Photochemistry of Triptycene-1,4-quinone
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DEPOSITORY MATERIAL

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SYNTHESIS AND PHOTOCHEMISTRY

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4a,9a,10-Tetrahydro-9,10|1',2'|benzenoanthracene-1,4-dione (A)

A Diels-Alder reaction was performed by refluxing recrystallized 1,4-benzoquinone (4.3 g.
39 mmol, Eastman Kodak Co.) and anthracene (7.0 g., 39 mmol, Eastman Kodak Co.) in 40 ml.
of mixed xylenes (o, p and m-isomers) for 2 h according to procedures described by Bartlett et
al. The mixture was cooled in an ice bath and the resulting brown solid was isolated by suction
filtration. This was then recrystallized two times from a mixture of xylenes (isomers) to yield pale
yellow crystals of adduct A (8.4 g., 29 mmol, 75%).

MP: 220-221 °C (lit. 221-222 °C).

IR (KBr) νmax : 1674 (C=O), 1611 (C=C) cm⁻¹.

MS m/z (relative intensity): 287 (M+, 0.4), 286 (M+, 2), 178 (100).

$^1$H NMR (200 MHz, CDCl$_3$) : δ 7.45-7.00 (m, 8H, aromatic H), 6.30 (s, 2H, vinyl H), 4.85 (s, 2H, bridgehead H$_9$ & H$_{10}$), 3.10 (s, 2H, bridgehead H$_{19}$ & H$_{20}$) ppm

$^{13}$C NMR (50 MHz, CDCl$_3$) : δ 198.34 (C=O), 141.54 (aromatic C), 140.59 (vinyl C-H), 139.69 (aromatic C), 126.73, 126.64, 124.73, 123.88 (aromatic C-H), 49.05 & 48.90 (bridgehead C-H) ppm

9,10-Dihydro[1',2']benzoanthracene-1,4-diol (B)

Adduct A (8.4 g, 29 mmol) was dissolved in 100 mL of boiling acetic acid (Fisher Scientific) and treated with 4 drops of HBr (48%, BDH) as described by Bartlett et al. A vigorous evolution of heat resulted and the solution turned orange. After 30 min of refluxing, the solution was cooled in an ice bath and a white solid precipitated which was filtered off by suction filtration. The resulting powder (B) was recrystallized from diethyl ether resulting in white needles (6.5 g, 23 mmol, 77%).

MP: 338-340°C (lit.: 338-340°C)

IR (KBr) ν$_{max}$: 3284 (O-H) cm$^{-1}$
MS m/e (relative intensity): 287 (M+1,24), 286 (M+,98), 269 (100), 268 (38), 256 (19), 239 (39), 226 (28), 202 (66).

Exact mass calculated for C_{20}H_{14}O_2: 286.0994. Found: 286.1001.

^1H NMR (200 MHz, d_6-acetone): δ 7.85 (s, 2H, OH), 7.50-7.35 (m, 4H, aromatic H), 7.05-6.90 (m, 4H, aromatic H), 6.39 (s, 2H, aromatic H), 5.95 (s, 2H, bridgehead H) ppm.

^13C NMR (50 MHz, d_6-acetone): δ 146.90, 146.00, 133.47 (aromatic C, aromatic C-OH), 125.48, 124.30 (aromatic C-H), 113.83 (aromatic C-H), 48.18 (bridgehead C-H) ppm.

9,10-Dihydro-9,10[1',2']benzoanthracene-1,4-dione (1)

Adduct B (6.5 g, 23 mmol) was dissolved in 60 ml of hot acetic acid according to Bartlett et al. procedures. A solution of KBrO_3 (1.3 g, 7.5 mmol, BDH) in 80 ml of hot water was added. The solution was refluxed for 5 min and 50 ml of hot water was added. The solution was cooled in an ice bath and the orange solid collected. This was then recrystallized from diethyl ether to give bright yellow crystals of 1 (4.5 g, 1.6 mmol, 70%).

IR (KBr) ν<sub>max</sub> : 1660 (C=O), 1581 (C=C) cm<sup>-1</sup>.

MS m/e (relative intensity) : 285 (M+1, 24), 284 (M<sup>+</sup>, 100), 255 (17), 226 (18), 202 (86).

Exact mass calculated for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub> : 284.0837. Found : 284.0837.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) : δ 7.50-7.35 (m, 4H, aromatic H), 7.10-6.95 (m, 4H, aromatic H),
6.59 (s, 2H, vinyl H), 5.79 (s, 2H, bridgehead H) ppm.

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) : δ 183.41 (C=O), 151.82 (vinyl C), 143.49 (aromatic C), 135.28 (vinyl C-H), 125.47, 124.32 (aromatic C-H), 47.27 (bridgehead C-H) ppm.

UV (acetonitrile) λ<sub>max</sub> : 404 (ε 357), 330 (ε 993), 251 (ε 14,884) nm.

PHOTOCHEMICAL STUDIES

Irradiation Sources

Photolysis experiments were conducted either with a 450 W Hanovia medium pressure mercury lamp at room temperature through various glass filters, namely Pyrex (λ ≥ 290 nm), quartz (λ ≥ 200 nm), Vycor (λ ≥ 240 nm) and uranium (λ ≥ 330 nm), or with a Rayonet Photochemical Chamber Reactor (Model RPR-100). This light source was equipped with up to 16 lamps at 3000 Å (21 watts), 2537 Å (35 watts) or 3360 Å (24 watts) and operated at a temperature of 35 °C.
Solution State Irradiation

Solution state irradiation studies were carried out by dissolving the samples ($10^{-2}$M) in spectral grade solvents (Fisher). Prior to analytical runs, the samples were degassed by three freeze-pump-thaw cycles and sealed under nitrogen. In the case of preparative scale photolyses, oxygen was purged by bubbling nitrogen through the solution 30 min before and during the irradiation period, while stirring it. The photoreactions were monitored by gas chromatographic analysis. Following irradiation, the solvent was removed in vacuo and the photoproducts isolated by column chromatography.

Solid State Irradiation

Solid state photolysis studies were carried out by crushing the crystals and distributing them evenly between two Pyrex or quartz glass plates. The samples were then placed in a polyethylene bag, which was sealed under nitrogen with a heat-sealing device. After irradiation, the samples were dissolved prior to gas chromatographic analysis and chromatographic isolation.
Photolysis of 9,10-Dihydro-9,10[1',2']benzeneanthracene-1,4-dione (1) in Acetonitrile

A solution of compound 1 (250 mg, 0.880 mmol) in anhydrous acetonitrile (400 ml.) was irradiated under nitrogen with a 450 W Hanovia medium pressure lamp through a Pyrex glass filter for 4 h. The solvent was removed and the remaining oil purified by column chromatography with ethyl acetate/petroleum ether (3 : 7) resulting in a light yellow crystalline photoproduct 3 (195 mg, 0.687 mmol, 78%). Compound 3 was characterized as 4b,8b,8c,8d-tetrahydrodibenzo[a,j]cyclopropa[cd]pentalene-8d,8c-benzo-1',4'-dione.

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\begin{align*} 
\text{MP} & : 167-169 \degree C \text{ (recryst from diethyl ether).} \\
\text{IR (KBr) } \nu_{\text{max}} & : 1677 (C=O), 1596 (C=C) \text{ cm}^{-1}. \\
\text{MS m/e (relative intensity): } & 285 (M^+ 1, 22), 284 (M^+, 100), 202 (12). \\
\text{Exact mass calculated for } & C_{20}H_{12}O_{4} : 284.0837. \text{ Found: } 284.0838. \\
\text{H NMR (200 MHz, CDCl}_3) & : \delta 8.05-7.97 (m, 1H, aromatic H), 7.35-7.03 (m, 7H, aromatic H), 6.65 (s, 2H, vinyl H), 5.13 \text{ & } 4.37 (s, 1H each, pentalene H) \text{ ppm.}
\end{align*} \]
$^{13}$C NMR (50 MHz, CDCl$_3$): δ 191.99 (C=O), 191.07 (C=O), 150.34, 149.03 (aromatic C), 138.46, 138.09 (vinyl C-H), 133.40, 131.41 (aromatic C), 128.72, 128.16, 127.10, 127.10, 126.14, 125.51, 121.82, 121.55 (aromatic C-H), 77.28 & 58.86 (pentalene C), 58.53 & 51.43 (pentalene C-H) ppm.

UV (acetone) λ$_{max}$: 378 (ε 791), 277 (ε 3,366) nm.

Anal. calculated for C$_{20}$H$_{12}$O$_2$: C, 84.48; H, 4.26. Found: C, 84.26 H, 4.30.

Photolysis of 9,10-Dihydro-9,10[1',2']benzenoanthracene-1,4-dione (1) in Air-Saturated Acetone

Compound 1 (275 mg, 0.968 mmol) dissolved in dry acetone (500 mL) was photolyzed for 15 h with a Rayonet Photoreactor (11 bulbs at 3000 Å) while saturating the solution with air. Evaporation of the solvent, followed by column chromatography (ethyl acetate / petroleum ether, 3:7), gave the yellow crystalline triketone 2 (52 mg, 0.173 mmol, 18%).
MP: 171-174 °C (recryst from petroleum ether / ethyl acetate).

IR (KBr) ν_max: 1709 (C=O), 1760 (C=O) cm⁻¹.

MS (DCI, NH₃, relative intensity): 318 (M+18, 100), 301 (M+1, 10), 215 (5), 189 (15), 178 (100)

Exact mass calculated for C₂₀H₁₂O₃ (M+1): 301.0864. Found: 301.0872.

¹H NMR (400 MHz, CDCl₃): δ 7.50-7.40 (m, 2H, aromatic H), 7.38 (s, 2H, vinyl H) 7.37-7.23 (m, 6H, aromatic H), 4.98 & 4.47 (s, 1H each, bridgehead H) ppm.

¹³C NMR (175 MHz, CDCl₃): δ 196.75 (C=O), 194.46 (C=O), 151.02 (vinyl C-H), 138.68, 135.65 (aromatic C), 127.55, 127.49, 125.78, 125.20 (aromatic C-H), 62.78 (bridgehead C), 61.89 & 49.61 (bridgehead C-H) ppm.