

Oxidation of 2,6-Dimethylphenol. 2,6-Dimethyl-*p*-benzoquinone **2b** was prepared in 63% yield following the above reaction procedure in acetone and pH 7.1 buffer. mp. 69-72°C (lit. 70-71°C)¹². ¹H-NMR (CDCl₃) δ 6.55 (s, 2H, ArH), 2.05 (s, 6H, CH₃), IR (KBr) 1651, 1614 cm⁻¹.

Oxidation of 2,6-Di-*tert*-Butylphenol. 2,6-Di-*tert*-butyl-*p*-benzoquinone **2c** was prepared in 76% yield following the above procedure in acetone and pH 9.3 buffer. mp. 64-66°C (lit. 65-66°C)¹². ¹H-NMR (CDCl₃) δ 6.50 (s, 2H, ArH), 1.25 (s, 18H, CH₃), IR (KBr) 1655, 1599 cm⁻¹.

Oxidation of 2,6-Dichlorophenol. To a solution of 0.30 g of 2,6-dichlorophenol in 10 ml acetone and 10 ml of pH 7.1 buffer, chlorine dioxide was passed through under the ice bath. The reaction was completed in 1.5 hr by the TLC. 100 ml of water added to the reaction mixture to facilitate the crystallization. The bright yellow needle product (0.3 g, 95% yield) was collected by the filtration. mp. 124-125°C (lit. 120-121°C)¹³. ¹H-NMR of **2d** (CDCl₃) δ 7.01 (s, 2H, vinyl proton from quinone). IR (KBr) 1701, 1649 cm⁻¹. Mass (EI) 176.

Oxidation of 2,4-Dimethylphenol. To a solution of 0.24 g of 2,4-dimethylphenol in 30 ml of acetone and pH 4.2 buffer, chlorine dioxide was passed through under the ice bath. After 30 min 100 ml of water was added and extracted with chloroform. Solvents was removed by the rotary evaporator to leave yellow oil which was triturated with hexane to yield 0.10 g (38%) of white crystal of phthalic acid **5**. The yellow product was separated by the column chromatography but failed to identify. mp. of **5**; 205-206°C dec. (lit. 210°C dec)¹⁴. ¹H-NMR of **5** (DMSO-d₆) δ 12.0-14.0 (br.s, 2H, OH), 7.54-7.68 (m, 4H, ArH), IR of **5** (KBr) 3000, 2654, 2526, 1691, 1585 cm⁻¹. Mass of **5** (EI) 166.

Oxidation of 2,4-Di-*tert*-Butylphenol. Following the reaction sequence described above, 45% of phthalic acid was prepared by the treatment of 2,4-di-*tert*-butylphenol with chlorine dioxide.

Oxidation of 2,4-Dichlorophenol. To a solution of 0.30 g of 2,4-dichlorophenol in 30 ml of acetone and 30 ml of pH 7.1 buffer, chlorine dioxide was passed through under the ice bath for 1 h. Following the usual work-up procedure 0.16 g (49%) of bright needle (which was identified as 2,6-dichloro-*p*-benzoquinone) was obtained after the column chromatography (eluent, chloroform : hexane = 7 : 3).

Oxidant of 1-Naphthol. To a solution of 0.30 g of 1-naphthol in 40 ml acetone, chlorine dioxide was passed through under the ice bath for 1.5 h. Evaporated the solvents and the residue was purified by the column chromatography (eluent, chloroform : hexane = 4 : 6) to yield 0.12 g (37%) of 2-chloro-1,4-naphthoquinone **8** and 0.07 g (22%) of 1,4-naphthoquinone **7**. mp. of **7**; 126-128°C (lit. 124-125°C)¹¹. ¹H-NMR of **7** (CDCl₃) δ 8.02 and 7.75 (m, 4H, ArH from aromatic), 6.95 (s, 2H, vinyl proton from quinone). IR of **7** (KBr) 1660, 1600 cm⁻¹. Mass spectrum of **7** (EI) 158. mp. of **8**; 114-116°C (lit. 112-115°C)¹⁴. ¹H-NMR of **8** (CDCl₃) δ 8.18, 8.10 and 7.80 (m, 4H, ArH from aromatic), 7.24 (s, 1H, vinyl proton from quinone). IR of **8** (KBr) 1670 and 1600 cm⁻¹. Mass spectrum of **8** (EI) 192.

Oxidation of 2-Naphthol. To a solution of 0.30 g of 2-naphthol in 20 ml chloroform, chlorine dioxide was passed through under the ice bath for 1 h. The white precipitate formed was collected by the suction filtration to yield 0.16

g (73%) of 2-carboxycinnamic acid **10** exclusively. mp. 213-215°C (lit. 217-219°C)⁹. ¹H-NMR (DMSO-d₆) δ 12.8 (s, 2H, OH), 8.35 and 6.45 (pair of d, 2H, -CH=CH-), 7.90 (d, 1H, ArH), 7.85 (d, 1H, ArH), 7.65 (t, 1H, ArH), 7.55 (t, 1H, ArH). ¹³C-NMR (DMSO-d₆) δ 168.01 and 167.28 (-CO₂H), 142.46, 134.76, 132.04, 130.89, 130.22, 129.62, 127.65, and 121.23 (ArH and vinyl carbons). IR (KBr) 2997, 1683, 1626, 1278 cm⁻¹. Mass spectrum (EI) 192.

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Photoaddition of *p*-Quinones to 1,4-Diethynylbenzenes

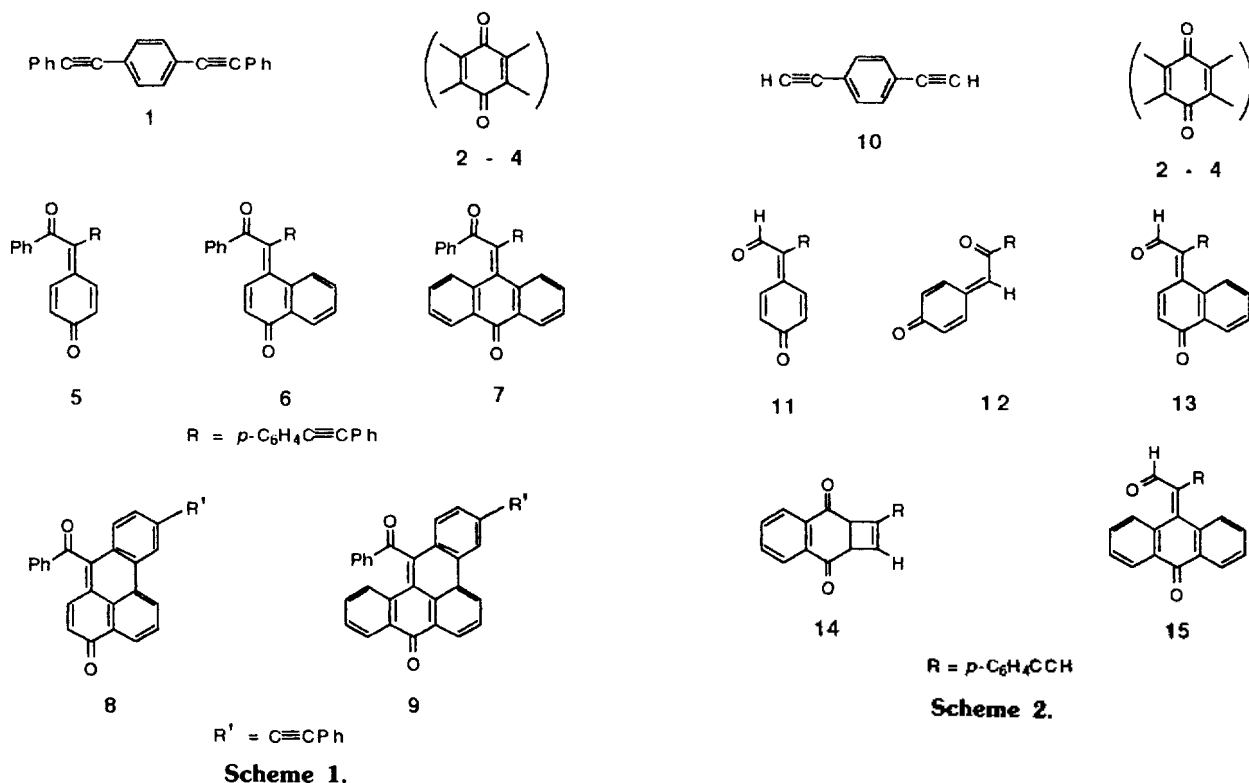
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Quinones are an important class of compounds in organic synthesis, in industry, and in Nature.¹ Due to their various



spectral properties, the photochemistry of quinones has been a subject of interest in many areas.²⁻⁶ The photoaddition of *p*-quinone to diphenylacetylene forms a quinone methide, through an unstable intermediate spiro-oxetene.⁷⁻¹⁰ The *p*-quinones are observed to form a single 1:1 adduct in the photochemical reaction with a conjugated diyne such as 1,4-diphenyl-1,3-butadiyne.¹¹

In connection with our investigation of the scope of these reactions, we have examined the photoaddition reactions of *p*-quinones to 1,4-diphenylethynylbenzene (DPEB, **1**) and to 1,4-diethynylbenzene (DEB, **10**), which have two carbon-carbon triple bonds separated by the central benzene ring. Preparative photochemical reactions were conducted in a photo-reactor composed of a water-cooled system and a pyrex reaction vessel with 350 nm UV lamps (Rayonet Photochemical Reactor).

Irradiation of a solution of 1,4-benzoquinone (**2**, 300 mg, 2.78×10^{-3} mole) and DPEB (**1**, 300 mg, 1.08×10^{-3} mole) in dichloromethane for 12 h gave a quinone methide (**5**) in 36% yield by 1,2-addition of a carbonyl group of the quinone.¹² The 1:1 adduct was isolated by column chromatography (silica gel, *n*-hexane and ethyl acetate (10:1, v/v)). The EI mass spectrum exhibits the molecular ion peak at *m/e* 386. The peaks at *m/e* 105 and *m/e* 77 prove the existence of benzoyl group. The two acetylenic carbons are observed at 88.6 ppm and 92.3 ppm in ¹³C-NMR spectrum.

Photoreactions of DPEB (**1**) with *p*-quinones, 1,4-naphthoquinone (**3**) and anthraquinone (**4**), in dichloromethane (12 h) gave compounds (**8**),¹³ 21% yield from **1** and **3**, and **9**,¹⁴ 37% yield from **1** and **4**), which are believed to be generated by secondary photoreactions of initially formed 1:1 photoadducts (**6** and **7**) respectively.

The photochemical reactions of DEB (**10**) with *p*-quinones

(**2-4**) were also studied in dichloromethane. A solution of 1,4-benzoquinone (**2**, 200 mg, 1.85×10^{-3} mole) and DEB (**10**, 100 mg, 7.94×10^{-4} mole) in dichloromethane (150 mL) was irradiated for 12 h. Two stereoisomeric 1:1 adducts (**11**, 17% yield and **12**, 15% yield) were obtained.^{15,16} ¹H-NMR spectrum of **11** shows two singlets at δ 3.10 ppm (acetylenic proton) and 9.73 ppm (aldehyde proton). The acetylenic carbons and aldehyde carbon were observed at 77.3 ppm and 78.1 ppm, and 197.8 ppm, respectively, in ¹³C-NMR spectrum. ¹H-NMR spectrum of **12** exhibits two singlets at δ 3.24 ppm (acetylenic proton) and 5.74 ppm (vinyl proton). The acetylenic carbons were observed at 77.3 ppm and 79.8 ppm in ¹³C-NMR spectrum.

1,4-Naphthoquinone (**3**) and DEB (**10**) gave not only a quinone methide (**13**, 23%) but also a cyclobutene (**14**, 9%).^{17,18} The 1:1 adduct (**13**) shows two ¹H signals of δ 3.20 ppm (acetylenic proton) and 10.27 ppm (aldehyde proton) in ¹H-NMR spectrum. A weak band at 2846 cm^{-1} is also found in IR spectrum, which is suggestive of aldehyde. The adduct (**14**) exhibits four ¹H signals at δ 3.15 ppm, 4.16 ppm, 4.53 ppm, and 6.61 ppm for the acetylenic proton, two methine protons, and vinyl protons, respectively. The methine carbons and acetylenic carbons were observed at 49.1 ppm and 52.0 ppm, and 78.7 ppm and 83.3 ppm, respectively, in ¹³C-NMR spectrum. The molecular ion peak was also observed at *m/e* 284 in the EI mass spectrum.

Anthraquinone (**4**, 370 mg, 1.78×10^{-3} mole) and DEB (**10**, 100 mg, 7.94×10^{-4} mole) in dichloromethane (200 mL) gave a quinone methide (**15**) in 35% yield.¹⁹ The adduct (**15**) shows two ¹H signals at 3.14 ppm (acetylenic CH) and 10.03 ppm (aldehyde CH) in ¹H-NMR spectrum. The acetylenic carbons and aldehyde carbon were observed at 78.1 ppm and 83.2 ppm, and 191.6 ppm, respectively, in ¹³C-NMR spectrum. Carbonyl carbon was observed at 184.5 ppm. Peaks at 3280 cm^{-1} and 2868 cm^{-1} are observed, which are due

to the acetylenic C-H bond and aldehyde C-H bond, respectively. The molecular ion peak was observed at m/e 334 in the EI mass spectrum. The photoproducts (**13** and **15**) were also oxidized to the corresponding photocyclized products.

Attempts to get 1:2 adduct from 1:1 adduct and *p*-quinone have been unsuccessful, which would be used in many areas such as organic colorants, metal complexes, etc.^{20,21} The results suggest that *p*-quinones react with alkynes (**1** and **10**) forming only 1:1 adducts in significant quantity, and that the adducts are photolabile. Although 1:2 adducts of the alkynes (**1** and **10**) and *p*-quinones have not been isolated yet, extension of the investigation to get the 1:2^{*} adducts in significant yields, and to study the properties of the photoproducts will be continued.

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- (a) Spectral data of **5**; IR (KBr), 3070, 2214, 1667, 1635, 1599, 1263, 1194, 832, 764, 699 cm^{-1} ; UV (MeOH), λ_{max} 349, 304, 300, 288, 249 nm; $^1\text{H-NMR}$ (CDCl_3), δ 6.91-6.95 (3H, m), 7.36-7.79 ppm (15H); $^{13}\text{C-NMR}$ (CDCl_3), δ 88.6 and 92.3 (acetylenic $\underline{\text{C}}$'s), 115.3, 115.4, 128.2, 128.4, 129.8, 130.0, 131.4, 131.7, 132.1, 132.5, 132.9 and 133.0 (18 or 12 kinds of $\underline{\text{C}}\text{H}$'s), 122.7, 127.2, 129.2, 131.0, 137.2 and 138.1 (6 $\underline{\text{C}}$'s), 195.4 and 196.3 ppm (2 $\underline{\text{C}}=\text{O}$'s); Mass (EI), m/e 77 (C_6H_6), 105 ($\text{C}_6\text{H}_5\text{CO}$), 281 (M-105), 386 (M, 100%); (b) Similar 1:1 adduct of DPEB **1** and tetrachloro-*p*-benzoquinone was also isolated; IR (KBr), 3054, 2221, 1691, 1677, 1595, 1510, 1236, 835, 758, 695 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 7.87-7.36 ppm (14H); Mass (EI), m/e 77 (C_6H_5), 105 ($\text{C}_6\text{H}_5\text{CO}$, 100%), 522 (M).
- Spectral data of **8**; IR (KBr), 3055, 2214, 1663, 1636, 1595, 1255, 1169, 866, 756, 691 cm^{-1} ; UV (MeOH), λ_{max} 358, 326, 292, 278, 226 nm; $^1\text{H-NMR}$ (CDCl_3), δ 6.72 (1H, d, $J=10\text{Hz}$), 7.39-9.12 ppm (17H); Mass (EI), m/e 77 (C_6H_5), 105 ($\text{C}_6\text{H}_5\text{CO}$), 329 (M-105), 357 (M-77), 406 (M-CO), 434 (M, 100%).
- Spectral data of **9**; IR (KBr), 3055, 1667, 1641, 1588, 1259, 1178, 862, 757, 689 cm^{-1} ; UV (MeOH), λ_{max} 362, 312, 300, 280, 272, 242 nm; $^1\text{H-NMR}$ (CDCl_3), δ 7.29-9.11 ppm (20H); Mass (EI), m/e 77 (C_6H_5), 105 ($\text{C}_6\text{H}_5\text{CO}$), 379 (M-105), 407 (M-77), 456 (M-CO), 484 (M, 100%).
- Spectral data of **11**; IR (KBr), 3303, 3022, 2853, 1721, 1672, 1602, 1510, 1215, 1173, 835, 751, 667 cm^{-1} ; UV (MeOH), λ_{max} 270, 254, 243, 210 nm; $^1\text{H-NMR}$ (CDCl_3), δ 3.10 (1H, s, $\underline{\text{C}}\text{H}$), 6.85 (2H, m), 7.23 (2H, m), 7.40 (2H, d, aromatic), 7.51 (2H, d, aromatic), 9.73 ppm (1H, s, $\underline{\text{C}}\text{H}=\text{O}$); Mass (EI), m/e 101 ($\text{C}_6\text{H}_4\text{CCH}$), 205 (M-CHO), 234 (M).
- Spectral data of **12**; IR (KBr), 3267, 3063, 1672, 1595, 1510, 1250, 1173, 835, 772, 674 cm^{-1} ; UV (MeOH), λ_{max} 272, 230, 211 nm; $^1\text{H-NMR}$ (CDCl_3), δ 3.24 (1H, s, $\underline{\text{C}}\text{H}$), 5.74 (1H, s, $=\underline{\text{C}}\text{H}$), 6.91 (2H, m), 7.59 (2H, m), 7.72 (2H, d, aromatic), 7.77 ppm (2H, d, aromatic); $^{13}\text{C-NMR}$ (CDCl_3), δ 77.3 and 79.8 (2 acetylenic $\underline{\text{C}}$'s), 115.2 (2 $\underline{\text{C}}$'s), 129.6 (2 $\underline{\text{C}}$'s), 131.9 (2 $\underline{\text{C}}$'s) and 132.8 (2 $\underline{\text{C}}$'s) and 130.9 (9 $\underline{\text{C}}\text{H}$'s), 126.2, 128.8 and 138.1 (3 $\underline{\text{C}}$'s), 194.6 and 196.3 ppm (2 $\underline{\text{C}}=\text{O}$'s); Mass (EI), m/e 77 (C_6H_5), 101 ($\text{C}_6\text{H}_4\text{CCH}$), 129 (HCCC $\text{C}_6\text{H}_4\text{CO}$), 234 (M).
- Spectral data of **13**; IR (KBr), 3249, 3069, 2846, 1658, 1637, 1588, 1293, 1264, 1166, 835, 758, 660 cm^{-1} ; UV (MeOH), λ_{max} 363, 300, 278, 243, 241 nm; $^1\text{H-NMR}$ (CDCl_3), δ 3.20 (1H, s, $\underline{\text{C}}\text{H}$), 6.53 (1H, d, $=\underline{\text{C}}\text{H}$, $J=10\text{Hz}$), 7.11-8.33 (9H), 10.27 ppm (1H, s, $\underline{\text{C}}\text{H}=\text{O}$); Mass (EI), m/e 255 (M-CHO), 284 (M, 100%).
- Spectral data of **14**; IR (KBr), 3247, 3064, 1679, 1581, 1271, 828, 786, 702 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 3.15 (1H, s, $\underline{\text{C}}\text{H}$), 4.16 (1H, dd), 4.53 (1H, d, $J=4.8\text{Hz}$), 6.61 (1H, s, $=\underline{\text{C}}\text{H}$), 7.46 (2H, d), 7.51 (2H, d), 7.76 (2H, m), 8.04 (1H, d), 8.10 ppm (1H, d); $^{13}\text{C-NMR}$ (CDCl_3), δ 49.1 and 52.0 (methine $\underline{\text{C}}\text{H}$'s), 78.7 and 83.3 (acetylenic $\underline{\text{C}}$'s), 192.5 and 195.3 (2 $\underline{\text{C}}=\text{O}$'s), 122.7-148.2 ppm (9 $\underline{\text{C}}\text{H}$'s and 5 $\underline{\text{C}}$'s); Mass (EI), m/e 255 (M-29), 284 (M, 100%).
- Spectral data of **15**; IR (KBr), 3280, 3084, 2868, 1665, 1588, 1307, 843, 779, 688 cm^{-1} ; UV (MeOH), λ_{max} 351, 289, 253, 231 nm; $^1\text{H-NMR}$ (CDCl_3), δ 3.14 (1H, s, $\underline{\text{C}}\text{H}$), 6.92-8.23 (12H), 10.03 ppm (1H, s, $\underline{\text{C}}\text{H}=\text{O}$); $^{13}\text{C-NMR}$ (CDCl_3), δ 78.1 ($-\underline{\text{C}}\text{C}\text{H}$), 83.2 ($-\underline{\text{C}}\text{C}\text{H}$), 184.5 ($\underline{\text{C}}=\text{O}$), 191.6 ($\underline{\text{C}}\text{H}=\text{O}$), 121.9-145.8 ppm (12 $\underline{\text{C}}\text{H}$'s and 8 $\underline{\text{C}}$'s); Mass (EI), m/e 305 (M-CHO), 334 (M, 100%).
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