

PHOTOCHEMICAL FORMATION OF ISOMERIC QUINONE METHIDES FROM *o*-QUINONES AND ONE-WAY ISOMERIZATION

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Abstract—Irradiation (300 nm) of 1,2-benzoquinones **1** and diphenylacetylene **2** in dichloromethane yielded two isomeric quinone methides, **6** and **7**. The same types of quinone methides, **9** and **10** (or **12** and **13**) were obtained from the photocycloadditions of 9,10-phenanthrenequinone **8** (or acenaphthenequinone **11**) to diphenylacetylene **2**. One-way photoisomerizations were observed between each isomeric adducts, (**6**, **7**), (**9**, **10**) and (**12**, **13**).

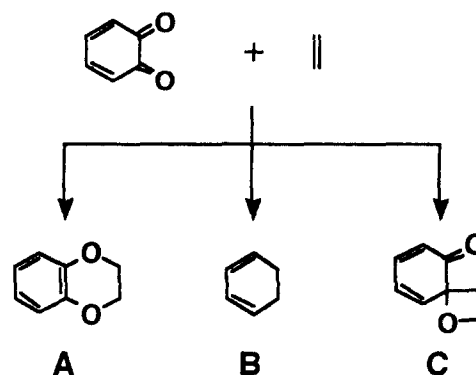
INTRODUCTION

Quinones are an important class of compounds in organic synthesis, in industry, and in nature. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas.¹⁻² It has been known that photocycloaddition of *o*-quinone to olefin generally gives three types of adducts; 1,4-dioxene (type A), 1,3-cyclohexadiene (type B) and keto-oxetane (type C), as shown in Scheme 1.¹⁻⁵

Bryce-Smith *et al.* have reported that irradiation (>400 nm) of tetrachloro-1,2-benzoquinone **1a** (X=Cl) and diphenylacetylene **2** in acetone or acetonitrile gives dioxene **4**, as major product (Scheme 2).⁶ Our interest in the diverse reactivities of excited quinones has promoted us to investigate the type of the photoadducts of *o*-quinones and alkynes. Therefore we carried out the photocycloaddition of various *o*-quinones with diphenylacetylene in dichloromethane. Here, we wish to report an interesting fact on the irradiation (300 nm) of *o*-quinones, such as **1**, **8**, and **11**, and diphenylacetylene **2** generating two isomeric quinone methides.

MATERIALS AND METHODS

Materials. *o*-Quinones, such as tetrachloro-1,2-benzoquinone, tetrabromo-1,2-benzoquinone, diphenylacetylene, 9,10-phenanthrenequinone and acenaphthenequinone, were obtained from Aldrich Chemical Co. and used as received or recrystallized prior to use. Dichloromethane, *n*-hexane, ethyl acetate and methyl alcohol were distilled prior to use. Silica gel (Kieselgel 60 F254, Merck Co.) was used for thin layer chromatography and silica gel (Kieselgel 60, 230-400 mesh, Merck Co.) was used for column chromatography.



Scheme 1

Instruments. ¹H and ¹³C NMR spectra were recorded on a Jeol JMN EX NMR spectrometer. Proton chemical shifts, δ , were reported in parts per million (ppm) downfield from tetramethylsilane (TMS). IR spectra were recorded on a Nicolet 5-DX 13 Fourier Transform spectrophotometer in KBr pellets or NaCl cells. UV spectra were obtained on a Beckmann DU 7500 spectrophotometer. Mass spectra were recorded on a Hewlett Packard 5985 GC/MS system using electron impact method.

General Procedure for Photocycloadditions of Diphenylacetylene to *o*-Quinones. Preparative photoreactions were conducted in a photochemical reactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208). Irradiation was carried out after degassing with dry nitrogen gas for 30 min. The reaction was followed by TLC. The residue obtained from the evaporation was chromatographed over silica gel with *n*-hexane and ethyl acetate as the eluents.

Irradiation of tetrachloro-1,2-benzoquinone and diphenylacetylene. The quinone **1a** (246 mg, 1.0 mmol) and

diphenylacetylene **2** (178 mg, 1.0 mmol) in dichloromethane (100 mL) with 300 nm UV light for 24 h gave quinone methides **6a** and **7a**, in 26% and 28% yield, respectively: **6a**: UV(MeOH) λ_{\max} 366, 325, 297, 258 nm; IR(KBr) 3060, 2923, 1703, 1689, 1592, 1451, 1038 cm^{-1} ; 400 MHz $^1\text{H-NMR}$ (CDCl_3), δ 7.81-7.28 (10H, Ph); $^{13}\text{C-NMR}$ (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). **7a**: UV(MeOH), λ_{\max} 366, 327, 294, 259 nm; IR (KBr), 3064, 2915, 1670, 1655, 1510, 1449, 1022, 875 cm^{-1} ; 400 MHz $^1\text{H-NMR}$ (CDCl_3), δ 8.08-7.47 (10H, Ph); $^{13}\text{C-NMR}$ (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.

Irradiation of tetrabromo-1,2-benzoquinone and diphenylacetylene. The quinone **1b** (424 mg, 1.0 mmol) and diphenylacetylene **2** (178 mg, 1.0 mmol) in dichloromethane (100 mL) with 300 nm UV light for 24 h yielded **6b** and **7b**, in 29% and 30% yield, respectively: **6b**: UV(MeOH) λ_{\max} 351, 321, 275, 253 nm; IR(KBr) 3062, 2963, 1696, 1596, 1444, 1032, 934 cm^{-1} ; 400 MHz $^1\text{H-NMR}$ (CDCl_3), δ 7.79-7.27 (10H, Ph); $^{13}\text{C-NMR}$ (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. **7b**: UV(MeOH), λ_{\max} 351, 324, 280, 256 nm; IR (KBr), 3064, 2960, 1671, 1591, 1449, 1072, 939 cm^{-1} ; 400 MHz $^1\text{H-NMR}$ (CDCl_3), δ 7.99-7.50 (10H, Ph); Mass (EI), m/e 602 (M), 282 (M-4Br), 105.

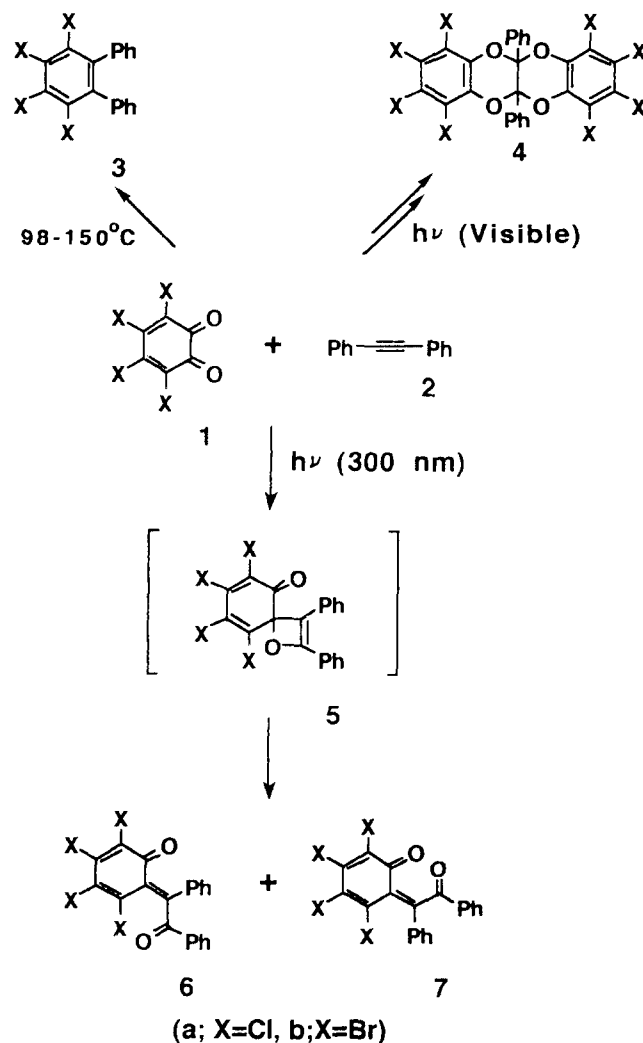
Irradiation of 9,10-phenanthrenequinone and diphenylacetylene. The quinone **8** (208 mg, 1.0 mmol) and diphenylacetylene **2** (89 mg, 0.5 mmol) in dichloromethane (100 mL) with 300 nm UV light for 48 h yielded **9** and **10**, in 26% and 27% yield, respectively: **9**: IR (KBr) 3063, 2963, 2850, 1704, 1595, 1447, 1221, 1184, 735, 694 cm^{-1} ; UV (MeOH) λ_{\max} 330, 306, 296, 256, 249 nm; $^1\text{H-NMR}$ (CDCl_3) δ 7.82-7.30 (18H, aromatic); $^{13}\text{C-NMR}$ (CDCl_3) δ 207.0, 186.7, 139.5, 133.3, 131.7, 131.2, 130.2, 130.0, 129.0, 128.1, 126.0; MS (EI) m/e 386 (M), 105. **10**: IR (KBr) 3063, 2929, 1677, 1595, 1449, 1211, 1175, 875, 720, 692, 643 cm^{-1} ; UV (MeOH) λ_{\max} 330, 256, 249 nm; $^1\text{H-NMR}$ (CDCl_3) δ 8.10-7.50 (18H); $^{13}\text{C-NMR}$ (CDCl_3) δ 194.6, 134.9, 133.0, 130.0, 129.2, 129.0, 128.8, 128.7, 128.4; Mass (EI), m/e 386 (M), 105.

Irradiation of acenaphthenequinone and diphenylacetylene. The quinone **11** (91 mg, 0.5 mmol) and diphenylacetylene **2** (89 mg, 0.5 mmol) in dichloromethane (200 mL) with 300 nm UV light for 48 h gave **12** and **13**, in 24% and 26% yield, respectively: **12**: IR (KBr) 3062, 2923, 2852, 1702, 1647, 1446, 1219, 735, 692 cm^{-1} ; UV(MeOH) λ_{\max} 330, 296, 286, 278, 256, 251 nm; $^1\text{H-NMR}$ (CDCl_3) δ 7.82-7.30 (16H, aromatic); $^{13}\text{C-NMR}$ (CDCl_3) δ 207.0, 186.7, 133.3, 131.1, 129.8, 129.0, 128.1, 126.0; Mass (EI), m/e 360 (M), 105. **13**: IR (KBr) 3440, 3061, 2924, 1718, 1677, 1595, 1448, 1279, 1209, 1174, 717 cm^{-1} ; UV (MeOH) λ_{\max} 330, 253, 248 nm; $^1\text{H-NMR}$ (CDCl_3) δ 8.10-7.50 (16H, aromatic); $^{13}\text{C-NMR}$ (CDCl_3) δ 194.6, 134.9, 133.7, 132.9, 130.0, 129.1, 129.0, 128.8, 128.4; Mass (EI) m/e 360, 105.

RESULTS AND DISCUSSION

As described before, Bryce-Smith *et al.* have reported that tetrachloro-1,2-benzoquinone **1a** reacts photochemically with diphenylacetylene **2** to give dioxene **4**, like type A, as shown in Scheme 2.⁶ The photoaddition reaction was carried out in acetone or acetonitrile solvent using visible light (> 400 nm). Heating of **1** and **2** at 98-150 °C gave rise to **3**, via [4 + 2]-cycloaddition followed by bisdecarbonylation, like type B in Scheme 1.

Our interest in the diversity of the reactivity of excited *o*-quinones has promoted us to investigate the type of the photoadducts of *o*-quinones and alkynes. Here, we have found an interesting fact that irradiation (300 nm) of tetrahalo-1,2-benzoquinones **1** and diphenylacetylene **2** in dichloromethane gives two isomeric quinone methides, **6** and **7**. Irradiation of a dichloromethane solution (100 mL) of tetrachloro-1,2-benzoquinone **1a** (246 mg, 1.0 mmol) and diphenylacetylene **2** (178 mg, 1.0 mmol) with 300 nm UV light for 24 h afforded two isomeric quinone methides, **6a** (26%) and **7a** (28%), via



Scheme 2

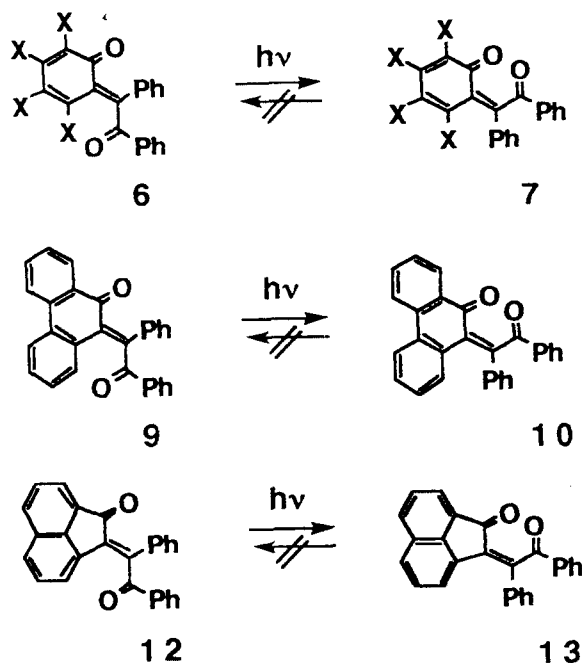
unstable intermediate spiro-oxetene **5a**.^{2,7} The R_f values of **6a** and **7a** on TLC plates (silica gel, Kieselgel 60 F₂₅₄, 0.25 mm, Merck Co.) in the eluent system of *n*-hexane and ethyl acetate (9:1, v/v) were 0.54 and 0.41, respectively.

This type of quinone methides were also found and isolated from the photoreaction of tetrabromo-1,2-benzoquinone **1b** and diphenylacetylene **2**. Irradiation of tetrabromo-1,2-benzoquinone **1b** (424 mg, 1.0 mmol) and diphenylacetylene **2** (178 mg, 1.0 mmol) in dichloromethane (100 mL) with 300 nm UV light for 24 h yielded same types of quinone methides, **6b** and **7b**, in 29% and 30% yields, respectively.^{2,7} When developed using TLC plates (silica gel, 0.25 mm), R_f values of **6b** and **5b** in the eluent system of *n*-hexane and ethyl acetate (9:1, v/v) were 0.53 and 0.40, respectively.

As like enedione systems, the irradiation of a dichloromethane solution (200 mL) of 9,10-phenanthrenequinone **8** (208 mg, 1.0 mmol) and diphenylacetylene **2** (89 mg, 0.5 mmol) with 300 nm UV light afforded two isomeric quinone methides, **9** (27%) and **10** (29%), as shown in Scheme 3.^{2,7} Irradiation of acenaphthenequinone **11** (91 mg, 0.5 mmol) and diphenylacetylene **2** (89 mg, 0.5 mmol) in dichloromethane (200 mL) with 300 nm UV light gave two isomeric enediones **12** (24%) and **13** (26%).

Interestingly, one-way *E-to-Z* photoisomerization was observed in the two isomeric quinone methides **6** and **7**. Irradiation of 20 mg (4.7×10^{-5} mol) of *E*-isomer **6a** in 15 mL of dichloromethane with 300 nm UV light for 24 h gave *Z*-isomer **7a** (23%), whereas irradiation of **7a** did not give **6a**. The same result was obtained between two isomers, **9** and **10**, and also **12** and **13**.

In conclusion, the irradiation of tetrahalo-1,2-benzoquinones, **1a** and **1b**, and diphenylacetylene **2** are irradiated using 300 nm UV light, instead of visible light, generated two isomeric quinone methides **6** and **7**, as like enedione systems. Two isomeric quinone methides, **9** and **10** (or **12** and **13**), are also produced when irradiated 9,10-phenanthrenequinone **8** (or

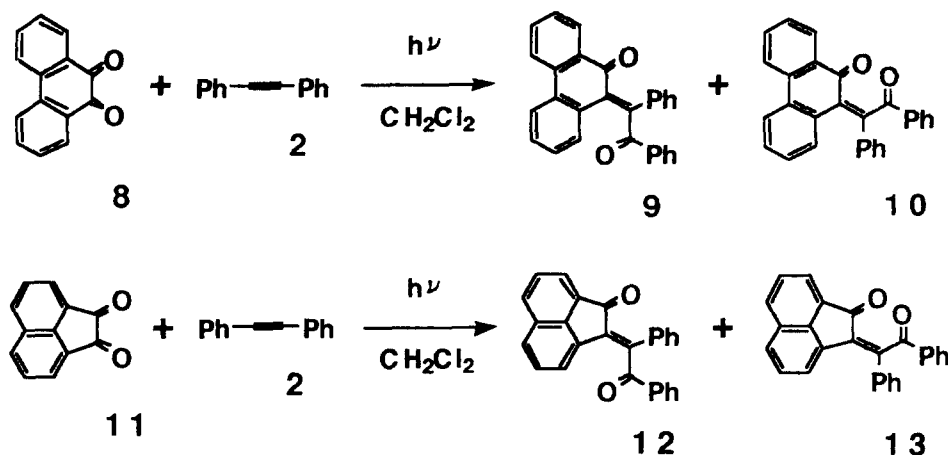


Scheme 4

acenaphthenequinone **11**) and diphenylacetylene **2** in dichloromethane with 300 nm UV light. It is also interesting to note that one-way *E-to-Z* photoisomerization is observed in these cases.

Extension of the chemical properties of various *o*-quinones and their photoproducts, and of the quantitative investigation of the one-way isomerization of the photoreactions will be investigated.

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Scheme 3

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