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Facile Formation of Semi-Reduced Radicals of cis-N,N'-Diacylindigos by Visible-Light-Induced One-Electron Transfer from Tertiary Amines

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N,N'-Oxalyl and N,N'-malonyl derivatives of indigo and 6,6'-di-tbutylindigo were reduced with high quantum efficiencies to their semireduced radicals by visible light irradiation in the presence of tertiary amines. These semi-reduced radicals were reversibly autoxidized and thus oxidative dealkylation of tertiary amines was catalyzed photochemically by these indigos.

Photo-induced electron transfer reactions driven by visible light absorption of dyes such as metalloporphyrins,<sup>1)</sup> ruthenium tris(bipyridine),<sup>2)</sup> and xanthene dyes<sup>3)</sup> have been attracting much interest from the viewpoint of solar energy conversion. Thioindigo was demonstrated to undergo photo-reduction to leucothioindigo in the presence of tertiary amines,<sup>4)</sup> and we have recently shown that irradiation of N,N'-dialkylindigos in a deaerated benzene solution containing triethylamine with visible light brings about a one- or a two-electron transfer depending on whether they are in a cis or a trans form.<sup>5)</sup> In this communication are reported new findings that (i) N,N'-oxalyl and N,N'-malonyl derivatives of indigos are photo-reduced with high quantum efficiencies to their semi-reduced radicals, which, in turn, are autoxidized in a completely reversible process and (ii) oxidative dealkylation of tributylamine takes place by using N,N'-oxalyl-6,6'-di-t-butylindigo as a photo-catalyst under aerobic conditions.

When a deaerated benzene solution of N,N'-malonylindigo<sup>6)</sup> (<u>1</u>) (6.7 ×  $10^{-5}$  mol dm<sup>-3</sup>) and triethylamine (6.7 ×  $10^{-2}$  mol dm<sup>-3</sup>) was irradiated through a band-pass filter (Toshiba KL-43, transparence maximum 427 nm) with a 200-W tungsten lamp, the absorption maximum at 433 nm due to <u>1</u> shifted to 418 nm with showing an isosbestic





Figs. 1 and 2. Spectral changes upon photolysis of benzene solutions of <u>1</u> and <u>4</u>, respectively, at 427 nm in the presence of triethylamine. Spectra were recorded at 3 minutes' intervals in Fig. 1 and at 30 seconds' intervals in Fig. 2.

This photolyzed solution showed an intense ESR point at 317 nm (see Fig. 1). signal at g=2.003 and could be air-oxidized to regenerate 1. A leuco form which was prepared by treating 1 with zinc in acetic acid showed an absorption maximum at 377 nm in EtOH, and this spectrum changed under aerobic conditions to that of 1. These observations clearly demonstrate that a semi-reduced radical (1-H) is formed exclusively upon visible-light-induced electron transfer from triethylamine. N,N'-Malonyl-6,6'-di-t-butylindigo<sup>7)</sup> (2) showed nearly the same spectral change as that of 1 under the same photolysis conditions in support of the formation of a semireduced radical (2-H). Although the photochemical behavior of N,N'-oxalylindigo<sup>8</sup>) (3) is not studied due to its solubility problem in organic solvents, we have found that  $N,N'-oxalyl-6,6'-di-t-butylindigo^{9}$  (4) undergoes one-electron photo-reduction to a semi-reduced radical (4-H). Thus, irradiation of a degassed benzene solution of 4 (5.1 ×  $10^{-5}$  mol dm<sup>-3</sup>) and triethylamine (5.1 ×  $10^{-2}$  mol dm<sup>-3</sup>) through a bandpass filter (Toshiba KL-43) with a 200-W tungsten lamp caused a spectral change as shown in Fig. 2. Absorption bands at 430 and 315 nm due to 4 decreased and those at 525, 387, and 337 nm increased with three isosbestic points at 451, 424, and 323 nm being maintained. The resulting benzene solution showed an intense ESR signal at g=2.004 (Fig. 3) and quickly regenerated 4 upon autoxidation.



Fig. 3. ESR spectrum of 4-H in benzene at room temperature generated photochemically in the presence of triethylamine ( $10^3$ -fold molar).



Fig. 4. Cyclic voltammograms of <u>1</u> and <u>5</u> in  $CH_3CN$  at a glassy carbon. (vs. Ag/AgCl, scan rate 100 mV s<sup>-1</sup>).

In contrast to these cis-fixed N,N'-diacylindigos, N,N'-diacetylindigo (5) which takes predominantly a trans form underwent two-electron photo-reduction to a leuco form under the same reaction conditions. The photolysis of 5 resulted in the decrease of the absorption bands at 562, 390, and 313 nm due to 5 with concomitant increase of a band at 335 nm. The ultimate spectrum turned out to be substantially the same as that of N,N'-diacetylleucoindigo  $(5-H_2)$  prepared by the treatment of 5 with zinc in ethanol.

We have already shown that cis-N,N'-1,3-propanoindigo is converted to the semi-reduced radical under the conditions where trans-N,N'-dimethylindigo undergoes two-electron photo-reduction to the leuco form.<sup>5)</sup> The stability of the semi-reduced radicals of these cis-fixed indigos is explainable in terms of the effective intramolecular hydrogen bonding between the oxygen radical center and the OH proton, which gives rise to a seven-membered cyclic system with facile delocalization of the unpaired electron.

Cyclic voltammograms of 1 and 5 were measured in acetonitrile containing ca. 0.1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NClO<sub>4</sub> at a glassy carbon electrode relative to an Ag/AgCl couple in order to obtain their redox profiles. They showed two reduction waves at -0.68 V and -1.03 V for 1 and at -0.62 V and -1.04 V for 5. The corresponding two oxidation waves were observed at -0.85 V and -0.13 V for  $\underline{1}$  and at -0.80 V and -0.49 V for 5. A small anodic peak at -0.10 V observed for 5 is attributable to the cis isomer of 5 (see Fig. 4). The two pairs of redox waves in both cases likely correspond to two stepwise one-electron transfers and, therefore, it is important to note that the first redox couple  $E_{k}^{1}$  for <u>1</u> is by 150 mV more positive than that for 5 while the second redox couples  $E_{\frac{1}{2}}^2$  for 1 and 5 are similar. This suggests that disproportionation of semi-reduced radicals is less favorable in a cis form than in a trans form. Table 1 summarizes these redox potentials and the quantum yields which were determined relative to ferrioxalate actinometry in the presence of 10<sup>3</sup>-fold molar amounts of triethylamine in benzene. The highest quantum yield observed for the photo-reduction of  $\underline{4}$  is probably due to the most strongly electron-withdrawing effect of the N,N'-oxalyl group among the N-acyl groups used here. It should be emphasized that the semi-reduced radicals of cis-N,N'-diacylindigos are reversibly autoxidized whereas the semi-reduced radical of cis-N,N'-1,3-propanoindigo decomposes to colorless materials under aerobic conditions.<sup>5)</sup> Therefore, photo-reduction of 4 was found to take place even in the presence of  $10^2$ -fold molar amounts of tributylamine and  $10^3$ -fold molar amounts of water under

		Quantum yield <sup>a)</sup>	Redox potentials b)				
Indigo	Reduced form	(wavelength/nm)	$E_{\frac{1}{2}}^{1}/V$	E <sup>2</sup> /V			
1	<u>1</u> -н	$4.4 \times 10^{-2}$ (427)	-0.41	-0.94			
2	<u>2</u> -H	$1.1 \times 10^{-1}$ (427)					
<u>4</u>	<u>4</u> -H	$7.2 \times 10^{-1}$ (427)					
<u>5</u>	<u>5</u> -н <sub>2</sub>	9.1 × $10^{-2}$ (546)	-0.56	-0.92			

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a) Measured relative to ferrioxalate actinometry at the wavelength noted in the parentheses. b) Relative to an Ag/AgCl couple.

aerobic conditions and dibutylamine was detected by GLC analysis of the photolized solution, suggesting the occurrence of a photo-catalytic dealkylation of tributylamine. After the irradiation for 90 min when the reaction ceased, 39% of tributylamine was consumed and 22% yield of dibutylamine was obtained on the basis of the converted tributylamine. The use of  $\underline{4}$  in 2 mol-% amounts relative to tributylamine improved the conversion up to 50% and the yield of dibutylamine up to 44% after 3 h irradiation period. Although the quantum yield for the photo-reduction of  $\underline{1}$  is lower than that of  $\underline{5}$ , the semi-reduced radical  $\underline{1}$ -H is reoxidized much faster than the leuco  $\underline{5}$ -H<sub>2</sub>. Accordingly,  $\underline{5}$  could not catalyze the photo-dealkylation of tributylamine at all while 6% conversion of tributylamine was observed by using  $\underline{1}$  as a photo-catalyst under the same conditions.

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References

- A. Harriman, G. Porter, and M.-C. Richoux, J. Chem. Soc., Faraday Trans. 2, <u>77</u>, 833 (1981); K. Kalyanasundaram and M. Grätzel, Helv. Chim. Acta, <u>63</u>, 478 (1980); M.-C. Richoux and A. Harriman, J. Chem. Soc., Faraday Trans. 1, <u>78</u>, 1873 (1982).
- 2) M. Grätzel, Acc. Chem. Res., 14, 376 (1981) and references therein.
- K. Hashimoto, T. Kawai, and T. Sakata, Chem. Lett., <u>1983</u>, 709; T. Shimidzu, T. Iyoda, and Y. Koide, J. Am. Chem. Soc., 107, 35 (1985).
- 4) K. S. Schanze, C. Giannotti, and D. G. Whitten, J. Am. Chem. Soc., <u>105</u>, 6326 (1983).
- 5) J.-i. Setsune, T. Matsuura, T. Fujiwara, and T. Kitao, Chem. Lett., <u>1984</u>, 1755.
- 6) This compound was obtained in 21% yield from indigo and malonyl chloride according to the procedure described for N,N'-oxalylindigo.<sup>8)</sup> Mp 270-271 °C; NMR(CDCl<sub>3</sub>) & 4.01(s, 2H), 7.29-8.34(m, 8H); IR(KBr) 1650, 1600 cm<sup>-1</sup>; UV-vis(benzene)  $\lambda_{max}(\epsilon)$  435(7000), 350(3300), 292(25000); Mass(m/e) 330. Found: C, 68.78; H, 2.66; N, 8.46%. Calcd for C<sub>19</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 69.09; H, 3.05; N, 8.48%.
- 7) This compund was obtained in 80% yield from 6,6'-di-t-butylindigo<sup>10)</sup> and malonyl chloride in benzene containing 2,6-lutidine. Mp 183-187 °C; NMR(CDCl<sub>3</sub>)  $\delta$  1.40(s, 18H), 4.10(s, 2H), 7.50(dd, 2H), 7.85(d, 2H), 8.60(d, 2H); IR(KBr) 1720, 1600 cm<sup>-1</sup>; UV-vis(benzene)  $\lambda_{max}(\epsilon)$  431(5200), 296(23000); Mass(m/e) 442. Found: C, 73.28; H, 5.92; N, 6.33%. Calcd for C<sub>27</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>: C, 73.06; H, 5.91; N, 6.00%.
- 8) G. M. Wyman and A. F. Zenhausern, J. Org. Chem., <u>30</u>, 2349 (1965).
- 9) This compound was obtained in 97% yield from 6,6'-di-t-butylindigo and oxalyl chloride according to the method used for 2. Mp 268-269 °C; NMR(CDCl<sub>3</sub>)  $\delta$  1.40(s, 18H), 7.60(dd, 2H), 7.95(d, 2H), 8.80(d, 2H); IR(KBr) 1700, 1650, 1600 cm<sup>-1</sup>; UV-vis(benzene)  $\lambda_{max}(\epsilon)$  431(11000), 290(23000); Mass(m/e) 428. Found: C, 72.97; H, 5.74; N, 6.97%. Calcd for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>: C, 72.88; H, 5.65; N, 6.54%.
- 10) H. Meier and W. Luttke, Justus Liebigs Ann. Chem., 1981, 1303.

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