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7. Physical data: **2**; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.85 (9H, s), 1.20 (6H, m), 3.35 (1H, dd, J=5.1, 3.4 Hz), 3.46 (1H, m), 4.24 (1H, m), 4.29 (1H, dd, J=10.3, 3.4 Hz), 4.79 (2H, m), 5.28 (1H, dd, J=10.3, 1.4 Hz), 5.43 (1H, dd, J=17.2, 1.4 Hz), 5.88-5.97 (1H, m), 10.32 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ −5.1, −4.2, 16.2, 17.9, 22.1, 25.6, 37.9, 56.3, 60.3, 65.3, 66.7, 119.2, 130.5, 141.9, 159.1, 172.1, 188.8.
3; mp 58-61 °C IR ($CDCl_3$) cm^{-1} 3403, 2957, 1779, 1465, 1386, 1275. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.09 (3H, s), 0.10 (3H, s), 0.89 (9H, s), 1.29 (3H, d, J=6.2 Hz), 1.30 (3H, d, J=7.3 Hz), 3.22 (1H, dd, J=6.2, 2.8 Hz), 4.07 (1H, m), 4.27 (2H, m), 4.82 (2H, m), 5.29 (1H, dd, J=10.5, 1.4 Hz), 5.46 (1H, dd, J=17.2, 1.4 Hz), 5.93-6.02 (1H, m), 7.51 (1H, d, J=3.0 Hz), 7.94 (1H, d, J=3.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.1, 17.0, 18.0, 22.5, 25.7, 43.5, 55.8, 59.9, 66.2, 118.7, 122.9, 127.3, 131.2, 142.1, 142.8, 158.4, 161.1, 172.8. HR EI-MS m/z calcd for $C_{22}H_{32}N_2O_4SSi$ 448.1857, Found 448.1877.
5; mp 93-95 °C IR ($CDCl_3$) cm^{-1} 3157, 2968, 1760, 1650, 1469, 1386, 1253. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.04 (3H, s), 0.06 (3H, s), 0.83 (9H, s), 1.14 (3H, d, J= 6.3 Hz), 1.16 (3H, d, J=7.0 Hz), 2.97 (1H, dd, J=4.7, 2.2 Hz), 3.12 (1H, m), 3.19 (3H, s), 3.70 (3H, s), 3.84 (1H, dd, J=4.7, 2.2 Hz), 4.18 (1H, m), 6.06 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.1, −4.4, 12.4, 17.8, 22.2, 25.6, 31.9, 37.7, 52.0, 61.3, 65.1, 168.4, 175.1. FAB-MS (m/z) 345 (M^+)
6a; mp 103-106 °C IR ($CDCl_3$) cm^{-1}; 3098, 2971, 1761, 1673, 1477, 1387, 1258. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (3H, s), 0.05 (3H, s), 0.86 (9H, s), 1.11 (3H, d, J= 6.3 Hz), 1.32 (3H, d, J=7.0 Hz), 3.07 (1H, dd, J=4.0, 2.2 Hz), 4.01 (1H, dd, J=5.1, 2.2 Hz), 4.16 (2H, m), 6.04 (1H, br), 7.74 (1H, d, J=3.0 Hz), 8.03 (1H, d, J=3.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.1, −4.4, 12.6, 17.8, 22.3, 25.7, 43.7, 51.6, 61.6, 64.9, 127.1, 144.8, 166.4, 168.2, 195.5. HR EI-MS m/z calcd for $C_{17}H_{28}N_2O_3SSi$ 368.1589, Found 368.1570.
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Formation of *o*-/*p*-Quinomethanes and *p*-Quinodimethanes from the Photoaddition of Diphenylacetylene to *o*-Quinones†

Ae Rhan Kim, Yoon Jung Mah, and Sung Sik Kim*

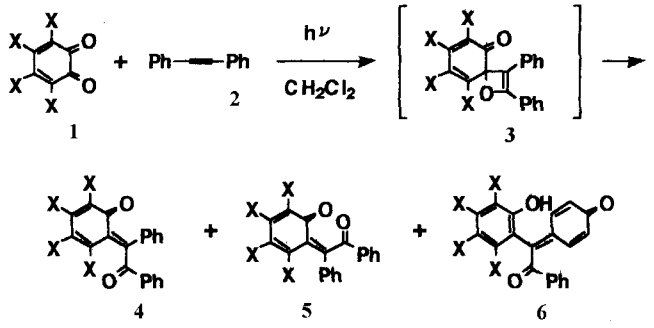
Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea

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.[1,2] Our interest in diverse reactivity of excited quinones has promoted us to investigate the type of the photoadducts of quinones.[3-5] Bryce-Smith *et al.* have reported that tetrachloro-1,2-benzoquinone **1a** reacts photochemically with diphenylacetylene (DPA) **2** to give dioxenes.[6] Photoreaction of **1a** and **2** in acetone or acetonitrile at >400 nm gave 1 : 2 adduct as 1,4-dioxene. We found that, when irradiated with 300 nm UV light, *o*-quinones add to **2** to give two isomeric *o*-quinomethanes, *i.e.*, **4** and **5**, **8** and **9**, and **12** and **13**, *via* spiro-oxetene intermediates, like **3**.[7]

Recently, we found an interesting fact that irradiation (300 nm) of tetrahalo-1,2-benzoquinones **1** and DPA **2** in dichloromethane gave new type of *p*-quinomethanes **6**, as well as two isomeric *o*-quinomethanes, **4** and **5**, as shown in Scheme 1. Preparative photochemical reactions were conducted in a photoreactor composed of a water-cooled system 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 photoproducts were isolated by flash column chromatography (silica gel, 230-400 mesh, Merck Co.) using *n*-hexane and ethyl acetate as the eluents (from 97 : 3 to 9 : 1, v/v).

Irradiation of a dichloromethane solution (100 mL) of tetrachloro-1,2-benzoquinone **1a** (246 mg, 1.0 mmol) and DPA **2** (178 mg, 1.0 mmol) with 300 nm UV light for 24 h afforded not only two isomeric *o*-quinomethanes, **4a** (26%) and **5a** (28%), *via* unstable spiro-oxetene **3a**, but also a novel *p*-quinomethane **6a** (17%).[8] The absorption peaks for

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



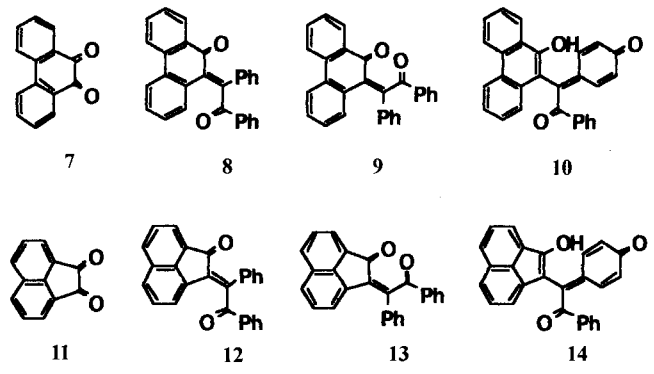
Scheme 1

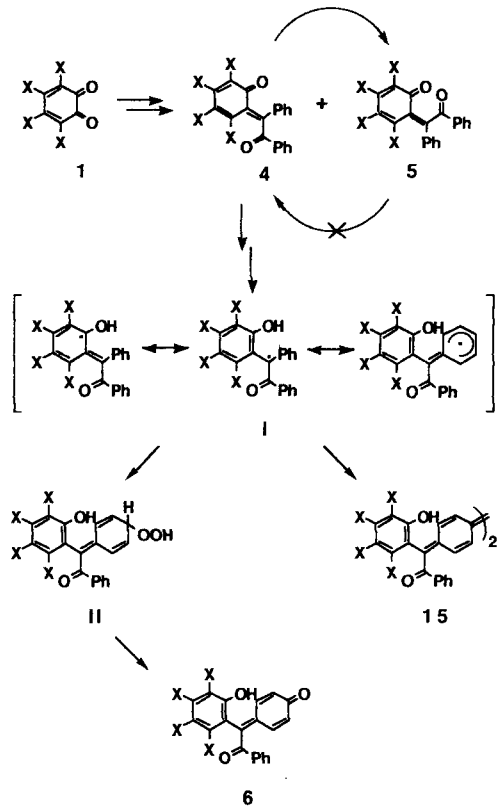
the four protons of quinone moiety in **6a** were observed at δ 7.57, 7.49, 7.10, and 6.91 as doublets (J=8.0 Hz) each in ^{1}H NMR spectrum ($CDCl_3$).

Irradiation of tetrabromo-1,2-benzoquinone **1b** (424 mg, 1.0 mmol) and DPA **2** (178 mg, 1.0 mmol) in dichloromethane (100 mL) with 300 nm UV light for 24 h yielded same types of quinomethanes, **4b, 5b**, and **6b**, in 29%, 30%, and 23% yields, respectively.[9] Two dimensional ^{1}H-^{1}H correlation spectrum ($CDCl_3$) of **6b** shows that the proton peaks of quinone moiety at δ 7.09 and 6.90 correspond to the peaks at δ 7.56 and 7.48, respectively.

It has been known that phenanthrenequinone **7** adds photochemically to alkynes to yield 1,4-dioxene, quinomethane, or 1,3-dioxole.[10,11] Irradiation of phenanthrenequinone **7** (208 mg, 1.0 mmol) and DPA **2** (89 mg, 0.5 mmol) in dichloromethane (200 mL) with 300 nm UV light for 48 h afforded a *p*-quinomethane **10** (26%), as well as two isomeric *o*-quinomethanes, **8** (27%) and **9** (29%).[12] The formation of **8** (or **9**) and **10** was confirmed from the mass spectra (EI), in which the molecular ions were found at m/e 386 and 402, respectively. Two dimensional ^{1}H-^{1}H correlation spectrum ($CDCl_3$) of **10** showed that the four absorption peaks of quinone moiety at δ 7.57 and 7.47 correspond to the peaks at δ 7.09 and 6.90, respectively. Two carbon peaks of **10** were observed at δ 207.0 and 205.5 in ^{13}C NMR spectrum ($CDCl_3$).

Irradiation of acenaphthenequinone **11** (91 mg, 0.5 mmol) and DPA **2** (89 mg, 0.5 mmol) in dichloromethane (200 mL) with 300 nm UV light for 48 h gave a *p*-quinomethane **14** (19%), as well as two isomeric *o*-quinomethanes, **12** (24%) and **13** (26%).[13] The exact structure of *o*-quinomethanes, such as **8, 9, 12**, and **13**, was also confirmed by irradiating in dichloromethane in the presence of molecular oxygen, in



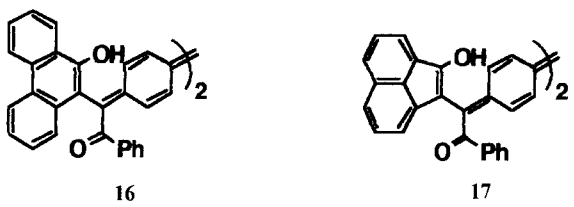


Scheme 2

which two benzene rings in the molecules was fused to give the corresponding oxidative photocyclization products. Purified **8** (or **12**) was irradiated with 300 nm UV light in dichloromethane to give **10** (or **14**). Irradiation of the other isomer **9** (or **13**) also gave rise to **10** (or **14**). Two dimensional ^{1}H-^{1}H correlation spectrum ($CDCl_3$) of **14** showed that the peaks at δ 7.58 and 7.40 correspond to the peaks at δ 7.06 and 6.80, respectively. Mass spectrum (EI) showed the molecular ion peak at m/e 376.

In order to elucidate the formation mechanism of **6a**, a dichloromethane solution of **4a** was purged with molecular oxygen for 30 min and irradiated in dichloromethane to give **6a**. Irradiation of **4** after degassing with freeze-pump-thaw method did not give **6**.

These results imply that the formation of *p*-quinomethane **6** proceeds *via* triplet state of the starting material **4**. It may be considered that irradiation of **4** leads to the formation of radical intermediate I, as shown in Scheme 2. The resonance-stabilized radical I can be alive until a molecular oxygen is added to give hydroperoxide II. The hydroperoxide II may be considered to decompose to yield the final product **6** as a novel *p*-quinomethane.



Irradiation of **1** and **2** in high concentration also gave rise to Chichibabin hydrocarbons **15** as a dimeric *p*-quinodimethane. The FAB mass spectrum of **15** (X=Cl) showed the molecular ion peak at m/e 845 (M+H). ^{1}H NMR spectrum ($CDCl_3$) showed hydroxyl protons and aromatic protons at δ 11.40 (s) and 7.99-7.59. The proton signals of *p*-quinodimethane moiety were observed at δ 7.57, 7.49, 7.10, and 6.91, in which all signals appeared as doublet (J=8.0 Hz) each. The same type of dimeric compounds, *i.e.,* **16** and **17**, were also observed and isolated from the photoreaction of **2** and **7** (or **11**), as shown below.[14,15]

Interestingly, one-way *E*-to-*Z* isomerization was observed between the two *o*-quinodimethanes, **4** and **5**.[7] Irradiation of 20 mg (4.7×10^{-5} mol) of *E*-isomer **4a** in 15 mL of dichloromethane with 300 nm UV light for 24 h gave *Z*-isomer **5a** (23%), and also **6a** (16%), whereas irradiation of **5a** did not give **4a**. The similar results were obtained in the case of **8** and **12**.

In conclusion, we have shown here that two isomeric *o*-quinomethanes are produced when *o*-quinones and DPA **2** are irradiated with 300 nm UV light, instead of visible light (>400 nm). It is also interesting to note that novel *p*-quinomethanes and *p*-quinodimethanes may be formed *via* the initially produced *o*-quinomethanes.

Extension of the chemical properties of various *o*-quinones and their photoproducts will be investigated.

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8. **6a**: 400 MHz ^{1}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); IR (KBr), 3369, 3064, 1732, 1682, 1030, 763 cm^{-1}; UV (MeOH), 334, 301, 279, 253, 245 nm; Mass (EI), m/e 438 (M), 333 (M-105), 105.
9. **6b**: 400 MHz ^{1}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); IR (KBr), 3382, 3061, 1734, 1682, 1038, 763 cm^{-1}; UV (MeOH), 336, 328, 283, 256, 245 nm; Mass (EI), m/e 614 (M), 105.
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12. **10**: 400 MHz ^{1}H NMR ($CDCl_3$), δ 11.4 (1H, s, hydroxy), 8.80-7.35 (13H, aromatic), 7.57 (1H, d, J=8.0 Hz), 7.47 (d, J=8.0 Hz), 7.09 (1H, d, J=8.0 Hz), 6.90 (1H, d, J=8.0 Hz); IR (KBr), 3440, 3065, 1742, 1671, 1093, 757 cm^{-1}; ^{13}C NMR ($CDCl_3$), 207.0, 205.5, 133.8, 130.2, 129.8, 129.4, 129.1, 129.0, 128.6, 128.5, 128.2, 127.5, 127.0, 126.3, 123.1, 122.9; UV (MeOH), 338, 301, 252 nm; Mass (EI), m/e 402 (M), 105.
13. **14**: 400 MHz ^{1}H NMR ($CDCl_3$), δ 11.4 (1H, s, hydroxy), 8.31-7.23 (13H, aromatic), 7.58 (1H, d, J=8.0 Hz), 7.40 (d, J=8.0 Hz), 7.06 (1H, d, J=8.0 Hz), 6.80 (1H, d, J=8.0 Hz); IR (KBr), 3440, 3059, 1734, 1687, 1014, 776 cm^{-1}; Mass (EI), m/e 376 (M), 271 (M-105), 105.
14. **16**: 400 MHz ^{1}H NMR ($CDCl_3$), δ 11.5 (1H, s, hydroxy), 8.80-7.35 (26H, aromatic), 7.57 (2H, d, J=8.0 Hz), 7.47 (d, J=8.0 Hz), 7.09 (1H, d, J=8.0 Hz), 6.90 (1H, d, J=8.0 Hz); IR (KBr), 3440, 3065, 1742, 756 cm^{-1}; Mass (FAB), m/e 773 (M+1).
15. **17**: 400 MHz ^{1}H NMR ($CDCl_3$), δ 11.5 (1H, s, hydroxy), 8.31-7.13 (22H, aromatic), 7.58 (2H, d, J=8.0 Hz), 7.40 (2H, d, J=8.0 Hz), 7.06 (2H, d, J=8.0 Hz), 6.90 (2H, d, J=8.0 Hz); IR (KBr), 3440, 3066, 1743, 757 cm^{-1}; Mass (FAB), m/e 721 (M+1).