation of 1;1 Adducts of Tetrahalo-1,2-benzoquinones and 1,3-Dienes. *Tetrahedron Lett.* **35(48)**, 9039-9042.

10. Kim, S. S., A. R. Kim, Y. J. Mah and S. C. Shim (1999) One-Pot Formation of a Cyclobutanes from the Double Photocycloaddition Reactions of 1,4-Diethynylbenzene to Some *o*-Quinones. *Chemistry Lett.* **5**, 395-396.

11. Reinhardt, B. A. and F. E. Arnold (1981) Synthesis and Properties of Conjugated Enyne Polysulfones. *J. Polymer Sci.* **19**, 271-285.

12. Kim, S. S., M. H. So and S-K. Park (1996) Photoaddition Reactions of 1,4-Diphenylbut-1-en-3-yne to *p*-Quinones. *J. Photosci.* **3(2)**, 61-64.

13. Kim, S. S., Y. J. Mah, A. R. Kim, D. J. Yoo and S. C. Shim (1996) Photoaddition Reactions of *o*-Benzoquinones to 1,4-Diphenylbut-1-en-3-yne: Formation of Phenanthrenes and Dihydrodioxins. *Bull. Korean Chem. Soc.* **17(7)**, 577-579.

14. Kim, S. S., D. Y. Yoo, A. R. Kim, S-K. Park and S. C. Shim (1996) Photoaddition Reactions of 9,10-Phenanthrenequinone and Acenaphthenequinone to Conjugated Molecules. *Bull. Korean Chem. Soc.* **17(11)**, 983-984.

(1989) Photoaddition Reactions of *p*-Quinones to Conjugated Diyne. *Bull. Koren Chem. Soc.* **10(1)**, 66-69.