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FORMATION AND OXIDATION OF 1:1 ADDUCTS OF TETRAHALO-1,2-BENZOQUINONES AND 1,3-DIENE

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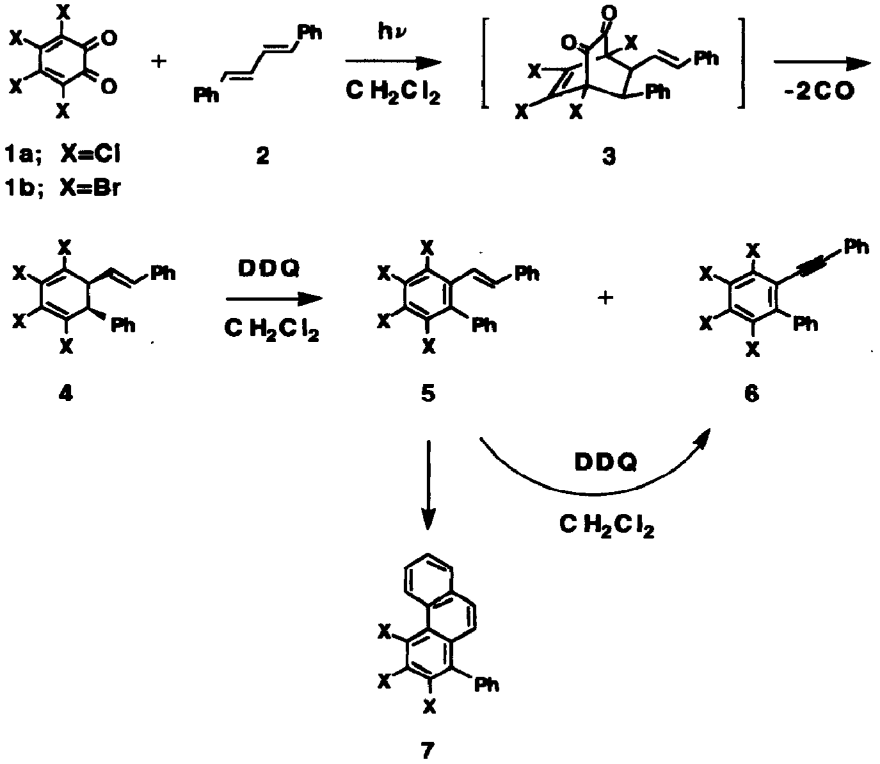
Abstract: Tetrahalo-1,2-benzoquinones, **1a** and **1b**, react with *trans,trans*-1,4-diphenyl-1,3-butadiene **2** to give 1:1 adducts **4** which are oxidized to **5** and **6**. Irradiation of **5** in the presence of oxygen yielded phenanthrene derivatives **7**.

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.[2-6] *o*-Quinones are known to react with olefins to give 1,4-dioxanes or oxetanes.[7-9] 9,10-Phenanthrenequinone reacts with *trans,trans*-1,4-diphenyl-1,3-butadiene (DPBe) **2** to give oxetane, a 1:1 adduct.[10] The adduct undergoes slow thermal dissociation at room temperature. In connection with our investigation of the scope of these reactions, we examined the photoreactions of *o*-quinones, such as tetrachloro-1,2-benzoquinone (*o*-TCBQ) **1a** and tetrabromo-1,2-benzoquinone (*o*-TBBQ) **1b** with conjugated systems, i.e., *trans,trans*-1,4-diphenyl-1,3-butadiene (DPBe) **2**, and the oxidation reaction of **4**, where we also found a convenient route to get phenanthrene derivatives, **7**.

Irradiation of a dichloromethane solution (200 mL) of *o*-TCBQ **1a** (246 mg, 1.0 mmol) and DPBe **2** (206 mg, 1.0 mmol) with 350 nm UV light for 2 h afforded tetrachloro-1,3-cyclohexadiene derivative **4a** quantitatively.[10,11] Irradiation of *o*-TBBQ **1b** (423 mg, 1.0 mmol) and DPBe **2** (206 mg, 1.0 mmol) for 2 h in the similar experimental condition also afforded **4b** quantitatively.[11] The formation of **4** probably proceeds via unstable [4+2] adducts **3** which would be expected to undergo rapid photobisdecarbonylation.[12,13] ^{1}H -^{13}C correlation spectrum of **4a** was obtained in chloroform-d. Carbon peaks at 135.2, 121.3, 80.13, and 78.77 ppm were correlated with proton peaks at 6.67 (PhC$\underline{H}$=CH-), 5.96 (PhCH=C$\underline{H}$-), 4.87 (PhC$\underline{H}$-CH-), and 4.70 ppm (Ph-CH-C$\underline{H}$-), respectively.



Refluxing a solution of **4a** (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 (DDQ, 35 mg, 0.15 mmol) for 24 h gave rise to **5a**[14] in 60 % yield, in which ca. 40 % of **4a** was recovered. ^{1}H - ^{13}C correlation spectrum ($CDCl_3$) was obtained to assign the exact positions of the carbon atoms of **5a**. Carbon peaks at 116.4 ppm and 130.1 ppm were correlated with proton peaks at 6.73 ppm (d, J = 15.4 Hz) and 7.08 ppm (d, J = 15.4 Hz). In contrast, treatment of **4a** with 4 eq. of DDQ gave **6a**[15] in 56 % yield as well as **5a** in 42 % yield, where the starting material **4a** was almost completely consumed. Refluxing a solution of **4a** (30 mg, 0.076 mmol) in dichloromethane (100 mL) in the presence of an excess of DDQ (500 mg, 2.2 mmol) for 48 h gave rise to **6a** in 98 % yield. Only trace amount of **5a** was observed in 400 MHz ^{1}H-NMR spectrum ($CDCl_3$) of the reaction mixture. Refluxing a solution of **5a** in dichloromethane in the presence of DDQ gave rise to **6a**. It was found that Ag_2O and chloranil were not useful to oxidize **4a** and **4b**, in which only small amount of oxidized products, **5** and **6**, were isolated.

The experimental evidence also shows that the 1:1 adducts, **4a** and **4b**, actually provide a convenient entry to phenanthrene derivatives, **7a** and **7b**, as well as the oxidized products, **5**[14] and **6**[15]. Irradiation of a dichloromethane solution (100 mL) of **5a** (98 mg, 0.25 mmol) with 350 nm UV light in the presence of molecular oxygen for 8 h afforded a phenanthrene derivative **7a** in 57 % yield.[16] This oxidative photocyclization reaction could be applied to tetrabromo compound **5b** to get tribromo phenanthrene **7b** in 55 % yield.[16]

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

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(11) **4a**: UV(n-hexane) λ_{max} 356, 338, 310, 302, 294, 270 nm; IR(KBr) 3029, 2917, 1560, 1426, 969, 786, 758, 695 cm^{-1}; ^{1}H-NMR($CDCl_3$), δ 7.39-7.23 (10H, m), 6.67 (1H, d, J=16.0 Hz, PhC$\underline{H}$=CH-), 5.96 (1H, dd, J=16.0 Hz and 5.92 Hz, Ph-CH=C$\underline{H}$-), 4.87 (1H, d, J=7.65 Hz, Ph-C$\underline{H}$-CH-), 4.70 ppm (1H, m, Ph-CH-C$\underline{H}$-); ^{13}C-NMR($CDCl_3$), δ 135.2 (Ph-$\underline{C}$H=CH-), 121.3 (Ph-CH=$\underline{C}$H-), 80.13 (Ph-$\underline{C}$H-CH-), 78.77 (Ph-CH-$\underline{C}$H-), 129.4 - 126.2 (10 $\underline{C}$H, 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).

(b) **4b** was also isolated and characterized with several spectral data. Carbon peaks at 135.6, 121.7, 80.50 and 79.14 ppm were correlated with proton peaks at 6.73 (1H, d, J = 15.6 Hz, Ph-CH=CH-), 5.97 (1H, dd, J = 15.8 Hz and 5.86 Hz, Ph-CH=CH-), 4.89 (1H, d, J = 8.06 Hz, Ph-CH-CH-), and 4.70 ppm (1H, m, Ph-CH-CH-), respectively.

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(14) (a) Spectral data of **5a**: UV(n-hexane), λ_{max} 282, 261, 236, 219 nm; IR (KBr), 3071, 3026, 2924, 1567, 1433, 1264, 1004, 948, 828, 751, 688 cm^{-1}; 400 MHz ^{1}H-NMR (CDCl$_3$), δ 6.73 (1H, d, J = 15.4 Hz, -CH=CH-Ph), 7.08 (1H, d, J = 15.4 Hz, -CH=CH-Ph), 7.23 - 7.56 ppm (10H, aromatic); ^{13}C-NMR (CDCl$_3$), δ 116.4 (-CH=CH-Ph) and 130.1 (-CH=CH-Ph), 126.8 (2CH's), 128.0, ca. 128.5 (4 CH's), 128.6 (2CH's) and 129.6 (10 CH's), 119.7, 126.9, 130.7 and 133.7 (4 C's), 136.3 and 136.6 ppm (3C's) (4 CCl's);

(b) **5b** was also isolated and characterized with several spectral data. Carbon peaks at 116.6 and 130.4 ppm were correlated with proton peaks at 6.75 (1H, d, J = 16.1 Hz, -CH=CH-Ph) and 7.14 ppm (1H, d, J = 16.1 Hz, -CH=CH-Ph), respectively.

(15) (a) Spectral data of **6a**: UV(n-hexane), λ_{max} 292, 285, 233, 223 nm; IR(KBr), 3064, 2959, 1595, 1461, 744, 702 cm^{-1}; ^{1}H-NMR(CDCl$_3$), δ 7.72 - 7.50 ppm (10H, aromatic); Mass (EI), m/e 390 (M).

(b) **6b** was also isolated and characterized with several spectral data. ^{1}H-NMR(CDCl$_3$), 7.72 - 7.50 ppm (10H, aromatic); Mass (EI), m/e 566 (M).

(16) (a) Spectral data of **7a**: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}; ^{1}H-NMR(CDCl$_3$), δ 7.08 - 8.17 ppm (11H, aromatic); Mass(EI), m/e 356 (M).

(b) Spectral data of **7b**: 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}; ^{1}H-NMR(CDCl$_3$), δ 7.09 - 8.17 ppm (11H, aromatic); Mass (EI), m/e 488 (M).

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