

6.92 (d, 2H, aromatic,  $J=9$  Hz) and 8.00 ppm (d, 2H, aromatic,  $J=9$  Hz), Mass (EI),  $m/e$  166 (M), 135 (M-OMe, 100%) and 107 (M-COOMe), IR (KBr), 1700 ( $\nu_{C=O}$ ) and 846  $\text{cm}^{-1}$  ( $\delta_{\text{CH(OOP)}}$ , aromatic).

## Photochemistry of Anthrone and Its Derivatives

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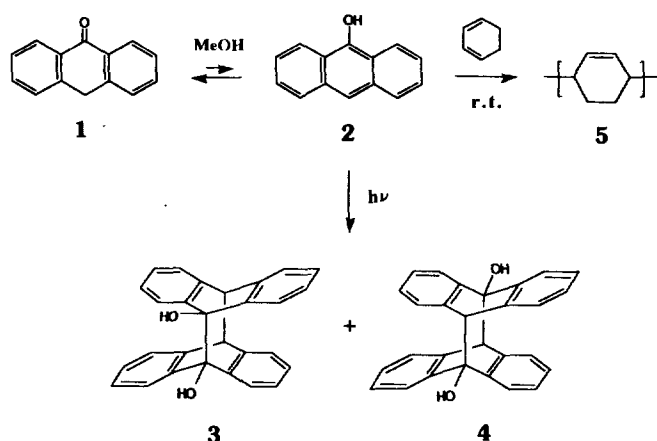
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There has been special interest in the energy-rich cyclodimers of aromatic hydrocarbons.<sup>1-5</sup> The synthesis of both the  $4\pi_s + 4\pi_s$  and  $4\pi_s + 2\pi_s$  adducts of arenes has allowed a study of orbital and state symmetry control in their thermal and photochemical cycloreversion.<sup>5,6</sup> The photochemistry of anthracene derivatives had enriched organic photochemistry with some remarkable novel structures, namely 9,9'-didehydrodianthracene and 9,9',10,10'-tetrahydrodianthracene, etc.<sup>7-10</sup> For some substituted anthracenes, the course of their intramolecular photolytic transformations is governed by the nature of the substituent and by their excited state interactions with the  $\pi$  system of anthrone. The photochemistry of 9-hydroxyanthracene (or anthranol **2**) is complicated not only because of the solvent-dependent ground-state equilibrium with anthrone **1**, but also by the facile formation of various autoxidation products.<sup>11-13</sup> Irradiation of anthranol **2** yielded  $4\pi_s + 4\pi_s$  dimers, *i.e.*, head-to-head and head-to-tail dimers.<sup>14</sup> Anthranol **2** can also be formed when anthrone **1** is dissolved in methanol.<sup>15</sup> In that case, enol content (*i.e.*, % **2**) is about 11% in methanol solution at room temperature.

We describe here the  $4\pi_s + 4\pi_s$  photodimers of 9-hydroxyanthracene derivatives using keto-enol tautomerization.<sup>16</sup> Anthrone **1** is not fluorescent, on the other hand, when dissolved in methanol, strong fluorescence bands of anthranol **2** were observed at 433.3 nm and 452.5 nm at room temperature. The fluorescence was quenched by some olefins, such as 1,3-cyclopentadiene, furan and thiophene. When a solution of 150 mg ( $7.7 \times 10^{-4}$  mole) of anthrone **1** and 10.0 mL (excess amount) of furan in 200 mL of dichloromethane was irradiated with 350 nm UV light, a dimer of anthrone, *i.e.*, 10,10'-bianthrone<sup>17</sup> was obtained as the major product. When the irradiation was carried out in methanol, the  $4\pi_s + 4\pi_s$  dimers (HH dimer **3** and HT dimer **4**) of anthranol and 1:1 adduct<sup>18</sup> of anthrone and furan, as well as bianthrone, were found in good yields (26, 15 and 35%, respectively). The photoproducts were isolated by column chromatography on



Scheme 1.

silica gel (70-230 mesh) using *n*-hexane and ethyl acetate as the eluent.  $R_f$  values of **3** and **4** were 0.23 and 0.49, respectively, in *n*-hexane and ethyl acetate (4 : 1, v/v). Hydroxyl protons and benzylic protons of HH dimer (and HT dimer) were observed at 2.36 ppm (and 2.41 ppm) and 4.42 ppm (and 4.60 ppm) in <sup>1</sup>H-NMR spectrum ( $\text{CDCl}_3$ ), respectively. The molecular ion peak was also found at  $m/e$  388 in EI mass spectrum. It is interesting to note that anthranol is formed *via* keto-enol tautomerization of anthrone in methanol solution. In fact, simply mixing anthrone **1** and 1,3-cyclohexadiene in methanol gave rise to white precipitate at room temperature, which was identified as heptamer **5** of 1,3-cyclohexadiene.<sup>19</sup> The formation of anthranol dimers, such as **3** and **4**, and heptamer **5** suggests that anthranol **2** is formed *via* keto-enol tautomerization, and also demonstrates that the protons produced during the tautomerization initiate the cationic polymerization reaction<sup>20</sup> of 1,3-cyclohexadiene to yield the heptamer **5**.

The irradiation (350 nm) of 100 mg of 10-nitroanthrone in 200 mL of dichloromethane gave only anthraquinone as the major product and 10,10'-bianthrone<sup>17</sup>. When the irradiation was carried out in methanol with visible light, the major product produced was 10,10'-bianthrone. As the nitro group was actually labile during the photoreaction, *i.e.*, photochemically unstable, visible light was used instead of UV light source. The  $4\pi_s + 4\pi_s$  dimer was not found in the reason of the photochemically unstable property.

When the irradiation of 1,8-dihydroxyanthrone (or dithranol or anthralin) was carried out in methanol, all the starting material was consumed. But only an unidentified compound was obtained in which benzylic protons were disappeared in <sup>1</sup>H-NMR spectrum ( $\text{CDCl}_3$ ). Irradiation of anthralin in dichloromethane gave bianthralin.<sup>21</sup>

In contrast to blue fluorescence of anthranol, very weak fluorescence emission bands of anthralin were observed at 497.5 nm, 525.0 nm and 565.0 nm in methanol. The ratio of fluorescence intensity, *i.e.*,  $I_f(\text{anthranol})/I_f(\text{anthralin})$ , was 13.6.<sup>22</sup> 10-Nitroanthrone was not fluorescent in the same experimental condition.

While the  $4\pi_s + 4\pi_s$  dimers could not be isolated from 10-nitroanthrone and anthralin at room temperature, the participation of enol form of anthrone **1** in the photoreaction could be used to the synthesis and application of highly unstable compounds such as 9,9',10,10'-tetrahydrodianthracene and

their related high-energy molecules.

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17. (a) The structure of 10,10'-bianthrone was characterized by <sup>1</sup>H-NMR, IR, and EI mass spectrum: <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) showed the presence of benzylic protons at 4.78 ppm. Peaks at m/e 386 (M) and m/e 193 (M/2) were observed in EI mass spectrum; (b) For the experimental data of 10,10'-bianthrone, see: O. L. Chapman and K. Lee, *J. Org. Chem.*, **34**, 4166 (1969).
18. (a) The 1:1 dimer was identified by <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>), IR spectrum (KBr) and mass spectrum (EI); Mass (EI), m/e 262 (M) and 194 (M-C<sub>4</sub>H<sub>4</sub>O, 100%). For this type of 2π<sub>s</sub>+2π<sub>s</sub> photodimer, i.e., oxetane adduct, see: S. S. Kim, D. Y. Yoo, and I. H. Cho, *Bull. Korean Chem. Soc.*, **9**(4), 257 (1988); (b) [4π<sub>s</sub>+4π<sub>s</sub>] Photodimer was also isolated as the major product from the photoreaction of anthrone and 1,3-cyclopentadiene in methanol. Mass spectrum (EI), m/e 260 (M), 194 (M-C<sub>5</sub>H<sub>6</sub>) and 66 (C<sub>5</sub>H<sub>6</sub>).
19. **5**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 5.68 (bs, -CH=), 2.02 (bs, -CH-) and 1.55 ppm (bs, -CH<sub>2</sub>-); Mass (EI), m/e 562 (M), 481 (M-C<sub>6</sub>H<sub>9</sub>), 401 (m/e 481-80), 321 (m/e 401-80), 241 (m/e 321-80), 161 (m/e 241-80), 81 and 79.
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21. Spectral data of bianthrone: <sup>1</sup>H-NMR (CDCl<sub>3</sub>), δ 11.73 (s, 4H, hydroxyl), 7.38 (dd, 4H, aromatic), 6.92 (d, 4H, aromatic), 6.39 (d, 4H, aromatic), 4.60 ppm (2H, benzylic); Mass (EI), m/e 450 (M) and 225 (100%).
22. Fluorescence emission spectra were recorded on a Jasco FP-770 Spectrofluorometer: anthrone (MeOH), λ<sub>em</sub> 433.3, 452.5 and 517.5 nm (shoulder); 1,8-dihydroxyanthrone (MeOH), λ<sub>em</sub> 497.5, 525.0 and 565.0 nm; anthranol dimer **3** (MeOH), λ<sub>em</sub> 432.5 and 455.0 nm (λ<sub>ex</sub> 375 nm).

### Radical Cyclization of α-Diazocarbonyl Compounds

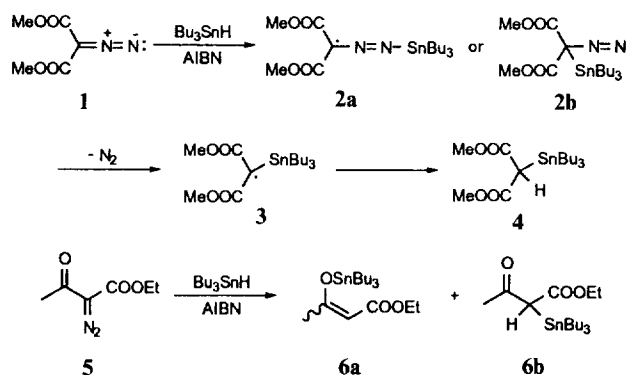
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Synthetic importance of α-diazocarbonyl compounds has been recently recognized in intramolecular carbenoid cyclization<sup>1</sup> and 1,3-dipolar cycloaddition.<sup>2</sup> However, radical reaction of diazo compounds has received little attention<sup>3</sup> and we are unaware of any studies on radical cyclization of α-diazocarbonyl compounds. Our interest in the development of new radical cyclization reactions involving the loss of N<sub>2</sub> prompted us to investigate the possibility of the use of α-diazocarbonyl compounds as radical precursors.<sup>4</sup> We envisioned that α-diazocarbonyl compounds under radical conditions (Bu<sub>3</sub>SnH/AIBN) would generate initially **2a** or **2b**, which would yield **3** by the loss of N<sub>2</sub> as shown in Scheme 1.

Our initial study was carried out with α-diazomalonnate and α-diazo β-keto ester. Reaction of **1** with Bu<sub>3</sub>SnH/AIBN in refluxing benzene-d<sub>6</sub> for 30 min afforded **4**, suggesting that the diazo group could be served as radical precursors. Similarly, **5** was converted into a mixture of **6a** and **6b** in a ratio of 92 : 8 according to <sup>1</sup>H-NMR analysis.<sup>5</sup> Furthermore, we examined the relative reactivity of diazomalonnate, the iodide and the bromide toward Bu<sub>3</sub>SnH/AIBN. The competi-



Scheme 1.