Photoinduced electron transfer retropinacol reaction of 4-(*N*,*N*-dimethylamino)phenyl pinacols in chloroform

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UV irradiation of 1,2-bis[4-*N*,*N*-(dimethylamino)phenyl]ethane-1,2-diol (1a) and 2,3-bis[4-(*N*,*N*-dimethylamino)phenyl]butane-2,3-diol (1b) in deaerated chloroform leads to central carbon–carbon bond cleavage (retropinacol reaction) forming 4-(*N*,*N*-dimethylamino)benzaldehyde (2a) and 4-(*N*,*N*-dimethylamino)acetophenone (2b), respectively, in high yields. Chemically induced dynamic nuclear polarization (CIDNP) and fluorescence quenching experimental results reveal that the reaction proceeds *via* a photoinduced electron transfer mechanism from the excited pinacols with a very fast dechlorination of the chloroform radical anion and fragmentation of the pinacol radical cation as crucial steps.

Introduction

The oxidative fragmentation of pinacols (retropinacol reaction) can be accomplished either thermally[1,2] or photochemically,[3–7] giving aldehydes or ketones as the main products. In general, the fragmentation does not occur by direct photolysis,[5a] and a strong electron-withdrawing sensitizer, such as 2,6,9,10-tetracyanoanthracene,[3] chloranil,[4a] 2,3,5,6-tetracyanobenzene[4b] or 1,4-dicyanonapthalene,[5,6] must be used to initiate the photoinduced electron transfer and to generate the pinacol radical cation which has been proposed to be the primary key intermediate for the fragmentation.[3–7] We report here an alternative version of the retropinacol reaction, *i.e.* exciting the pinacol donor instead of exciting the acceptor sensitizers. It was found that for 4-(*N*,*N*-dimethylamino)phenyl substituted pinacols the retropinacol reaction can take place in the absence of sensitizers in chloroform solvent, giving high yields of aldehydes or ketones. Chemically induced dynamic nuclear polarization (CIDNP) and fluorescence quenching experimental results suggest that this reaction proceeds *via* a photoinduced electron transfer mechanism from the excited pinacols, involving a very fast carbon–chlorine bond breaking of the chloroform radical anion and fragmentation of the pinacol radical cation. According to Whitten[7] and Maslak[8] and their co-workers, this reaction can be considered to be a double mesolytic fragmentation reaction since it involves both catiomesolytic and aniomesolytic processes.

Results

Photochemical reactions

Steady state photolysis of a dilute deoxygenated chloroform solution of 4-(*N*,*N*-dimethylamino)phenol pinacol **1a** or **1b** by UV light through a Pyrex filter afforded aldehyde **2a** or ketone **2b**, respectively, as the unique product in high yield (Scheme 1). Gas chromatographic analysis after removal of the aldehyde or ketone indicated quantitative formation of dichloromethane during the reaction. No substituted benzyl alcohol could be detected and no appreciable reaction took place when the (dimethylamino)phenyl pinacols were irradiated under similar conditions in acetonitrile of cyclohexane solvent in the absence of chloroform.

Fluorescence quenching

Pinacol **1a** showed strong fluorescence emission at 354 nm upon excitation at 306 nm in dilute acetonitrile. Addition of chloroform quenched the fluorescence effectively without showing a new emission (Fig. 1). The Stern–Volmer plot showed a good straight line from which the Stern–Volmer constant K_{SV} of 36.0 mol^{-1} dm^3 was deduced. The fluorescence life time, τ_0, was determined by a single photon counting technique as 2.2 ns. Thus the fluorescence quenching rate constant, k_q, was calculated to be 1.6×10^{10} dm^3 mol^{-1} s^{-1}. Pinacol **1b** showed similar fluorescence quenching behaviour. The photophysical para-

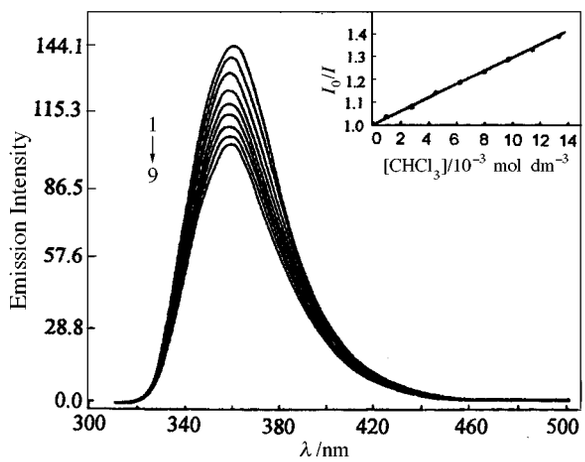
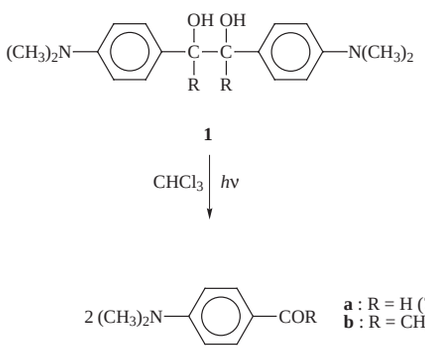


Fig. 1 Fluorescence spectra of **1a** (4.3×10^{-5} mol dm^{-3}) in acetonitrile with increasing concentrations of chloroform (for spectra 1–9: 0, 0.86, 2.58, 4.30, 6.03, 7.74, 9.46, 11.2, 12.9 mmol dm^{-3} respectively) under air. The inset shows the Stern–Volmer plot for the experiment.



Scheme 1

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Table 1 Thermodynamic and photophysical parameters for the photoinduced electron transfer retropinacol reaction in chloroform

Sensitizer	$E_{(D/D^{+})}$[a]/V *vs.* SCE	$E_{0,0}$[b]/eV	ΔG_{ET}[c]/kcal mol^{-1}	E_{IRP}[d]/kcal mol^{-1}	τ_0[e]/ns	$k_q/10^{10}$ dm^3 mol^{-1} s^{-1}
1a	0.66	3.7	−47.5	37.8	2.2	1.6 (1.0)[f]
1b	0.60	3.7	−48.9	36.4	1.9	1.7

[a] Determined in acetonitrile at a glassy carbon electrode with 0.1 mol dm^{-3} tetra-*n*-butyl ammonium perchlorate as supporting electrode. [b] Estimated from the fluorescence excitation and emission spectra. [c] Calculated by the Rehm–Weller equation,[11] $\Delta G_{ET} = 23.06\ [E_{(D/D^{+})} - E_{(A^{-}/A)} - E_{0,0} - E_{coul}]$, taking $E_{(A^{-}/A)} = -1.32$ V (*vs.* SCE) for chloroform[22] and $E_{coul} = 0.34$ eV for chloroform calculated by the Born equation.[23] [d] Calculated by $E_{IRP} = 23.06\ [E_{(D/D^{+})} - E_{(A^{-}/A)} - E_{coul}]$.[11] [e] Determined by single photon counting in acetonitrile, see text. [f] Determined in cyclohexane.

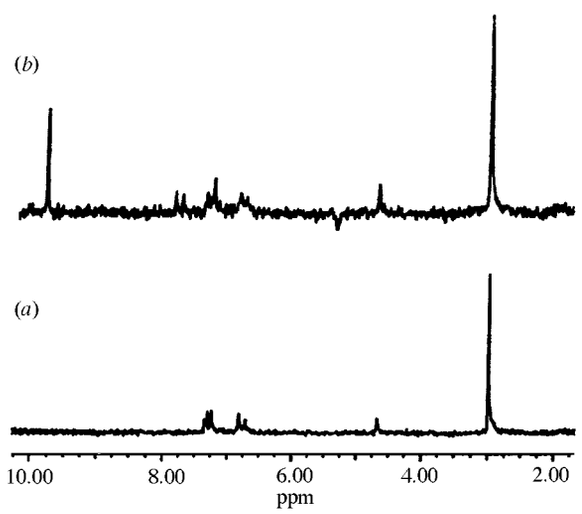


Fig. 2 ^{1}H NMR (80 MHz) spectra obtained (*a*) before and (*b*) during the UV irradiation of **1a** (5 mmol dm^{-3}) in $CDCl_3$

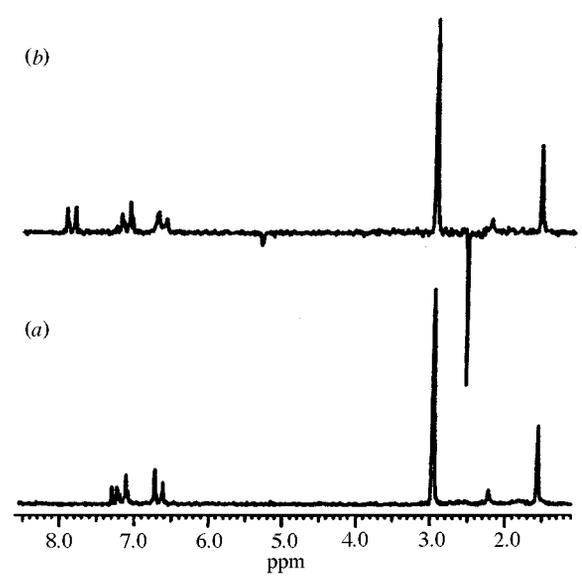


Fig. 3 ^{1}H NMR (80 MHz) spectra obtained (*a*) before and (*b*) during the UV irradiation of **1b** (5 mmol dm^{-3}) in $CDCl_3$

meters together with the thermodynamic parameters for the electron transfer process (*vide infra*) are listed in Table 1.

Chemically induced dynamic nuclear polarization (CIDNP)

Irradiation of a [^{2}H]chloroform solution of **1a** or **1b** (0.01 mol dm^{-3}) *in situ* with a 1000 W high-pressure Hg–Xe lamp gave rise to strong polarized NMR signals. The CIDNP spectrum of **1a** shows a strong enhanced absorption at 9.76 ppm, an enhanced absorption at 7.74 (doublet) and an emissive peak at 5.30 ppm (Fig. 2). The former two peaks are assigned to the aldehyde proton and aromatic protons respectively, of the product 4-(*N*,*N*-dimethylamino)benzaldehyde (**2a**) with reference to the NMR spectrum of the authentic sample of **2a**. The small emissive peak comes from [^{2}H]dichloromethane[9] (*vide infra*). The spectrum of **1b** shows similar enhanced absorptive peaks of the aromatic protons of **2b**, but the signal of the acetyl protons is strongly emissive. The emissive peak of $CHDCl_2$ at 5.30 ppm is also observed (Fig. 3). The polarization phases are summarized in Table 2.

Table 2 ^{1}H CIDNP results observed during the photoreaction of **1** in $CDCl_3$

Compound	Position	δ_H	A_i[a]	Γ_i[b]
2a	Aldehyde	9.76	−	A
	o-Aromatic	7.74 (d)	−	A
	m-Aromatic	6.70 (d)	+	*c*
	$CHDCl_2$	5.30	−	E
2b	*o*-Aromatic	7.95 (d)	−	A
	m-Aromatic	6.71 (d)	+	*c*
	$CHDCl_2$	5.30	−	E
	Acetyl	2.52	+	E

[a] The sign of hyperfine splitting constants in radical **3** and $\cdot CHCl_2$.[12,13b,16] [b] Polarization phase, A and E denote enhanced absorption and emission respectively, see eqn. (1). [c] Not observed because the hyperfine splitting constant is small and the peak overlapped with the aromatic peak of **1a** (6.73 ppm).

Discussion

It is well known that pinacols can be prepared by photochemical reduction of ketones,[10] hence they are generally persistent against direct photolysis.[5a] As a matter of fact, UV irradiation of pinacols **1a** or **1b** in cyclohexane or acetonitrile shows no appreciable reaction. However, the central carbon–carbon bond in pinacols and tetra-substituted ethanes can be significantly weakened by removing an electron from the molecule to form a radical cation,[3,8] and central carbon–carbon bond cleavage of pinacols has been accomplished by single electron transfer using a Fe^{III} complex[1] or tris(*p*-bromophenyl) aminium salts,[2] and by photoinduced electron transfer using electron-withdrawing sensitizers.[3–6] In the present study pinacols **1a** and **1b** fragment in the absence of any electron-withdrawing sensitizer, but participation of chloroform is indispensable. Since other pinacols not bearing a dimethylamino-substituent, *i.e.* less electron-donating than **1**, do not undergo appreciable photochemical reactions under identical experimental conditions, and the fluorescence of **1a** and **1b** can be effectively quenched by chloroform with a diffusion-limited rate (see Table 1), it is reasonable to assume that this reaction is a photoinduced electron transfer reaction. The free energy change for the electron transfer process is calculated by the Rehm–Weller equation[11] and listed in Table 1.

It can be seen from Table 1 that the electron transfer reactions between pinacols **1** and chloroform are energetically feasible. Therefore, there is little doubt that photoinduced electron transfer from excited **1** to chloroform is the primary stage of the reaction and the radical cation of the pinacol is the crucial intermediate for the bond cleavage. However, the detailed mechanism for the radical cation fragmentation is a point of controversy. Das and co-workers[5b] studied the dicyanonaphthalene (DCN) sensitized fragmentation of phenyl-substituted pinacols by laser flash photolysis and found that the lifetimes of the photochemically generated pinacol radical cations are extremely short (less than 10 ns), hence it was suggested that the

fragmentation is caused by homolytic cleavage of the central carbon–carbon bond *via* back electron transfer within the radical ion pair which produces two identical α-hydroxybenzyl radicals. Albini and Mella[6a] compared the quantum yields of DCN sensitized fragmentation of benzopinacols in the absence and in the presence of oxygen, and proposed that the in-cage proton transfer from the pinacol radical cation to DCN followed by fragmentation of the alkoxyl radical may take place concurrently with the homolytic cleavage process proposed by Das.[5b] An alternative pathway is the direct cleavage of the radical cation which produces an α-hydroxybenzyl carbocation and an α-hydroxylbenzyl radical, followed by proton transfer and hydrogen transfer respectively to the sensitizer to form the final product carbonyl compound.[5a,6b] Whitten and co-workers[3] studied the tetracyanoanthracene (TCA) sensitized fragmentation of 4-(*N*,*N*-dimethylamino)phenyl pinacols **1a** and **1b** and found that the fragmentation rate (5×10^5 s^{-1}) is considerably slower than the rate of back electron transfer (1.4×10^{10} dm^3 mol^{-1} s^{-1}) and the rate of separation of the initially formed radical ion pair (5×10^8 s^{-1}), hence suggesting that the fragmentation of the radical cation occurs after separation of the radical ions from the cage. Kochi and co-workers[4a,b] compared tetracyanobenzene (TCNB) and chloranil sensitized fragmentation of pinacols and found that the fragmentation of the pinacol radical cation may take place either in-cage or out-of-cage, depending on the character of the sensitizer (singlet or triplet). Recently Whitten and co-workers[7] found that the quantum efficiency of the fragmentation of aminopinacols can be improved by efficient fragmentable electron acceptors, such as organic bromides and carbon tetrachloride, and suggested an oxygen-mediated radical chain mechanism for the so-called 'double fragmentation' which is similar to the present reaction (*vide infra*).

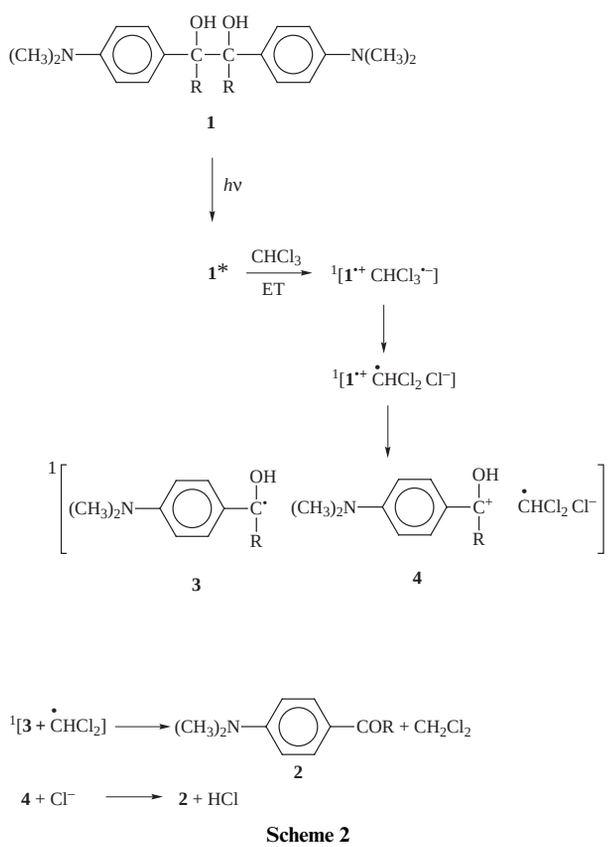
Chemically induced dynamic nuclear polarization (CIDNP) is a powerful tool for investigating reaction mechanisms dealing with radical pairs, and is especially useful for distinguishing between radical pair and radical ion pair intermediates.[12] CIDNP results can be qualitatively discussed using the Kaptein rule[13] and the amendments suggested by Roth and Shilling[14] and Closs and Czeropski.[15] The net CIDNP effect connects the polarization phase Γ_i of the nucleus i (positive for enhanced absorption and negative for emission) with four parameters *via* eqn. (1), where μ is the initial spin multiplicity of the radical

$$\Gamma_i = \mu\varepsilon\Delta g A_i \qquad (1)$$

pair [positive for triplet or random (free) pairs and negative for singlet pairs]; ε the type of the product (positive for cage products and negative for escape products; and negative for secondary pair recombination products[14]); $\Delta g = g_a - g_b$ (g_a pertains to the radical carrying the nucleus i); and A_i the sign of the radical hyperfine splitting constant (hfs) for the nucleus under observation.

From an initial consideration of the CIDNP spectra of **1a** and **1b** (Figs. 2 and 3) it can be concluded that the polarization does not stem from the aminium radical cation $\mathbf{1}^{\bullet+}$, but stems from a neutral carbon centred radical. This is due to the fact that the hyperfine splitting constants of the protons in the α- and β-positions of carbon centred radicals are negative and positive respectively,[13b,16] whereas those in α- and β-positions of aminium radical cations are all positive with the former very large and the latter very small (*e.g.* 37 G and <1 G respectively for triethylaminium radical cation[12]). Therefore, the lack of polarization from the parent pinacols clearly demonstrates that the radical ion pair does not contribute to the CIDNP effect. If this was the case, the parent pinacols would have showed strong enhanced absorption at the methyl protons of the dimethylamino group. The polarization also cannot stem from the homolytic central carbon–carbon bond cleavage, because two identical radicals would not generate a net CIDNP effect.[13] Therefore, we must invoke a fast fragmentation of the aminium radical cation which generates an α-hydroxybenzyl radical (**3**) and an α-hydroxybenzyl carbocation (**4**). Radical **3** then interacts with the dichloromethyl radical, which was formed from the dechlorination of the chloroform radical anion, to generate the polarization. The *g* value of $\mathbf{1}^{\bullet+}$ should be close to that of tertiary aminium radical cations (~2.004),[12] and the *g* value of **3** should be around 2.003.[12] They both are significantly smaller than that of the chloroform radical anion (2.0080)[16] or the dichloromethyl radical (2.0083),[13b] thus giving a negative value of Δg. The fluorescence of **1** is efficiently quenched by chloroform (*vide infra*) implying that the reaction originates from the singlet excited pinacol, thus μ is negative. Therefore, the enhanced absorptive polarization of the aldehyde proton of **2a**, as well as the emissive polarization of the ketone methyl protons of **2b** predict three possible reaction channels for the reaction: a singlet escape reaction or a triplet (or free pair) in-cage reaction according to the Kaptein rule,[13] or a secondary recombination reaction according to the amendment suggested by Roth and Shilling.[14] The hyperfine splitting constant of the dichloromethyl radical is −16.8 G,[16a,17] hence the emissive polarization of dichloromethane predicts the same possibilities as well, because the Δg is positive in this case. The enhanced absorption peaks of the *ortho*-protons of the aromatic ring are also consistent with the prediction because the *ortho*- and *meta*-protons of benzyl radicals possess large negative and small positive hyperfine splitting constants respectively.[16b] Since no 4-(*N*,*N*-dimethylamino)benzyl alcohol is produced from the reaction, the hydrogen abstraction of the intermediate **3** from the solvent, *i.e.* the singlet escape reaction, as well as the free pair reaction, can be excluded. The triplet energy of **1** is estimated to be *ca.* 68 kcal mol^{-1},[18] which is significantly higher than the radical ion pair energy of $[\mathbf{1}^{\bullet+}\ CHCl_3^{\bullet-}]$ (see Table 2), making the triplet recombination reaction unlikely to take place due to the unfavourable energetics. Therefore, the following mechanism is proposed for this retropinacol reaction (Scheme 2).

The critical step in this mechanism is the extremely fast dechlorination of the radical anion of chloroform. It is well



Scheme 2

known that alkyl and aryl halides are subject to reductive dissociation when accepting an electron either electrochemically or photochemically.[19] The carbon–chlorine bond energy was reported to be 77.2 and 34.5 kcal mol^{-1} for chloroform and the chloroform radical anion respectively,[20] and the lifetime of the chloroform radical anion was reported to be extremely short (less than a few picoseconds).[21] Therefore, electron transfer to alkyl and aryl halides may even take place concertedly with the carbon–halogen bond breaking.[19] These facts explain why no polarization could be observed from the back electron transfer of the $\mathbf{1}^{\bullet+}$ $CHCl_3^{\bullet-}$ radical ion pair. The timescale of $S–T_0$ mixing which is the origin for generating nuclear polarization is around 10^{-9}–10^{-8} s,[13b] hence the radical ion pair, even if formed, does not have enough time to generate nuclear polarization before the carbon–chlorine bond breaking.

Furthermore, the central carbon–carbon bond breaking in pinacols is also significantly facilitated by losing an electron,[1–6] and the lifetime of pinacol radical cations has been reported to be <10 ns,[5b] 0.1–0.2 ns[7] and <0.03 ns,[4b] depending on the structure of the pinacol and the sensitizer used. In the present case the lifetime of $\mathbf{1}^{\bullet+}$ must be less than 10^{-9} s; that would make the $S–T_0$ mixing of the $[\mathbf{1}^{\bullet+}\cdot CHCl_2]$ radical pair also impossible. In other words, $\mathbf{1}^{\bullet+}$ fragments directly to the α-hydroxybenzyl radical **3** and α-hydroxybenzyl cation **4** as proposed previously[5a,6] within the timescale of less than 10^{-9} s. Therefore, only the polarization from the secondary radical pair $[\mathbf{3}\cdot CHCl_2]$ could be observed. This mechanism demonstrates that the hydrogen abstraction by the dichloromethyl radical from the α-hydroxybenzyl radical is also a fast process and it is completed before the two radicals can escape from the cage. It explains why no reduction product, *i.e.* the corresponding benzyl alcohol, is produced, since the α-hydroxybenzyl radical **3** has no chance to diffuse out of the cage to abstract hydrogen from the solvent.

In conclusion, this work demonstrates that pinacols bearing (dimethylamino)phenyl substituents can be subject to fast oxidative fragmentation *via* photoinduced electron transfer with chloroform as the electron acceptor. The extremely fast dechlorination of the chloroform radical anion helps to circumvent the back electron transfer and makes feasible the fragmentation of the pinacol radical cation. Maslak and co-workers[8] have termed unimolecular fragmentation reactions of radical ions to radical and ions as mesolytic cleavages and illustrated the tremendous acceleration of carbon–carbon bond cleavages obtainable in mesolytic processes. The present reaction involves mesolytic cleavages of both radical cation (catiomesolysis) and radicals anion (aniomesolysis), hence, it can be considered as a double mesolytic fragmentation reaction which causes the very fast and efficient reaction. This strategy may be applicable to enhance the efficiency of other photoinduced electron transfer reactions.

Experimental

Materials

meso-1,2-Bis[4-(*N*,*N*-dimethylamino)phenyl]ethane-1,2-diol (**1a**) was prepared by reductive coupling of 4-(*N*,*N*-dimethylamino)benzaldehyde according to the published procedure.[3] The *meso*-isomer was separated from the (±)-isomer by recrystallization from ethanol and repeated column chromatography on silica gel with methylene chloride and diethyl ether as eluent. Mp 173–174 °C (uncorrected, lit. mp 178–179 °C);[3] $\delta_H(CDCl_3)$ 7.26 (d, *J* 8.4 Hz, 4H), 6.73 (d, *J* 8.4 Hz, 4H), 4.64 (s, 2H), 2.96 (s, 12H). *meso*-2,3-Bis[4-(*N*,*N*-dimethylamino)phenyl]butane-2,3-diol (**1b**) was prepared by a Grignard reaction of 4-bromo-*N*,*N*-dimethylanilene with butane-2,3-dione as described in the literature.[3] The *meso*-isomer was separated from the (±)-isomer by careful column chromatography on silica gel with methylene chloride containing 2.5% diethyl ether as eluent, followed by repeated recrystallization from absolute ethanol. Mp 190–191 °C (uncorrected, lit. mp 196–197 °C);[3] $\delta_H(CDCl_3)$ 7.14 (d, *J* 9.6 Hz, 4H), 6.65 (d, *J* 9.6 Hz, 4H), 2.95 (s, 12H), 2.20 (s, 2H) 1.54 (s, 6H). [^{2}H]Chloroform was obtained from Aldrich and used as received. Chloroform and other chemicals were commercial products and purified by conventional methods before use.

Photochemical reactions

An anhydrous chloroform solution (25 ml) of **1a** (0.36 g, 1.2 mmol) or **1b** (0.35 g, 1.1 mmol) was deaerated by argon bubbling and then was irradiated with a 500 W high pressure mercury lamp in a Pyrex bottle with a water-cooling jacket for 2 h. Then the reaction solution was washed with dilute sodium carbonate and water respectively, and dried over anhydrous potassium carbonate. After removing the solvent under reduced pressure the residue was chromatographed on preparative silica gel plates. The products were identified by ^{1}H NMR spectroscopy and compared with the authentic samples, and quantitatively determined with a Shimadzu CS-910 double-beam thin layer scanning fluorescence spectrophotometer. 4-(*N*,*N*-Dimethylamino)benzaldehyde (**2a**), mp 72–74 °C (uncorrected. lit. 73–75 °C);[24] $\delta_H(CDCl_3)$ 9.76 (s, 1H), 7.74 (d, *J* 8.2 Hz, 2H), 6.70 (d, *J* 8.2 Hz, 2H), 3.10 (s, 6H). 4-(*N*,*N*-Dimethylamino)-acetophenone (**2b**), mp 103–105 °C (uncorrected, lit. 105.5 °C),[25] $\delta_H(CDCl_3)$ 7.95 (d, *J* 9.4 Hz, 2H), 6.71 (d, *J* 9.4 Hz, 2H), 3.09 (s, 6H), 2.52 (s, 3H).

CIDNP

CIDNP experiments were performed at 80.131 MHz on a Bruker AC-80 spectrometer equipped with a photo-CIDNP probe with a 1000 W high pressure Hg–Xe lamp as described previously.[26] The deuterated chloroform solution of **1** (5 mmol dm^{-3}) was deaerated by argon bubbling before the experiment.

Fluorescence quenching

Steady state fluorescence spectra were recorded with a Hitachi M850 fluorescence spectrophotometer in acetonitrile solutions of **1a** and **1b** (4×10^{-5} mol dm^{-3}) with an increasing amount of chloroform (ranging from 8.6×10^{-4} to 1.3×10^{-2} and 6.2×10^{-4} to 8.4×10^{-2} mol dm^{-3} for **1a** and **1b** respectively). **1a** and **1b** were excited at 306.5 and 305 nm respectively.

Fluorescence lifetime

Time-resolved fluorescence spectra were recorded in acetonitrile (5×10^{-5} mol dm^{-3}) on a Horible NAES-1100 single photon counting fluorescence spectrophotometer. The fluorescence was excited and recorded at 306.5 and 354.0 nm for **1a**, and 305.0 and 353.5 nm for **1b**, respectively. Double exponential fitting gave the lifetime of the main component (>93%) as shown in Table 1.

Electrochemical determination

The oxidation potentials of **1a** and **1b** were measured by cyclic voltammetry with a PAR 173 potentiostat coupled with a PAR 175 universal programmer at room temperature, using a conventional three-electrode cell with a glassy carbon electrode as the working electrode and a platinum wire as an auxiliary electrode. The potentials were recorded with reference to a saturated calomel electrode (SCE).

Acknowledgements

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