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M. Matsuoka [a] & T. Hikida [a]
[a] Department of Applied Chemistry, University of Osaka, Prefecture Sakai, Osaka, 593, Japan
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PHOTOCHEMISTRY AND APPLICATIONS OF CYANINE BORATE IR DYES

M. MATSUOKA *, T. HIKIDA
Department of Applied Chemistry, University of Osaka Prefecture
Sakai, Osaka 593, Japan

Abstract Photoreduction of cyanine borate ir dye gave the corresponding *meso*-substituted leuco cyanine. One electron transfer from borate to the cyanine molecule in excited state, followed by recombination of the dye radical with the alkyl or phenyl radical, produced from *n*-butyl triphenylborate as a counter anion, gave the leuco dye. This photoreaction process can be applied as a photopolymerization of monomers induced by ir irradiation, and a photodecolorizable tonner for electrophotography.

INTRODUCTION

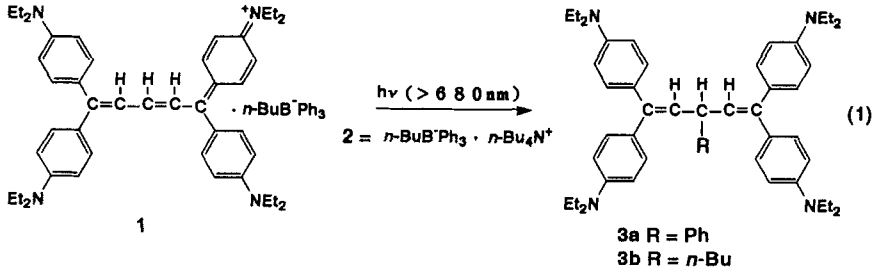
Recovery of paper as information recording media is currently important to save resources and to protect the environment. Paper is now consumed in large amounts as recording media for electrophotography, computer output and so on, but their recovery is not common and their recovery ratio is very low. If the recorded image can be decolored on the substrates, paper can be recycled in many times until quality becomes poor.

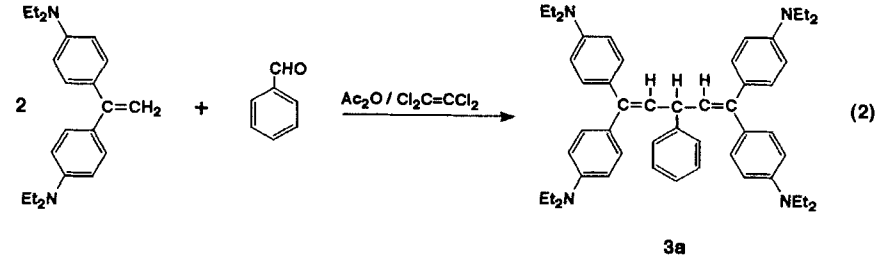
It was found that decolored *meso*-substituted leucocyanine was synthesized by the photoirradiation of the cyanine *n*-butyltriphenyl borate **1** in the presence of tetra *n*-butyl ammonium *n*-butyltriphenyl borate **2** (TBABTB). G. B. Schuster et al. have been studied the photoreduction of some cyanine borates in the similar process and proposed the reaction mechanism, but they could not isolate the reaction products[1].

In this paper, we report the photoinduced decoloration reaction of the cyanine borate and applied it as a decolorizable tonner for electrophotography. The photoreduction of the cyanine borates in various solvents was studied to know the reaction mechanism.

RESULTS AND DISCUSSION

The infrared absorbing cyanine borate **1** was decolored under irradiation of infrared light in the presence of TBABTB **2**; the mixture of cyanine borate **1** with **2** was irradiated with Xe lamp through a Toshiba R-69 filter under argon atmosphere gave the white solid (Equation 1). The product was identified as the meso-phenyl leucocyanine **3a**. Compound **3a** can also be synthesized by the reaction of 1,1 - bis (4-*N*,*N*-diethylaminophenyl) ethylene with benzaldehyde as shown in Equation 2.





While, photoirradiation of **1** and **2** in different solvents such as dichloromethane or alkylbenzenes predominantly gave the *meso*-butyl leucocyanine **3b** under similar conditions. The reactivity and the selectivity of the products in various solvents are summarized in Table 1.

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

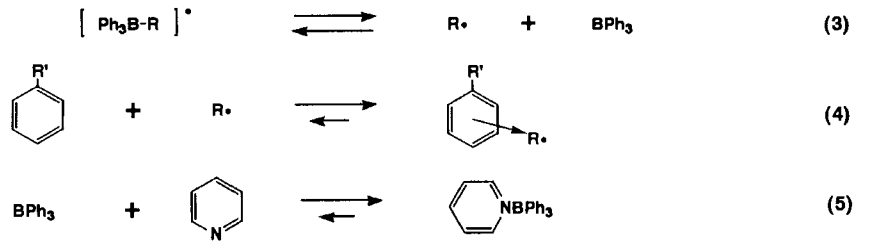
Run	Solvent	Reaction Time /h	Product (%)[c] 3a	3b
1	DMSO	40	100	0
2	CH_3CN	16	77	23
3	CH_3OH	37	40	60
4	THF	12	0	100
5	CH_2Cl_2	23	0	100
6	C_6H_6[b]	0.5	0	100
7	Toluene[b]	0.5	0	100
8	Xylene[b]	0.5	0	100
9	Tetraline[b]	0.5	0	100

[a] The mixture of **1** and **2** in solution was irradiated with Xe lamp through a Toshiba R-69 filter until the color of **1** was disappeared. The crude yields are about 80% in each case.

[b] **2** was not added.

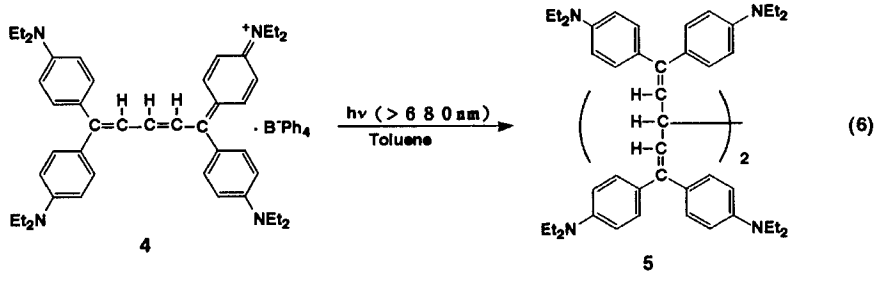
[c] The selectivity of the product was determined from the integration of ^1H NMR peaks of each product.

The reactivity and selectivity of photoreduction of **1** largely depend on the polarity of solvent. In alkylbenzenes, the photoreduction of **1** was very fast and gave only the meso-butyl leucocyanine **3b** even without **2**. From these results, alkylbenzenes can stabilize the butyl radical to form the π-complex as indicated in Equation 4. The reaction equilibrium shifts to right in alkylbenzene and the reaction is largely accelerated. The photoreduction was also accelerated by an addition of pyridine to the reaction mixture which is explained by the formation of the complex between the resulting boran and pyridine as indicated in Equation 5. The cleavage of C-B bond in Equation 3 will be the rate-determining step.



In less polar solvents such as acetonitrile or methanol, two products **3a** and **3b** were obtained (Runs 2,3). The selectivity of the product was affected by polarity of solvent, and the reaction was accelerated in nonpolar aromatic solvents (Runs 6-9).

On the other hand, the photoirradiation of cyanine tetraphenyl borate **4** in toluene gave a dimer **5** under argon atmosphere. This fact showed that cyanine radical formed as an intermediate under reaction conditions. Tetraphenyl borate moiety can donate one electron to cyanine dye in excited state but the borate moiety is quite stable against the cleavage of C-B bond, and consequently cyanine dye radical coupled in each other to give the dimer **5** in 83% yield. The dimer **5** was quite unstable and decomposed gradually in solution under atmospheric conditions.



In conclusion, the photoreduction of cyanine borate to give the *meso*-phenyl (**3a**) or the *meso*-butyl leucocyanine (**3b**) was elucidated. The reaction mechanism was same as proposed by Schuster[1] but we could confirm the mechanism by the isolation of the reaction products. That is the initial electron transfer from borate to cyanine dye in excited state followed by radical cleavage of the borate moiety to give butyl or phenyl radicals. The radical coupling of these radicals with the cyanine dye radical at *meso*

position gave the leuco cyanine. The cyanine borate **1** could be applied as a decolorizable tonner for electrophotography and the paper can be recycled in many times.

EXPERIMENTAL

Preparation of cyanine borate

Compound **1** was synthesized by the anion exchage reaction of cyanine tosylate **6** by the tetramethylammonium *n*-butyltriphenylborate **7**(TMABTB) in the mixture of acetonitrile and water (50:1,v/v). Compound **6** was synthsized by the reaction of 1,1-bis (4-*N*,*N*-diethylaminophenyl) ethylene with ethyl orthoformate in acetic anhydride in the presence of *p*-toluenesulfonic acid[2]. Compound **4** was synthesized by the anion exchage reaction of **6** with sodium tetraphenylborate in the similar method. Compounds **1** and **4** were purified by precipitation from dichloromethane solution with *n*-hexane.

Photoreduction of cyanine dyes

Cyanine borate **1**(0.1mmol) and **2**(0.2mmol) were placed in a 10ml reaction tube equipped with water jacket. The reaction tube was firstly substituted with argon gas and 4-5ml of distilled solvent was added. The mixture was stirred magnetically and irradiated with 500W Xe lamp (Ushio Electric Co.,Ltd) through a Toshiba R-69 filter for 0.5-40h. Reaction conditions are given in Table 1. The solvent was removed by evaporation under reduced pressure, and the resulting residue was separated by column chromatography to remove the raw material on silica gel using dichloromethane as an eluent, then ethyl acetate could be used to isolate the product from the resulting column. Product **3a** was obtained in about 80% yield in each case.

In the case of photoreduction of **4**, **4**(0.1mmol) in toluene(5ml) was irradiated with Xe lamp in the similar conditions. Toluene was removed by evaporation to dryness, and DMSO(20ml) was added to the residue and filtered. The precipitate was washed with water(20ml) and dried in vacuo at room temperature to give the dimer **5** in 83% yield.

Identification of compounds

The identification of compounds was conducted by usual methods; the ir spectra were recorded with a HORIBA FT-200 spectrometer. ^{1}H NMR spectra were determined on a JEOL JNM-GX 270 instrument with tetramethylsilane as internal standard. The mass spectra were recorded on a Finnigan MAT TSQ-70 spectrometer. The visible spectra were measured on a Shimadzu UV-265FS specrophotometer. Elemental analyses were conducted with a Yanaco CHN MT-3 recorder.

1: ^{1}H NMR (CDCl3) δ =1.0-1.3 (24H+6H, m), 3.43 (16H, q), 6.66 (8H,d), 6.84 (3H, t), 7.03 (6H, t), 7.14 (2H, d), 7.34 (8H, d), 7.45-7.55 (6H+1H,m) ;IR (KBr) 2976, 1583, 1498, 1408, 1344, 1271, 1174, 1117, 1072, 860, 748cm^{-1} ;Calcd for $C_{67}H_{83}N_4B$: C, 84.24; H, 8.76; N,5.87%. Found: C, 83.83; H, 8.91; N, 5.60%.

2: ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, t), 0.98 (12H, t), 1.11-1.29 (20H, m), 2.26 (10H, m), 6.86 (3H,t), 7.04 (6H,t), 7.46(6H,d) ; IR (KBr) 3057, 2962, 1578, 1481, 735, 708cm^{-1} ;Calcd for $C_{38}H_{51}NB$: C, 84.25; H,11.16; N,2.56%. Found: C, 83.82; H, 11.55; N, 2.54%.

3a: ^{1}H NMR (CDCl3) δ =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), 7.2-7.4 (5H,m) ; MS (EI) m/z 732 (M^+,13.4%) ;IR (KBr) 2970, 2889, 1608, 1520, 1353,1267, 1196, 817cm^{-1}.

3b: ^{1}H NMR ($CDCl_3$) δ =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), 7.2-7.4 (5H, m) ; MS(EI) m/z 712 (M^+,12.3%).

4: ^{1}H NMR ($CDCl_3$) δ =1.20 (24H, t), 3.41 (16H, q), 6.64 (8H,d), 6.88 (4H, t), 7.04 (8H, t), 7.10 (2H, d), 7.32 (8H, d), 7.41-7.48 (8H, m), 7.49 (1H, t); IR (KBr) 2972, 1583, 1498, 1408, 1344, 1271, 1174, 1115, 1070, 864, 748cm^{-1} ;Calcd for $C_{69}H_{79}N_4B$: C, 84.98; H, 8.17; N,5.75%. Found: C, 85.05; H, 8.31; N, 5.69%.

5: ^{1}H NMR ($CDCl_3$) δ =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), 7.05 (8H, d) ;MS(FAB) m/z 1312.1(M^+,3.4%) ; IR (KBr) 2970, 1608, 1520, 1356,1267, 816cm^{-1}

;Calcd for $C_{90}H_{118}N_8$: C, 82.39; H, 9.07; N, 8.54%. Found: C, 82.48; H, 9.26; N, 8.33%.

6: ^{1}H NMR (DMSO-d_6) δ =1.15 (24H, t), 2.28 (3H, s), 3.45 (16H, q), 6.85 (8H, d), 7.10 (2H, d), 7.3-7.4 (8H+2H+1H, m), 7.47 (2H, d) ;Calcd for $C_{69}H_{79}N_4B$: C, 84.98; H, 8.17; N,5.75%. Found: C, 85.05; H, 8.31; N, 5.69%.

7: ^{1}H NMR (DMSO-d_6) δ =0.7-1.0 (7H, m), 1.16 (2H, m), 3.08 (12H, s), 6.73 (3H, t), 6.89 (6H,t), 7.19 (6H,d)

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