Photoaddition Reaction of 1,4-Diethynylbenzene to Tetramethyl-1,4-benzoquinone and Photochemical Transformation of the Photoadducts

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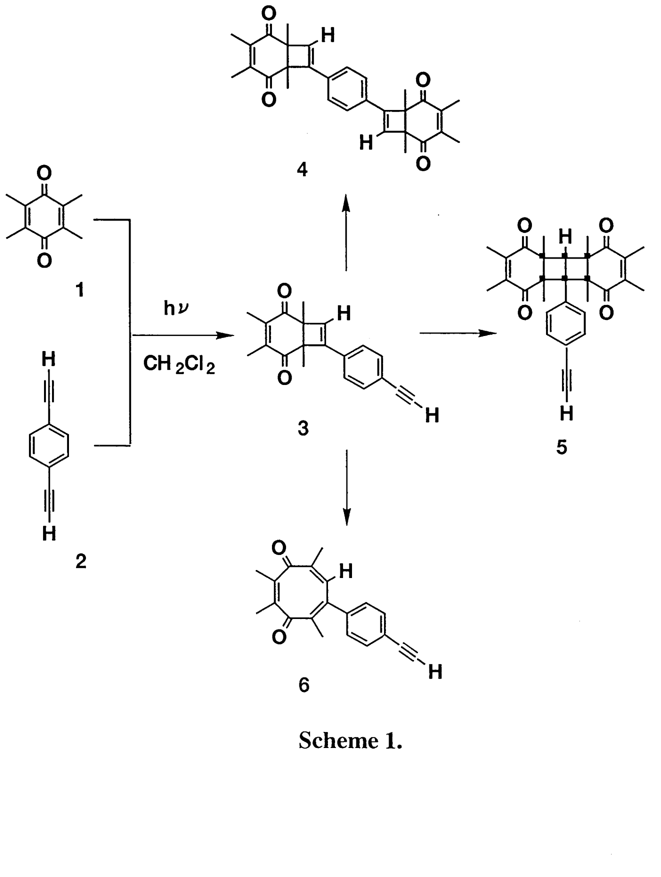
Irradiation of a dichloromethane solution of tetramethyl-1,4-benzoquinone and 1,4-diethynylbenzene with 300 nm UV light yields three kinds of photoadducts which are interconverted photochemically into their corresponding isomers.

Quinones are an important class of compounds in organic synthesis, in industry, and in nature.[1] Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas.[2-4] Photoaddition of *p*-quinones to alkynes yields quinone methides, *via* an unstable intermediate spiro-oxetenes.[5-6] The *p*-quinones also add to a conjugated diyne such as 1,4-diphenyl-1,3-butadiyne to give 1:1 adducts.[7] Recently, we have examined the photoaddition reactions of 1,4-diethynylbenzenes to *p*-quinones.[8] In connection with our investigation of the scope of these reactions, we examined the photochemical reaction of tetramethyl-1,4-benzoquinone (duroquinone) **1**[9] with 1,4-diethynylbenzene **2** which has two carbon-carbon triple bonds separated by the central benzene ring.

Preparative photochemical reactions were conducted in a photochemical reactor composed of a water-cooled system and a pyrex (or a quartz) reaction vessel with 300 nm (or 254 nm) UV lamps (Rayonet Photochemical Reactor, Model RPR-208). Irradiation of a dichloromethane solution (200 mL) of duroquinone **1** (197 mg, 1.2 mmol) and 1,4-diethynylbenzene **2** (76 mg, 0.60 mmol) with 300 nm UV light for 25 h afforded not only 1:1 adducts, **3** and **6**, but also two kinds of 1:2 adducts, **4** and **5**, in 17, 19, 30, and 15% yield, respectively.



Scheme 1.

The photoproducts were isolated by flash column chromatography (silica gel, 230 - 400 mesh) using *n*-hexane and ethyl acetate (9:1, v/v) as the eluents. ^{1}H-NMR spectrum ($CDCl_3$) of 1:1 adduct **3**[10] shows two singlets at δ 6.52 (vinyl proton) and 3.13 (acetylenic proton). The carbon signals containing vinyl proton and acetylenic proton were observed at δ 134.9 and 78.50, respectively. The CI mass spectrum gave (M+1) peak at m/e 291 (100%).

Irradiation (254 nm) of **3** (20 mg, 0.068 mmol) in dichloromethane (20 mL) for 1 h afforded the electrocyclic reaction product **6**[11] in 32% yield, as well as the starting materials, **1** and **2** in 20% yield. Irradiation (300 nm) of **6** in dichloromethane gave rise to the formation of the original 1:1 adduct **3**. ^{1}H-NMR spectrum ($CDCl_3$) of **6** shows a vinyl proton and an acetylenic proton at δ 7.60 (s) and 3.13 (s), respectively. The carbon signals containing vinyl proton and acetylenic proton were found at δ 159.2 and 78.34, respectively.

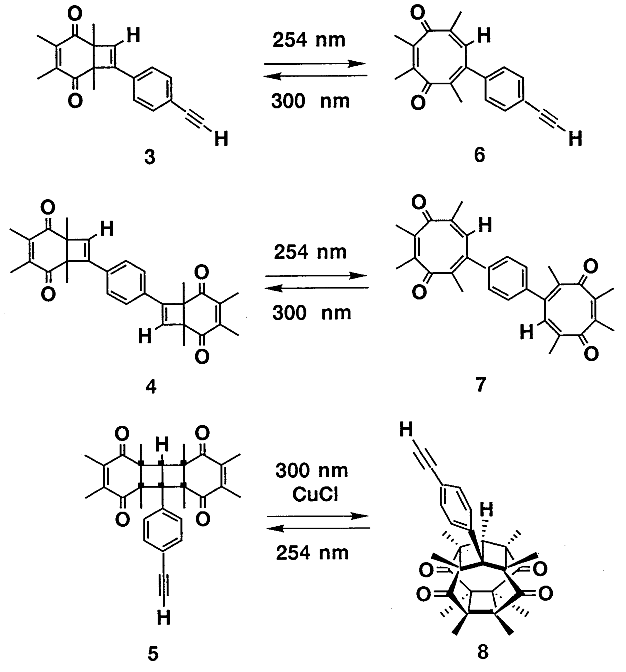
Two-dimensional ^{1}H-^{13}C correlation spectrum ($CDCl_3$) of 1:2 adduct **4**[12] shows that the peaks at δ 134.5 and 125.8 in the ^{13}C dimension correspond to the vinyl protons (δ 6.49) and the aromatic protons (δ 7.38) in the ^{1}H dimension, respectively. The CI mass spectrum also gave (M+1) peak at m/e 455 (100%). It was found that the chemical yield of 1:2 adduct **4** increases with increasing the irradiation time.

Irradiation (254 nm) of **4** (20 mg, 0.044 mmol) in dichloromethane (20 mL) for 1 h yielded **7**[13] containing two eight-membered rings in 54% yield. Irradiation (300 nm) of **7** in dichloromethane also gave rise to the original 1:2 adduct **4**. ^{1}H-NMR spectrum ($CDCl_3$) of **7** shows vinyl protons and aromatic protons at δ 7.61 (s, 2 x 1H) and 7.72 (s, 4H), respectively. The carbon signals containing vinyl protons and aromatic protons were observed at δ 158.9 and 127.3, respectively. These types of electrocyclic reaction to eight-membered ring compounds, such as **6** and **7**, depend upon the steric hindrance of the structure. A 1:2 adduct prepared from the photoreaction of duroquinone and 1,4-diphenylbutadiyne did not undergo such conversion in the similar condition.[14]

Another type of 1:2 adduct **5**[15] shows two proton signals at δ 5.45 (methine proton) and 3.13(acetylenic proton) in ^{1}H-NMR spectrum ($CDCl_3$). The carbon signals containing methine proton and acetylenic proton were observed at δ 126.9 and 78.15, respectively, in ^{1}H-^{13}C correlation spectrum ($CDCl_3$). The structure of **5** was characterized not only by a weak (M+1) peak at m/e 455 but by a peak at m/e 291 as well in the CI mass spectrum. The base peak at m/e 291 may be due to the elimination of a duroquinone moiety from the molecular ion.

Irradiation of **5** (16 mg, 0.036 mmol) in dichloromethane (20 mL) in the presence of copper(I) chloride (16 mg, 0.16 mmol) with 300 nm UV light gave rise to cage molecule **8**[16] in 90% yield. **8** was also found to go back to **5**, when irradiated with 254 nm

UV light. Instead of copper(I) chloride, using copper (I) iodide or copper (II) triflate also yielded the cage molecule **8** in 80-92% yield. ^{1}H-NMR spectrum (CDCl$_3$) of **8** shows a methine proton and an acetylenic proton at δ 5.28 and 3.12, respectively. The carbon signals containing methine proton and acetylenic proton were found at δ 112.7 and 78.05, respectively. The UV spectrum (MeOH) of **8** shows characteristic absorption bands at 280, 269, 266, 252, 244, and 233 nm, which are partly due to phenyl acetylene moiety of the structure.



Scheme 2.

We have shown above that three kinds of photocycloadducts can be prepared from the photoreaction of duroquinone **1** with 1,4-diethynylbenzene **2**. It is also interesting to note that the three adducts each undergo reversible photochemical transformation into their corresponding isomers. Extension of some properties of these photochromic molecules will be investigated.

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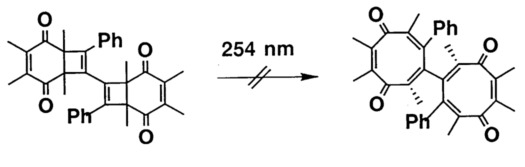
10 Spectral data of **3**; mp 118-119 °C; IR (KBr) 3296, 3043, 2980, 2108, 1700, 1658, 1454, 1377, 835 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 290, 280, 256 nm; ^{1}H-NMR (CDCl$_3$) δ 7.42 (2H, d, J = 8 Hz), 7.39 (2H, d, J = 8 Hz), 6.52 (1H, s, vinyl), 3.13 (1H, s, acetylenic), 1.99 (3H, s, Me), 1.97 (3H, s, Me), 1.63 (3H, s, Me), 1.49 (3H, s, Me); ^{13}C-NMR (CDCl$_3$) δ 200.4 (C=O), 199.8 (C=O), 152.6, 142.7, 142.5, 134.9 (CH, vinyl), 131.8 (2CH's, aromatic), 125.9, 125.8 (2CH's, aromatic), 123.6, 83.47 (C, acetylenic), 78.50 (CH, acetylenic), 58.25, 56.11, 16.90 (Me), 16.55 (Me), 13.80 (Me); 13.56 (Me); MS (CI) m/e 291 (M+1).

11 Spectral data of **6**; mp 160-62 °C; IR (KBr) 3296, 3043, 2973, 2108, 1700, 1658, 1447, 1377, 842 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 336, 285, 256 nm; ^{1}H-NMR (CDCl$_3$) δ 7.66 (2H, d, J = 8 Hz), 7.47 (2H, d, J = 8 Hz), 7.60 (1H, s, vinyl), 3.13 (1H, s, acetylenic), 2.11 (3H, s, Me), 1.67 (3H, s, Me), 1.38 (3H, s, Me), 1.37 (3H, s, Me); ^{13}C-NMR (CDCl$_3$) δ 205.9 (C=O), 204.3 (C=O), 168.8, 159.2 (CH, vinylic), 136.8, 134.5, 132.2 (2CH's, aromatic), 131.1, 129.9, 127.1 (2CH's, aromatic), 125.8 122.5, 83.31 (C, acetylenic), 78.34 (CH, acetylenic), 16.87 (Me), 16.26 (Me), 12.89 (Me), 8.34 (Me); Mass (CI), m/e 291 (M+1).

12 Spectral data of **4**; mp 184-185 °C; IR (KBr) 3057, 2973, 1700, 1665, 1454, 1377, 835 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 290, 280, 257 nm; ^{1}H-NMR (CDCl$_3$) δ 7.38 (4H, s), 6.49 (2H, s, vinyl), 1.97 (6H, s, 2Me's), 1.93 (6H, s, 2Me's), 1.60 (6H, s, 2Me's), 1.48 (6H, s, 2Me's); ^{13}C-NMR (CDCl$_3$) δ 200.4 (C=O), 199.8 (C=O), 152.6, 142.6, 142.5, 134.5 (2CH's, vinyl), 132.0, 125.8 (4CH's, aromatic), 58.25, 56.08, 16.93 (2Me's), 16.55 (2Me's), 13.80 (2Me's), 13.56 (2Me's); Mass (CI), m/e 455 (M+1).

13 Spectral data of **7**; IR (KBr) 3043, 2924, 1700, 1644, 1454, 1377, 842 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 336, 294, 254, 240 nm; ^{1}H-NMR (CDCl$_3$) δ 7.72 (4H, s, aromatic), 7.61 (2H, s, vinyl), 2.14 (6H, s, 2Me's), 1.71 (6H, s, 2Me's), 1.41 (6H, s, 2Me's), 1.40 (6H, s, 2Me's); ^{13}C-NMR (CDCl$_3$) δ 206.0 (C=O), 204.5 (C=O), 168.8, 158.9 2CH's, vinyl), 137.0, 132.3, 131.1, 130.9, 128.8, 127.3 (4CH's, aromatic), 16.90 (2Me's), 16.28 (2Me's), 12.91 (2Me's), 8.34 (2Me's); Mass (CI), m/e 455 (M+1).

14 Irradiation of duroquinone and 1,4-diphenylbutadiyne in dichloromethane with 300 nm UV light yielded 1:2 [2+2] photoadduct as shown below. Spectral data; IR (KBr), 3064, 2931, 1728, 1658, 1447, 1377, 786, 695 cm^{-1}; UV (MeOH), $\lambda_{\max}$ 259, 270 nm; ^{1}H-NMR (CDCl$_3$) δ 7.28-7.04 (10H, m), 2.04 (6H, s), 1.89 (6H, s), 1.66 (6H, s), 1.62 (6H, s); Mass (EI) m/e 202, 530 (M).



15 Spectral data of **5**; mp 190-192 °C; IR (KBr) 3296, 3043, 2931, 2108, 1707, 1658, 1454, 1377, 842 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 280, 268, 254, 244 nm; ^{1}H-NMR (CDCl$_3$) δ 7.55 (2H, d, aromatic, J = 8 HZ), 7.20 (2H, d, aromatic, J = 8 Hz), 5.45 (1H, s, -C-C-H), 3.13 (1H, s, acetylenic), 1.65 (6H, s, 2Me's), 1.24 (12H, s(overlapped), 2x2Me's), 1.18 (6H, s, 2Me's); ^{13}C-NMR (CDCl$_3$) δ 200.4 (C=O), 199.8 (C=O), 136.3, 135.4, 132.8 (2CH's, aromatic), 129.9 (2CH's aromatic), 126.9 (-C-C-H), 125.3, 122.8, 83.31 (C, acetylenic), 78.15 (CH, acetylenic), 59.27, 57.30, 52.69, 45.01, 16.18 (6H, 2Me's), 7.89 (12H, 4Me's), 6.23 (6H, 2Me's); Mass (CI) m/e 455 (M+1), 291 (M-duroquinone+1).

16 Spectral data of **8**; IR (KBr) 3296, 3015, 2924, 2108, 1728, 1454, 1384, 835 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 280, 269, 266, 252, 244, 233 nm; ^{1}H-NMR (CDCl$_3$) δ 7.49 (2H, d, J = 8 Hz), 7.18 (2H, d, J = 8 Hz), 5.28 (1H, s, -C-C-H), 3.12 (1H, s, acetylenic), 1.92 (6H, s, 2Me's), 1.32 (6H, s, 2Me's), 0.84 (6H, s, 2 Me's), 0.82 (6H, s, 2Me's).