

PHOTOADDITION REACTIONS OF *o*- BENZOQUINONES TO SOME OLEFINS AND ALKYNES †

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Abstract – Photoaddition reactions of *o*-benzoquinones to some organic molecules were investigated to yield three types of photoadducts. Irradiation (350 nm UV light) of a dichloromethane solution of tetrahalo-1,2-benzoquinones and 1,4-diphenylbutadiene yielded 1,3-dienes, which was found to be used to synthesize 1-phenylphenanthrenes. The 1,3-dienes were also produced, when irradiated tetrahalo-1,2-benzoquinones and 1,4-diphenylbut-1-en-3-yne in the similar conditions, which was applied to get 9-phenylphenanthrenes. An enolic compound came from the tautomerization of dibenzoylmethane was found to add to *o*-benzoquinones to give 1,4-dioxenes and 1,5-diketones as the major products. Although diphenylbutadiyne did not add to *o*-benzoquinones, diphenylacetylene added to *o*-benzoquinones to give *p*-quinomethanes as well as two isomeric *o*-quinomethanes. One-way photoisomerism was observed for the two isomeric *o*-quinomethanes.

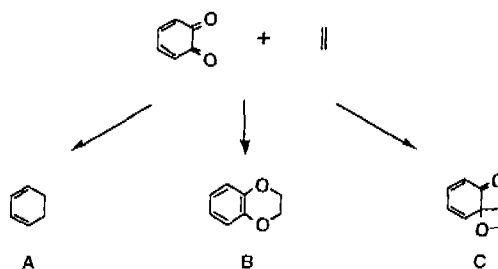
INTRODUCTION

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. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas.¹⁻⁶ It has been known that photocycloaddition of *o*-quinones to olefins gives mainly three types of products, 1,3-diene (*type A*), 1,4-dioxene (*type B*) and keto-oxetane (*type C*) as shown in Scheme 1, along with H-abstraction products.^{2,3,7-12} Our interest in the diversity of the reactivity of excited *o*-quinones has promoted us to investigate the type of the photoproducts of *o*-quinones and alkynes.

We have reported that tetrahalo-1,2-benzoquinones **1** and 1,4-diphenylbutadiene **2** could be utilized for the synthesis of phenanthrenes *via* the initially formed 1,3-dienes (*type A*).⁹ Bryce-Smith *et al.* reported that tetrachloro-1,2-benzoquinone **1a** reacts photochemically with diphenylacetylene **19** to give dioxenes (*type B*).⁷ Whereas, we found that irradiation (300 nm UV light) of *o*-quinones and alkynes in dichloromethane leads to keto-oxetenes (*type C*), which undergo rearrangement to give *o*-quinomethanes.¹¹ We describe here that three types of photoadducts are produced from the photo-addition of *o*-benzoquinones to some organic molecules, such as dienes, alkynes, enynes and enolic tautomers of 1,3-diketones.

MATERIALS AND METHODS

Materials. Tetrachloro-1,2-benzoquinone, tetrabromo-1,2-



Scheme 1.

benzoquinone, 1,4-diphenylbutadiene, diphenylacetylene, 1,4-diphenylbutadiyne, dibenzoylmethane, 1-phenyl-1,3-butanedione, 2,4-pentanedione, phenanthrenequinone, acenaphthenequinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were purchased from Aldrich Chemical Co. and used as received or recrystallized prior to use. 1,4-Diphenylbut-1-en-3-yne was synthesized from phenylacetylene. Dichloromethane, *n*-hexane, ethyl acetate and benzene were distilled prior to use. Silica gel (Kieselgel 60, 230-400 mesh, Merck Co.) 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. ¹H and ¹³C NMR spectra were recorded on a Jeol JMN EX NMR spectrometer. Chemical shifts, δ , were reported as parts per million (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 Hitachi 556 spectrophotometer. Mass (MS) spectra were determined on a Hewlett Packard 5985 GC/MS system using electron impact method. Fast atom bombardment (FAB) mass spectra were obtained with thioglycerol as the reagent gas.

*General Procedure for Photocycloadditions of Alkynes to *o*-*

† This paper is dedicated to Prof. Sang Chul Shim on the occasion of his 60th birthday.

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Benzoquinones. Preparative photoreactions were conducted in a photoreactor composed of a water-cooled inner condenser and a Pyrex reaction vessel with 300 nm or 350 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging with nitrogen gas (purity; 99.9%) for 30 min. The reaction mixture was concentrated in vacuo and chromatographed over silica gel with *n*-hexane and ethyl acetate as the eluent.

Irradiation of a dichloromethane solution (200 mL) of tetrachloro-1,2-benzoquinone **1a** (246 mg, 1.0 mmol) and 1,4-diphenylbutadiene **2** (206 mg, 1.0 mmol) with 350 nm UV light for 2 h afforded 1,3-diene **3a** quantitatively. Refluxing a solution of the diene **3a** (60 mg, 0.15 mmol) in dichloromethane (100 mL) in the presence of 1 eq. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (35 mg, 0.15 mmol) for 24 h gave stilbene derivative **4a** in 60% yield. The oxidized product **4a** (98 mg, 0.25 mmol) was irradiated with 350 nm UV light in the presence of molecular oxygen for 8 h to give a phenanthrene derivative **5a** in 57% yield. Tribromo compound **5b** was also obtained when irradiated tetrabromo-1,2-benzoquinone **1b** and 1,4-diphenylbutadiene **2** with 350 nm UV light in dichloromethane.

3a: UV(*n*-hexane) λ_{\max} 356, 338, 302, 294, 270 nm; IR(KBr) 3029, 2917, 1560, 1426, 969, 786, 758, 695 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.39-7.23 (10H, m), 6.67 (1H, d, $J = 16.0\text{Hz}$, Ph-CH=CH-), 5.96 (1H, dd, $J = 16.0\text{Hz}$ and 5.92 Hz, Ph-CH=CH-), 4.87 (1H, d, $J = 7.65\text{Hz}$, Ph-CH-CH-), 4.70 ppm (1H, m, Ph-CH-CH-); ^{13}C NMR(CDCl_3) δ 135.2 (Ph-CH=CH-), 121.3 (Ph-CH=CH-), 80.13 (Ph-CH-CH-), 78.77 (Ph-CH-CH-), 129.4-126.2 (10 CH, aromatic), 135.6 and 136.0 (2 C's), 138.0 and 140.1 ppm (3 C's) (4 CCl's); Mass(EI) m/e 394 (M). **3b** was also isolated and characterized with several spectral data. Carbon peaks at δ 135.6, 121.7, 80.50 and 79.14 ppm were correlated with proton peaks at δ 6.73 (1H, d, $J = 15.6\text{Hz}$, Ph-CH=CH-), 5.97 (1H, dd, $J = 15.8\text{Hz}$ and 5.86 Hz, Ph-CH=CH-), 4.89 (1H, d, $J = 8.06\text{Hz}$, Ph-CH-CH-), and 4.70 ppm (1H, m, Ph-CH-CH-), respectively. **5a:** UV(*n*-hexane) λ_{\max} 315, 280, 250, 245, 242, 236 nm; IR(KBr) 3064, 1630, 1595, 1447, 1384, 1307, 1089, 997, 899, 779, 695 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.08-8.17 (11H, aromatic); Mass(EI) m/e 356 (M). **5b:** UV(*n*-hexane) λ_{\max} 318, 308, 272, 250, 242, 230, 223 nm; IR(KBr) 3064, 1630, 1595, 1489, 1440, 1398, 1314, 1046, 962, 892, 765, 695 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.09-8.17 (11H, aromatic); Mass(EI) m/e 488 (M).

Irradiation (300 nm) of tetrachloro-1,2-benzoquinone **1a** (246 mg, 1.0 mmol) and 1,4-diphenylbut-1-en-3-yne **6** (204 mg, 1.0 mmol) in dichloromethane (50 mL) for 24 h afforded 1,3-diene **7a** (8%) and diphenylacetylene derivative (5%) **8a**, as well as dioxene **10a** (55%). In contrast, irradiation (300 nm) of tetrabromo-1,2-benzoquinone **1b** (424 mg, 1.0 mmol) and 1,4-diphenylbut-1-en-3-yne **6** (204 mg, 1.0 mmol) in dichloromethane (50 mL) for 24 h yielded dioxene **10b** (45%), a diphenylacetylene derivative **8a** (7%) and 9-phenylphenanthrene **9b** (13%).

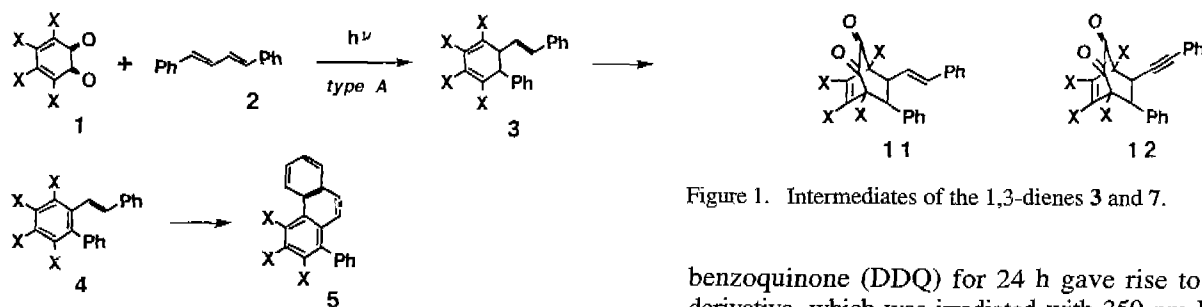
7a: ^1H NMR(CDCl_3) δ 7.51-7.29 (10H), 4.94 (d, 1H, $J = 7.3\text{Hz}$), 4.87 (d, 1H, $J = 7.3\text{Hz}$); IR(KBr) 3057, 2968, 2926, 2229, 1556, 1441, 1384, 1285, 1015, 760, 695 cm^{-1} ; UV(MeOH) λ_{\max} 301, 252, 242, 235, 219 nm; Mass(EI) m/e 392 (M), 77. **9a:** ^1H NMR(CDCl_3) δ 7.88 (d, 1H, $J = 7.3\text{Hz}$), 7.87 (d, 1H, $J = 7.3\text{Hz}$), 7.79 (dd, 2H, $J = 7.3\text{Hz}$, $J = 1.5\text{Hz}$), 7.49-7.43 (5H), 7.05 (s, 1H); Mass(EI) m/e 390 (M), 77. **9b:** UV(*n*-hexane) λ_{\max} 395, 389, 272,

212 nm; IR(KBr) 3064, 1553, 765, 667 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.88 (d, 1H, $J = 7.3\text{Hz}$), 7.87 (d, 1H, $J = 7.3\text{Hz}$), 7.78 (dd, 2H, $J = 7.3\text{Hz}$, $J = 1.5\text{Hz}$), 7.49-7.43 (5H), 7.06 (s, 1H); ^{13}C NMR(CDCl_3) δ 129.6 (CH), 129.3 (CH), 129.1 (2 CH?), 128.6 (3 CH's), 124.8 (2 CH's), 107.7 (CH); Mass(EI) m/e 566 (M), 77. **10a:** ^1H NMR(CDCl_3) δ 7.51-7.30 (10H), 5.15 (d, 1H, $J = 7.3\text{Hz}$), 5.02 (d, 1H, $J = 7.3\text{Hz}$); IR(KBr), 3064, 2966, 2924, 2235, 1257, 1025, 751, 688 cm^{-1} ; UV(MeOH) λ_{\max} 301, 253, 242, 234, 218 nm; Mass(EI) m/e 448 (M), 204, 77. **10b:** ^1H NMR(CDCl_3) δ 7.53-7.31 (10H), 5.16 (d, 1H, $J = 7.3\text{Hz}$), 5.01 (d, 1H, $J = 7.3\text{Hz}$); IR(KBr), 3064, 2966, 2924, 2235, 1257, 1025, 751, 688 cm^{-1} ; UV(MeOH) λ_{\max} 302, 280, 253, 243, 224 nm; Mass(EI) m/e 624 (M), 204, 77.

When solution of **1a** (123 mg, 0.5 mmol) and dibenzoylmethane **13** (135 mg, 0.6 mmol) in dichloromethane was irradiated with 300 nm UV light for 7 days, the consumption of starting material was associated with the formation of two photoproducts. Separation and isolation of both products were accomplished by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (10:1, v/v) as the eluent to give 1,4-dioxene **14a** (18%) and 1,5-diketone **16a** (7%). Irradiation of a dichloromethane solution (200 mL) of **1b** (X=Br, 212 mg, 0.5 mmol) and dibenzoyl methane **11** (135 mg, 0.6 mL) with 300 nm UV light for 7 days also afforded **14b** (12%) and **16b** (5%). **14a:** UV(MeOH) λ_{\max} 310, 280, 231, 212 nm; IR(KBr) 3630, 3020, 2922, 1679, 1590, 1287 cm^{-1} ; 400 MHz ^1H -NMR(CDCl_3) δ 9.81 (1H, OH, s), 8.20-7.04 (10H, aromatic), 6.24 (1H, s); Mass (EI), m/e 470 (M). **16a:** UV(MeOH) λ_{\max} 300, 222 nm; IR(KBr) 3060, 2923, 1703, 1689, 1592, 1451, 1038 cm^{-1} ; 400 MHz ^1H -NMR(CDCl_3) δ 8.20-7.51(10H, aromatic), 5.48(2H, s); Mass (EI), m/e 470(M).

Irradiation of tetrachloro-1,2-benzoquinone **1a** (246 mg, 1.0 mmol) and diphenylacetylene **19** (178 mg, 1.0 mmol) in dichloromethane(100 mL) with 300 nm UV light for 24 h gave not only two isomeric quinomethanes, **21a** (26%) and **22a** (28%), but also a *p*-quinomethane **24a** (17%). Irradiation of tetrabromo-1,2-benzoquinone **1b** (424 mg, 1.0 mmol) and **19** (178 mg, 1.0 mmol) in dichloromethane (100 mL) with 300 nm UV light for 24 h yielded **21b**, **22b** and **24b**, in 29%, 30% and 23% yields, respectively.

21a: UV(MeOH) λ_{\max} 366, 325, 297, 258 nm; IR(KBr) 3060, 2923, 1703, 1689, 1592, 1451, 1038 cm^{-1} ; 400 MHz ^1H -NMR(CDCl_3) δ 7.81-7.28 (10H, Ph); ^{13}C -NMR(CDCl_3) δ 186.0 (C=O, overlapped), 133.3, 131.0, 130.0, 129.0, 128.0, 126.0 (aromatic CH's); Mass (EI) m/e 424 (M). **21b:** UV(MeOH) λ_{\max} 351, 321, 275, 253 nm; IR(KBr) 3062, 2963, 1696, 1596, 1444, 1032, 934 cm^{-1} ; 400 MHz ^1H -NMR(CDCl_3) δ 7.79-7.27 (10H, Ph); ^{13}C -NMR(CDCl_3) δ 189.0, 186.0(C=O), 133.2, 131.4, 131.2, 129.0, 128.0, 126.6 (aromatic CH's); Mass (EI) m/e 602 (M), 105. **22a:** UV(MeOH) λ_{\max} 366, 327, 294, 259 nm; IR (KBr) 3064, 2915, 1670, 1655, 1510, 1449, 1022, 875 cm^{-1} ; 400 MHz ^1H -NMR (CDCl_3) δ 8.08-7.47 (10H, Ph); ^{13}C -NMR (CDCl_3) δ 189.0 (overlapped), 134.9, 129.9, 129.0 (aromatic CH's); Mass (EI), m/e 424 (M), 353 (M-2Cl), 105. **22b:** UV(MeOH) λ_{\max} 351, 324, 280, 256 nm; IR (KBr) 3064, 2960, 1671, 1591, 1449, 1072, 939 cm^{-1} ; 400 MHz ^1H -NMR (CDCl_3) δ 7.99-7.50 (10H, Ph); Mass (EI) m/e 602 (M), 282 (M-4Br), 105. **24a:** UV(MeOH) λ_{\max} 334,



Scheme 2.

301, 279, 253, 245 nm; IR (KBr) 3369, 3064, 1732, 1682, 1030, 763 cm^{-1} ; 400 MHz $^1\text{H-NMR}$ (CDCl_3) δ 11.4 (1H, s, hydroxy), 7.99-7.59 (5H, aromatic), 7.57 (1H, d, $J = 8.0$ Hz), 7.49 (1H, d, $J = 8.0$ Hz), 7.10 (1H, d, $J = 8.0$ Hz), 6.91 (1H, d, $J = 8.0$ Hz); Mass (EI) m/e 438 (M), 333 (M-105), 105. **24b**: UV(MeOH) λ_{max} 336, 328, 283, 256, 245 nm; IR (KBr) 3382, 3061, 1734, 1682, 1038, 763 cm^{-1} ; 400 MHz $^1\text{H-NMR}$ (CDCl_3) δ 11.4 (1H, s, hydroxy), 7.99-7.57 (5H, aromatic), 7.56 (1H, d, $J = 8.0$ Hz), 7.48 (1H, d, $J = 8.0$ Hz), 7.09 (1H, d, $J = 8.0$ Hz), 6.90 (1H, d, $J = 8.0$ Hz); Mass (EI) m/e 614 (M), 105.

RESULTS AND DISCUSSION

We have been interested in the photoaddition reactions of quinonoid compounds with some conjugated molecules for many years. *p*-Quinones are generally added to olefins and alkynes to give spiro-oxetanes and spiro-oxetenes, respectively, in which the latter undergo rearrangement to yield *p*-quinomethanes.^{1-3, 13-15} On the other hand, the reactivity of *o*-quinones are more diverse than those of *p*-quinones.^{1-3, 7-12} As shown in Scheme 1, *o*-quinones add photochemically to olefins to give 1,3-diene (type A), 1,4-dioxene (type B), or spiro-oxetane (type C). We have found that tetrahalo-1,2-benzoquinones **1** add to 1,4-diphenylbutadiene **2** to give 1,3-diene **3** as 1:1 adduct, when irradiated with 300 nm UV light (see Scheme 2).⁹

We found that the 1,3-dienes **3** may be utilized for the synthesis of phenanthrene derivatives **5**, as shown in Scheme 2.⁹ Refluxing a solution of **3a** in dichloromethane in the presence of 1 eq. of 2,3-dichloro-5,6-dicyano-1,4-

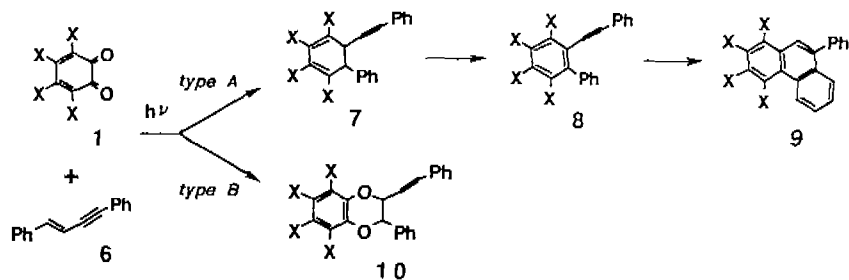
benzoquinone (DDQ) for 24 h gave rise to a stilbene derivative, which was irradiated with 350 nm UV light in the presence of molecular oxygen for 8 h to give 1-phenylphenanthrene **5a**. This oxidative photocyclization reaction could be applied to tetrabromo-1,2-benzoquinone **1b** to get a tribromo phenanthrene **5b**.

The similar type of 1:1 adducts **7** were found and isolated from the photoaddition of **1** to 1,5-diphenylbut-1-en-3-yne (DBE) **6**, although the adducts **7** were isolated as the minor products, in which the major products were found to be 1,4-dioxanes **10**.¹⁰ The 1,3-diene **7a** can be oxidized to diphenylacetylene derivative **8a**. The excitation of the oxidized product **8a** yielded 9-phenylphenanthrenes **9a**, which may be produced via the initial formation of transoid excited intermediate, cyclization and [1,5]-hydrogen shift to yield 9-phenylphenanthrene **9a**. It was found that tetrabromo-1,2-benzoquinone **1b** is more efficient than tetrachloro compound **1a** to give the corresponding phenanthrenes **9b**, where one-pot photochemical formation of **9b** (37%) was observed when irradiated **1b** and **6** in benzene solution.

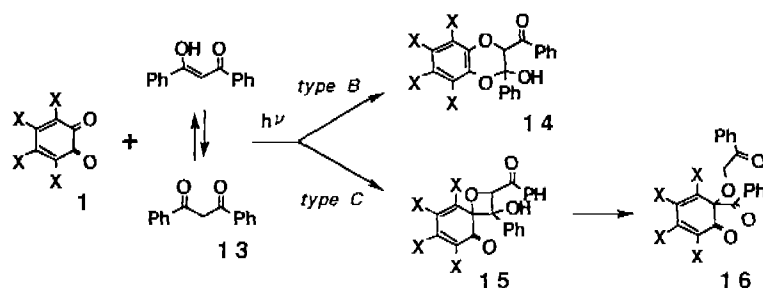
The 1,3-dienes **3** and **7** may be rationalized by way of the formation of unstable [4+2]-adducts **11** and **12**, as shown in Figure 1, followed by photobisdecarbonylation.^{9, 10}

The formation of 1,4-dioxenes **10** may be interpreted by way of the formation of stable 1,4-diradical intermediate, followed by the formation of 1,6-diradicals and coupling to yield 1,4-dioxene **10** as the final products. Phenanthrenequinone was found to add to 1,4-diphenylbutadiene **2** and 1,4-diphenylbut-1-en-3-yne **6** to give type C and type B adduct, respectively.¹² It was also found that acenaphthenequinone add to **2** and **6** to yield type C adduct.¹² The type B adduct, 1,4-dioxene, was isolated when irradiated 9,10-phenanthrenequinone and **6** in dichloromethane with 300 nm UV light.

We have been interested in the tautomerism of 1,3-



Scheme 3.



diketones **13**, *i.e.*, isomerization between **13_{Keto}** and **13_{Enol}**, in order to find out the participation of enolic tautomer **13_{Enol}** in the photoaddition of the quinonoid compounds to 1,3-diketone (see Scheme 4).¹⁶ *p*-Benzoquinones were found to add to dibenzoylmethane to give 1,5-diketones, *via* β -hydroxyketones as 1:1 photoadduct.¹⁷

Tetrahalo-1,2-benzoquinones **1** and dibenzoylmethane **13** were irradiated in dichloromethane with 300 nm UV light to yield 1,4-dioxenes **14** as the major products (type B adducts) and 1,5-diketones **16** as the minor products, in which **16** was formed *via* **15** (type C adducts), as shown in Scheme 5.¹⁸ In contrast, the photoaddition of 9,10-phenanthrenequinone or acenaphthenequinone to **13** led to 1,5-diketones, like **16**, as the major products. 1,4-Dioxenes were not found in these photoreactions.¹⁸

The formation of six-membered ring compound **14** as the major products reveals that stable 1,6-diradicals were produced from the more stable 1,2-diradicals **17** having ketyl like tertiary radical. An alternative diradical **18** is less stable than **17**. The formation of 1,5-diketones **16** may be rationalized *via* the formation of 1,4-diradical **17** having stable ketyl radical, followed by the coupling to give β -hydroxyketones **15** and retro-aldolization process to yield 1,5-diketones **16**. Attempts to get such types of adducts by using 1-phenyl-1,3-butanedione, 2,4-pentanedione and dimethyl malonate were unsuccessful.

It was reported that irradiation (visible light) of tetrachloro-1,2-benzoquinone **1a** and diphenylacetylene **19** with visible light yields 1,4-dioxenes as the major products.⁷ On the other hand, we found that irradiation of a dichloromethane solution (100 mL) of tetrachloro-1,2-benzoquinone **1a** (246 mg, 1.0 mmol) and diphenylacetylene **19** (178 mg, 1.0 mmol) with 300 nm UV light for 24 h affords not only two isomeric quinone methides, **21a** (26%) and **22a** (28%), *via* unstable spiro-oxetene **20a** (see Scheme 6), but also *p*-quinomethane **24a** (17%).¹¹ The photoproducts were

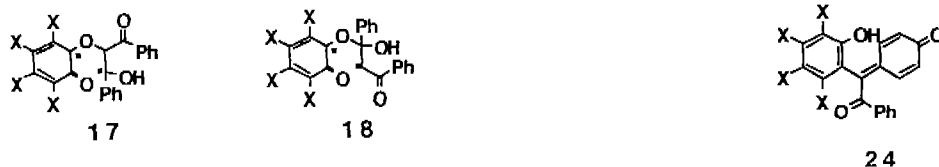


Figure 2. Diradical intermediate **17** of the photoadducts **14** and **16**. An alternative diradical **18** is less stable than **17**.

This type of a novel quinone methide was also found and isolated from the photoreaction of tetrabromo-1,2-benzoquinone **1b** and diphenylacetylene **19**. Irradiation of tetrabromo-1,2-benzoquinone **1b** and diphenylacetylene **19** in dichloromethane with 300 nm UV light yielded same types of *o*-quinomethanes, **21b** and **22b**, and *p*-quinomethane **24b**, in 29%, 30% and 23% yields, respectively. When developed using TLC plates (silica gel, 0.25 mm), R_f values of **21b** and **22b** in the eluent system of *n*-hexane and ethyl acetate (9:1, v/v) were 0.53 and 0.40, respectively.

Although it has been known that diphenylbutadiyne adds photochemically to some olefins to give [2+2]-adducts,^{19,20} no adduct was observed when irradiated *o*-benzoquinones **1** and diphenylbutadiyne **22** in dichloromethane with 300 nm UV light.

Interestingly, one-way *E*-to-*Z* photoisomerization was also observed in the two isomeric *o*-quinomethanes, **21** and **22**. Irradiation of 20 mg (4.7x10⁻⁵ mol) of *E*-isomer **21a** in 15 mL of dichloromethane with 300 nm UV light for 24 h gave *Z*-isomer **22a** (23%), whereas irradiation of **22a** did not give **21a**.¹¹ The same result was obtained in the case of **21b** and **22b**. The formation of *p*-quinomethanes **24** may be rationalized as follows. The excitation of the initially formed *o*-quinomethanes, **21** and **22**, may result in the resonance-stabilized radical intermediates **23**, to which molecular oxygen may add to the intermediates to give unstable peroxides. The peroxides may be stabilized to the more stable *p*-quinomethanes **24**. In fact, the *p*-quinomethanes **24** were not produced, when irradiated the *o*-quinones **1** and diphenylacetylene **19** after degassing the solution with freeze-pump-thaw method. Irradiation of the starting materials in the presence of molecular oxygen also gave the *p*-quinomethanes **24**.

The exact structure of **21** and **22** could also be verified by the formation of **25** and **26**, the corresponding oxidative photocyclization products, as shown in Scheme 5.

In conclusion, we have shown here that three types of photoadducts of *o*-benzoquinones may be formed when irradiated *o*-benzoquinones and some olefins or alkynes with UV light. We also found that the 1,3-dienes **3** and **7** can be applied to synthesize phenanthrenes **5** and **9**. It is also interesting to note that the enol form of dibenzoylmethane **13** can be used to synthesize 1,5-diketones **16**. Some alkynes were found to add to *o*-benzoquinones to give *o*-quinomethanes, **21** and **22**, and *p*-quinomethanes **24**.

Extension of the chemical properties of the photoproducts and the photochemical syntheses of quinomethanes will be investigated.

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