

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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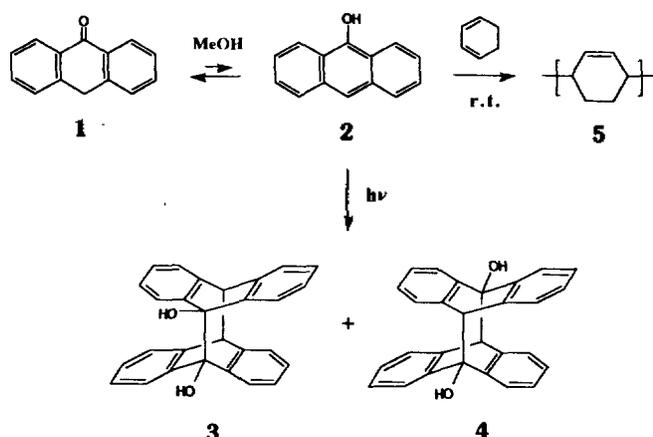
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Received July 22, 1993

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.

**Acknowledgement.** We appreciate the financial support of this work by the Korea Science and Engineering Foundation (KOSEF). And, this was supported by the Organic Chemistry Research Center (OCRC) sponsored by the Korea Science and Engineering Foundation (KOSEF).

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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>6</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

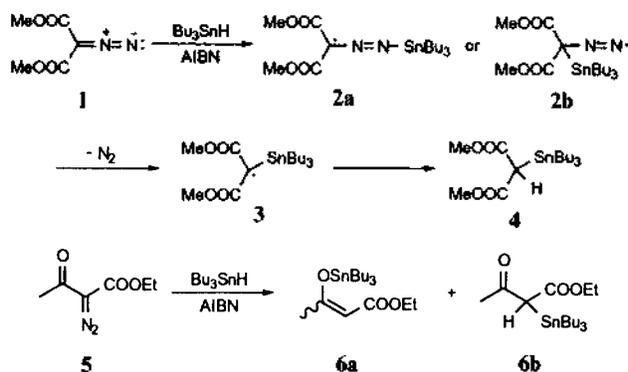
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Synthetic importance of α-diazocarbonyl compounds has been recently recognized in intramolecular carbenoid cyclization<sup>1</sup> and 1,3-dipolar cycloaddition.<sup>2</sup> However, radical reaction of diazo compounds has received little attention<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.