Photoreduction of Cyanine Borate Infrared Absorbing Dyes

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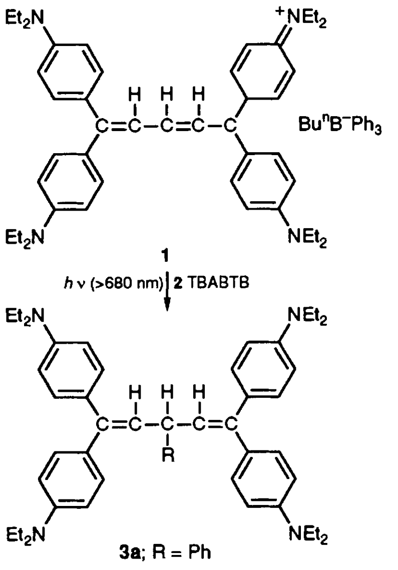
Photoreduction of cyanine borate infrared absorbing dyes gave the *meso*-substituted leuco cyanines; single electron transfer from borate to the cyanine molecule in an excited state, followed by combination of the dye radicals with alkyl or phenyl radicals produced from the n-butyltriphenylborate counter anion, gave the leuco dye.

Infrared absorbing dyes are of current interest as organic media for information recording systems.[1] Recovery of paper used as recording media is currently important to save resources and to protect the environment. Large amounts of paper are now consumed as recording media for electrophotography, computer output *etc.*, but there is a low rate of recycling of this paper. If images can be decoloured on a substrate, it may be possible to recycle paper many times until its quality becomes too poor.

We have found for the first time that decoloured *meso*-



Scheme 1

substituted leuco cyanines may be synthesized by photoirradiation of the cyanine n-butyltriphenylborate **1** in the presence of tetra-n-butylammonium n-butyltriphenylborate **2** (TBABTB). Schuster *et al.*[2] have studied the photopolymerization of monomers induced by some cyanine borates and proposed a reaction mechanism, but were unable to isolate the products. We now report the photoinduced decolouration of cyanine borates and its potential for application as a decolourizable toner for electrophotography. The photoreduction of the cyanine borates in various solvents was studied to gain insight into the reaction mechanism.

A mixture of the cyanine borate **1** and TBABTB **2** was irradiated with an Xe lamp through a Toshiba R-69 filter under argon atmosphere and gave a white solid (Scheme 1).† The product was identified as the *meso*-phenyl leuco cyanine **3a**. Compound **3a** can be synthesized by an alternative route involving the reaction of 1,1-bis(4-*N*,*N*-diethylaminophenyl)ethylene with benzaldehyde in the presence of acetic anhydride in tetrachloroethylene.

Photoirradiation of **1** and **2** in various solvents such as dichloromethane or alkylbenzenes exclusively gave the *meso*-butyl leuco cyanine **3b** under similar conditions. The reactivity and selectivity of the photoreduction of **1** depend on solvent polarity, as shown by results for various solvents summarized in Table 1. In the highly polar dimethyl sulfoxide, **3a** was obtained exclusively (run 1), but a decrease in solvent polarity led to mixtures of **3a** and **3b** (runs 2 and 3). Less polar solvents gave **3b** as the only product (runs 4–10). In alkylbenzenes (runs 7–10), the photoreduction of **1** was very fast and gave only the *meso*-butyl leuco cyanine **3b** even in the absence of **2**. From these results, we propose that alkylbenzenes can stabilize the butyl radical to form a π-complex as indicated in eqn. (2). The equilibrium in eqn. (1) shifts to the right in alkylbenzenes and the reaction is accelerated. Cleavage of the C–B bond in eqn. (1) will be the rate-determining step.

$$[\mathrm{Ph_3B{-}R}]^\bullet \rightleftharpoons \mathrm{R}^\bullet + \mathrm{BPh_3} \qquad (1)$$

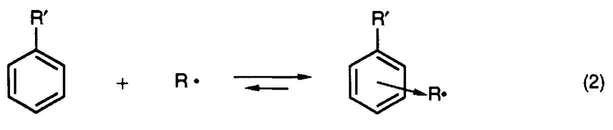
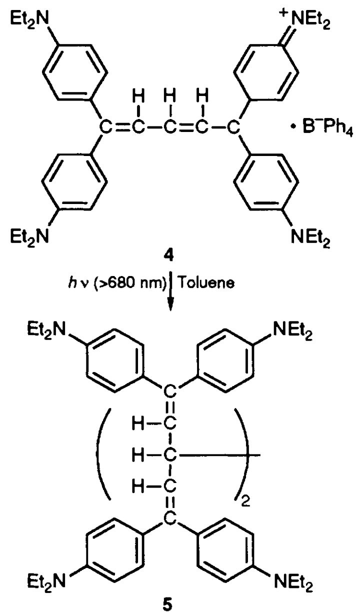


Table 1 Photoreduction of **1** with **2** in various solvents[a]

Run	Solvent	ε[b]	μ[c]/ Debye	Reaction time/h	Product (%)[d]	
					3a	**3b**
1	DMSO[f]	46.7	3.9	40	100	0
2	MeCN	37.5	1.2	16	77	23
3	MeOH	32.7	2.9	18	40	60
4	Pyridine	12.4	2.4	12	0	100
5	THF[f]	8.9	1.1	12	0	100
6	CH_2Cl_2	7.6	1.8	10	0	100
7	C_6H_6[e]	2.2	0	0.5	0	100
8	Toluene[e]	2.4	0.3	0.5	0	100
9	Xylene[e]	2.6	0.5	0.5	0	100
10	Tetraline[e]	2.8	0.6	0.5	0	100

[a] The mixture of **1** (0.1 mmol) and **2** (0.2 mmol) in solution (5 ml) was irradiated with an Xe lamp through a Toshiba R-69 filter until the colour of **1** disappeared. The crude yields are about 80% in each case. [b] Relative permittivity. [c] Dipole moment. [d] The selectivity of the product was determined from the integration of ^{1}H NMR peaks of each product. [e] **2** was not added. [f] DMSO = dimethyl sulfoxide; THF = tetrahydrofuran.



Scheme 2

On the other hand, photoirradiation of the cyanine tetraphenylborate **4** in toluene gave the dimer **5** under argon (Scheme 2). This fact confirmed that the cyanine radical formed by single electron transfer from borate in an excited state is a reaction intermediate. The tetraphenylborate moiety is stable towards C–B bond cleavage in comparison with the results of Scheme 2, and consequently cyanine dye radicals coupled with each other to give the dimer **5** in 83% yield. The dimer **5** was unstable and decomposed gradually in solution under atmospheric conditions.

The photoreduction of the cyanine borate **1** to give the *meso*-phenyl **3a** or the *meso*-butyl leuco cyanine **3b** has thus been elucidated. The mechanism is similar to that proposed by Schuster,[2] as we have confirmed by isolation of the products; initial electron transfer from borate to cyanine dye in an excited state followed by radical cleavage of the borate moiety

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† Satisfactory elemental analysis were obtained for **1**, **3a**, **4** and **5**. M.p.s (T/°C): **1**, 109; **3a**, 163; **4**, 139.4–141.3; **5**, 134. *Selected spectroscopic data*: **3a**, ^{1}H NMR δ ($CDCl_3$) 1.13 (24H, m), 3.31 (16H, m), 4.74 (1H, t), 5.94 (2H, d), 6.41 (4H, d), 6.58 (4H, d), 6.90 (4H, d), 7.17 (4H, d) and 7.2–7.4 (5H, m); *m/z* 732 (M$^+$, 13.4%); ν_{max}/cm^{-1} 2970, 2889, 1608, 1520, 1353, 1267, 1196 and 817. **5**, ^{1}H NMR δ($CDCl_3$) 1.13 (48H, m), 3.29 (32H, m), 3.64 (2H, m), 5.78 (4H, d), 6.36 (8H, d), 6.51 (8H, d), 6.72 (8H, d) and 7.05 (8H, d); ^{13}C NMR δ($CDCl_3$) 12.8, 44.7, 45.7, 111.3, 127.2, 128.5, 128.8, 131.3, 132.6, 139.5, 146.2 and 146.4; *m/z* 1312.1 (M$^+$, 3.2%); ν_{max}/cm^{-1} 2970, 1608, 1520, 1356, 1267 and 816.

gives butyl or phenyl radicals. Coupling of these radicals with the cyanine dye radical at the *meso* position gave the leuco cyanine **3**. The cyanine borate **1** may have application as a decolourizable toner for electrophotography.

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References

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2 S. Chatterjee, P. D. Davis, P. Gottshalk, M. E. Kurz, B. Sauerwein, X. Yang and G. B. Schuster, *J. Am. Chem. Soc.*, 1990, **112**, 6329.