Photoinduced benzylation of 1,4-dimethoxynaphthalene by benzyl halides

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Irradiation of 1,4-dimethoxynaphthalene (DMNH) in the presence of 4-substituted benzyl chlorides (X–$C_6H_4CH_2Cl$, X = H, Cl, CN or NO_2) in either acetonitrile or benzene solution results in benzylation of DMNH, predominantly at position 2 and to a lesser extent on the unsubstituted ring. Steady-state and flash photolysis studies show that charge transfer between singlet excited DMNH and the chlorides is involved. The reaction occurs predominantly in-cage *via* concerted electron transfer and carbon–chlorine bond cleavage with X = H or Cl, while with X = NO_2 fragmentation of the benzyl chloride radical anion occurs out-of-cage, but the process in this case is much less efficient due to competing back electron transfer.

Introduction

The large change in redox potential occurring on electronic excitation of a molecule makes electron transfer involving excited states an efficient process[1] which has been commonly used for the preparation of radical ions in solution. Although back electron transfer limits their lifetimes, such species often react so rapidly that an efficient chemical process results. A typical reaction is fragmentation of a σ-bond which becomes severely weakened upon ionisation. The resulting radical cation frequently fragments to yield a neutral radical.[2a] When the acceptor is a substituted aromatic molecule (A–Z), this often results in photosubstitution on the ring.[2b] Thus, following radical ion pair formation [eqn. (1)], the donor-derived radical
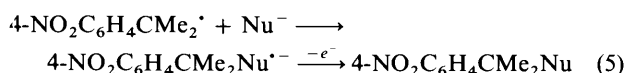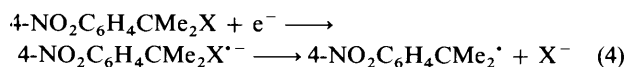
$$A-Z^* + R-X \longrightarrow A-Z^{\cdot -} + R-X^{\cdot +} \qquad (1)$$
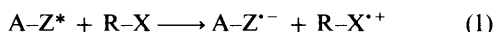
(R·) formed by fragmentation of the radical cation (R–X·⁺) [eqn. (2)] commonly couples with the radical anion (A–Z·⁻)

$$R-X^{\cdot +} \longrightarrow R^{\cdot} + X^{+} \qquad (2)$$
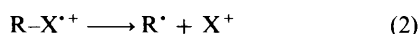
to yield an anion (R–A–Z⁻), which eliminates the original substituent to yield a differently substituted aromatic (A–R) [eqn. (3)].

$$A-Z^{\cdot -} + R^{\cdot} \longrightarrow R-A-Z^{-} \longrightarrow A-R + Z^{-} \qquad (3)$$
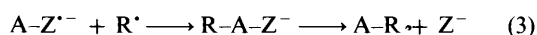
Formation of an alkyl radical is similarly possible by loss of a nucleofugal group from a radical anion. For example, the 4-nitrocumyl radical is the key intermediate in the $S_{RN}1$ type nucleophilic substitution in the benzylic position observed on photostimulation of various 4-nitrocumyl derivatives. [eqns. (4) and (5)].[3]

$$4\text{-}NO_2C_6H_4CMe_2X + e^- \longrightarrow$$
$$4\text{-}NO_2C_6H_4CMe_2X^{\cdot -} \longrightarrow 4\text{-}NO_2C_6H_4CMe_2^{\cdot} + X^- \qquad (4)$$

$$4\text{-}NO_2C_6H_4CMe_2^{\cdot} + Nu^- \longrightarrow$$
$$4\text{-}NO_2C_6H_4CMe_2Nu^{\cdot -} \xrightarrow{-e^-} 4\text{-}NO_2C_6H_4CMe_2Nu \qquad (5)$$

By analogy with eqns. (1)–(3) the photoalkylation of an aromatic donor molecule (D–H) might be anticipated to occur by the mechanism suggested in eqns. (6)–(8) where the electrofugal group is a proton.

$$D-H^* + R-Z \longrightarrow D-H^{\cdot +} + R-Z^{\cdot -} \qquad (6)$$
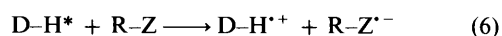
Table 1 Products from the preparative irradiation of DMNH in the presence of benzylic chlorides 1a–d

Benzyl chloride	Solvent	Product (% yield)[a]
1a	Acetonitrile	2a (32)
1a	Benzene	2a (24)
1b	Acetonitrile	2b (90), 3b (5)
1b	Benzene	2b (25), 3b (3)
1c	Acetonitrile	2c (40), 3c (17)[b]
1c	Benzene	2c (28), 4c (4), 5c (2)
1d	Acetonitrile	2d (57), 4d (4), 5d (10)
1d	Benzene	2d (39), 4d (7), 5d (13)

[a] Based on DMNH consumed. [b] Mixture of dibenzylated derivatives.

$$R-Z^{\cdot -} \longrightarrow R^{\cdot} + Z^- \qquad (7)$$

$$D-H^{\cdot +} + R^{\cdot} \longrightarrow R-D-H^{+} \longrightarrow D-R + H^{+} \qquad (8)$$
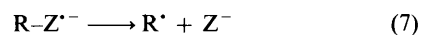
However, such a process has not been reported to date, although photosolvolysis of benzyl halides has been extensively investigated and mechanistically characterised, particularly in intramolecular examples,[4a] and it has also been reported[4b] that they quench the fluorescence of 2,6-dimethoxynaphthalene. We have been interested in evaluating the synthetic potential and the mechanistic characteristics of such an alkylation, and report here our studies on the photochemistry of a donor–acceptor system involving 1,4-dimethoxynaphthalene (DMNH) and various 4-substituted benzyl chlorides as potential participants in such a process.

Results

Preparative irradiation

Solutions of DMNH (10^{-2} mol dm⁻³) in either acetonitrile or benzene were irradiated in the presence of benzyl chloride (1a). When most of the DMNH had been consumed, chromatographic separation of the photolysate gave a product identified as 2-benzyl-1,4-dimethoxynaphthalene (2a) (Scheme 1, Table 1).

Similar irradiation of DMNH in the presence of 4-chlorobenzyl chloride (1b) gave the corresponding 2-benzyl derivative 2b as well as a small amount of a dibenzylated (2,6- or 2,7-) naphthalene 3b (Scheme 1, Table 1).

With 4-cyanobenzyl chloride 1c the 2-benzyl derivative 2c

Table 2 Product distribution in low (< 20%) conversion runs

| Benzyl chloride | Product (relative ratio) | | | | | |
| | In acetonitrile | | | In benzene | | |
	2	4	5	2	4	5
1a	79	12	9	94	3	3
1b	69	17	14	79	13	8
1c	66	20	14	74	17	9
1d	73	15	12	a	a	a

[a] Slow reaction.

Table 3 Steady-state parameters

Benzyl chloride	Solvent	$K_{fluorescence}/$ mol^{-1}	ϕ_{lim}	$K_{product}/$ mol^{-1}
1a	Acetonitrile	8.5	0.14	10
	Benzene	5	0.05	8
1b	Acetonitrile	28	0.11	40
	Benzene	25	0.08	20
1c	Acetonitrile	83	0.3	100
	Benzene	63	0.05	80
1d	Acetonitrile	a	0.05[b]	—
	Benzene	a	0.0005[b]	—

[a] Curved plots. [b] [1d] = 1 × 10^{-3} mol dm^{-3}.

Scheme 1

was again the main product. From irradiation in benzene two minor components were isolated and identified as the 5- and 6-(4-cyanobenzyl)-1,4-dimethoxynaphthalenes **4c** and **5c**. In acetonitrile a further fraction was obtained and, although the individual components could not be separated, the spectra supported their structure as the four isomeric 2,5-, 2,6-, 2,7- and 2,8-dibenzylated derivatives **3c** (Scheme 1, Table 1).

With 4-nitrobenzyl chloride (**1d**) the main product obtained was the 2-substituted derivative **2d** with minor amounts of the 5- and 6-substituted compounds **4d** and **5d** (Scheme 1, Table 1).

Steady-state measurements

Separate experiments at low conversion were carried out and investigated by vapour phase chromatography. In this way, it was possible to ascertain that with all four benzyl chlorides the products initially formed were the three isomeric benzyl-1,4-dimethoxynaphthalenes **2**, **4** and **5**. The relative ratios of the products were quite similar in each case and product yields corresponded to >90% of the DMNH consumed (Table 2). Products not containing the naphthalene moiety were also present in small amounts. For example, in the case of **1b**, 1,2-di(4-chlorophenyl)ethane and 2-(4-chloro-benzyl)-4-chlorobenzyl chloride were also identified by GC–MS.

Under these conditions the quantum yield for product formation ($\phi_{product}$) and its dependence on [1], the benzyl chloride concentration, were also measured. Table 3 lists the parameters obtained from these experiments, viz. the quantum yield at infinite **1** concentration, (ϕ_{lim}), and the Stern–Volmer coefficients ($K_{product} = k_q/k_d$), the intercept vs. slope ratios from the plots of $1/\phi_{product}$ vs. $1/[1]$.

Furthermore, quenching of DMNH fluorescence by compounds **1a–d** was determined. For compounds **1a–c** linear plots of ϕ_0/ϕ vs. [1] were obtained. Table 3 lists the corresponding Stern–Volmer coefficients ($K_{fluorescence}$), the gradients of these plots. Compound **1d** in contrast gave curved plots. In this latter case the formation of a ground state complex could be deduced from the appearance of a new absorption, tailing to ca. 470 nm, upon mixing the reagents in acetonitrile.

Similar experiments in acetonitrile involving benzophenone sensitisation of DMNH ($E_T^{Ph_2CO}$ = 69 kcal mol^{-1}; E_T^{DMNH} = 60.3
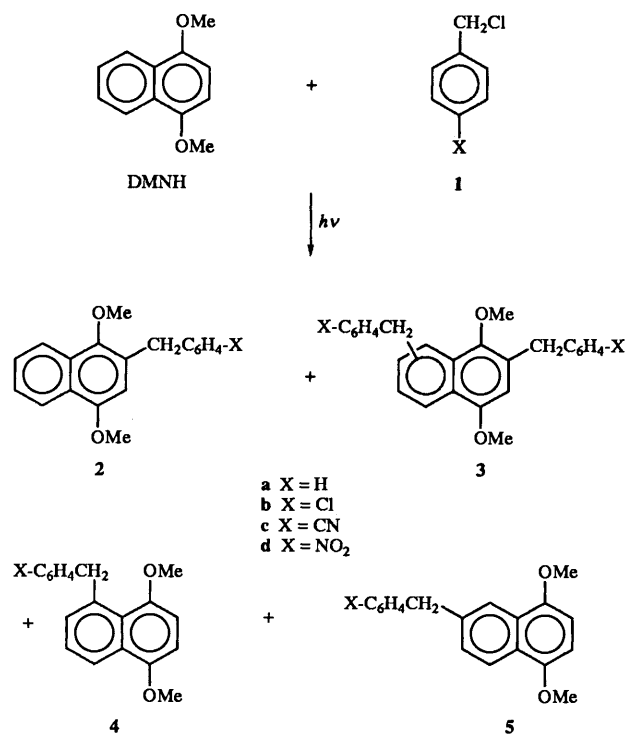
kcal mol^{-1}) in the presence of compounds **1a–d**, under conditions in which only benzophenone absorbed the light, did not lead to photoproduct formation. When the irradiation of DMNH and **1b** or **1d** in acetonitrile was carried out in the presence of dodecylthiol (0.06 mol dm^{-3}), there was a 15% decrease in benzylation in the case of **1b**, but a complete quenching of the benzylated products, with simultaneous formation of 4-nitrotoluene, in the case of **1d**.

Flash photolysis

Pulsed laser irradiation of DMNH in acetonitrile resulted in the appearance of a transient absorption on the long-wavelength side of the very strong DMNH fluorescence (τ_s 8.1 ns, in agreement with a previously reported value for the DMNH singlet lifetime).[5] The species giving rise to this transient had a lifetime of 3.5 μs (estimated at 480 nm, interference from the DMNH fluorescence prevented investigation at shorter wavelengths) and was quenched by oxygen, suggesting it to be triplet DMNH. Irradiation of 4-methoxyacetophenone (0.12 mol dm^{-3}) in the presence of DMNH (2 × 10^{-4} mol dm^{-3}) led to quenching of the 4-methoxyacetophenone triplet (E_T 71.5 kcal mol^{-1})[6] and generation of the DMNH triplet (E_T 60.3 kcal mol^{-1}).[7] This latter transient had a lifetime of 5.7 μs and an absorption spectrum similar to that observed by others[8] and to that of the longer-lived transient observed on pulsed irradiation of DMNH.

In the presence of **1a–d** a different transient absorption (λ_{max} 435–440 nm, lifetime in the μs range) was observed, essentially independent of the particular benzyl chloride in its shape and intensity. At λ > 400 nm the spectrum (Fig. 1) is very similar to that reported for the DMNH radical cation.[7] In the cases of **1a** and **1b** the transient absorption was not changed in air saturated solution, whereas some reduction in signal intensity took place with **1c** and **1d**.

Addition of N,N-dimethylaniline (DMA:[9] E_{ox} = 0.79 V; cf. DMNH:[5] E_{ox} = 1.10 V) to a degassed solution of DMNH–**1c** completely quenched the previously mentioned transient. A much longer-lived transient was formed (λ_{max} = 465 nm, $\tau \approx$ 1 ms), with an absorption spectrum (Fig. 2) very similar
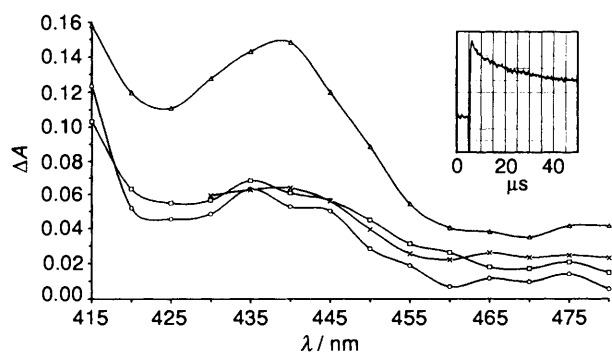
Fig. 1 Absorption observed 1 μs after pulsed laser excitation of DMNH (0.01 mol dm⁻³ in acetonitrile solution in the presence of benzyl chloride (2.0 mol dm⁻³), 4-chlorobenzyl chloride (0.4 mol dm⁻³), 4-cyanobenzyl chloride (0.4 mol dm⁻³), or 4-nitrobenzyl chloride (0.003 mol dm⁻³). Spectra are shown for degassed solutions, except for 4-nitrobenzyl chloride for which the spectrum in air-saturated solution is shown. In degassed solution this latter halide displays an additional maximum at 430 nm, close to that of the ground-state charge-transfer complex. *Inset:* transient decay of the absorption at 440 nm following pulsed excitation of a degassed acetonitrile solution of DMNH (0.01 mol dm⁻³) and benzyl chloride (0.4 mol dm⁻³). (□) Benzyl chloride; (○) 4-chlorobenzyl chloride; (△) 4-cyanobenzyl chloride; (×) 4-nitrobenzyl chloride.
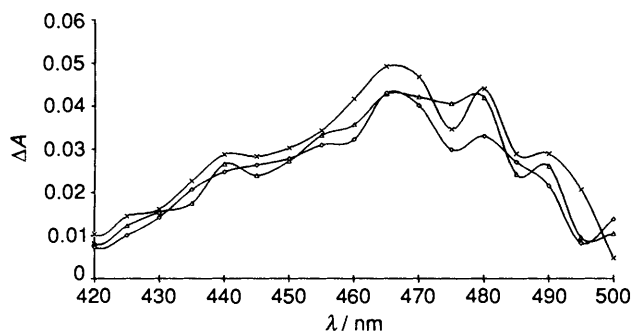
Fig. 2 Absorption spectra of the transients generated by pulsed laser excitation of DMNH (0.01 mol dm⁻³) in the presence of 4-cyanobenzyl chloride (0.1 mol dm⁻³) and *N,N*-dimethylaniline (0.005 mol dm⁻³), measured after 2 (×), 8 (△) and 20 μs (◇) delay intervals

to that previously reported for the *N,N*-dimethylaniline radical cation.[10] On the contrary, added 1,2,3-trimethoxybenzene (E_{ox} 1.42 V)[11] had no effect on the DMNH–1c system.

Discussion

The reported reactions involve the singlet excited state of DMNH. This is supported by the effective quenching of the DMNH fluorescence in the steady-state experiments, by the correspondence (Table 3) between the Stern–Volmer coefficients from independent fluorescence ($K_{fluorescence}$) and quantum yield ($K_{product}$) measurements, and finally by the negative evidence from the triplet sensitisation attempts (failure to sensitise photoproduct formation in the preparative experiments, coupled with the demonstration that triplet energy transfer from 4-methoxyacetophenone to DMNH occurred in the laser pulsed experiments).

That quenching of singlet excited DMNH by the benzyl chlorides involves a charge transfer interaction is suggested by the increasing efficiency of fluorescence quenching along the series **1a** to **1d**, and firmly established by detection of the DMNH radical cation by flash photolysis. Indeed, the transient absorption observed with λ_{max} at 435 nm is clearly distinguished from the triplet DMNH absorption, and selective quenching by *N,N*-dimethylaniline (but not by 1,2,3-trimeth-

oxybenzene) offers final evidence for its assignment as being due to the DMNH radical cation, in agreement with a previous proposal.[7]

Singlet excited DMNH has strong reducing properties, its oxidation potential being estimated as $E_{ox}(S_1) = E_{ox}(S_0) - E_{ex} = -2.41$ V *vs.* SCE, with E_{ex} being estimated from the fluorescence spectrum. Electron transfer to the benzyl chloride involves the π* orbital of such substrates, and the one-electron reduction potential can be approximated by that of the corresponding toluenes. In the case of parent **1a** this is *ca.* −3 V *vs.* SCE in acetonitrile,[12] and thus SET from DMNH¹* is endothermic. On the other hand, the nitro derivative **1d** is much easier to reduce ($E_{red} = 1.14$ V *vs.* SCE)[13] and electron transfer to the singlet is markedly exothermic ($\Delta G_{et} = -29$ kcal mol⁻¹); in this case ΔG_{et} is negative also for the DMNH triplet (−9 kcal mol⁻¹), but quenching of the singlet is too efficient to permit the operation of a triplet pathway.

Mere consideration of the driving force for SET is insufficient for complete discussion of the present reactions. Extensive studies of the electrochemical reductive cleavage of benzyl halides have shown that a stepwise mechanism involving the intermediacy of the radical anion is followed in the case of **1d** [eqn. (9)]. However, for less electron-withdrawing substituents

$$ArCH_2Cl + e^- \longrightarrow ArCH_2Cl^{\cdot-} \longrightarrow ArCH_2^{\cdot} + Cl^- \quad (9)$$

and for the parent chloride **1a**, the radical anion (which would be a strongly dissociative species, $E_d(\mathbf{1a}^{\cdot-}) = -50$ kcal mol⁻¹)[12] is not an intermediate, and the reaction occurs *via* a concerted electron-transfer/bond-breaking mechanism [eqn. (10)].

$$ArCH_2Cl + e^- \longrightarrow ArCH_2^{\cdot} + Cl^- \quad (10)$$

As a result, electrochemical reduction of **1a** and **1c** occurs at a less negative potential than would be expected for the pure electron transfer process, while the mechanism in eqn. (9) operates for **1d**. Dissociative electron transfer has been discussed in terms of a modified Marcus–Hush model,[13,14–18] and a quantitative agreement between experimental parameters and those calculated on this basis has been found both for electrochemical reduction and for homogeneous electron transfer from organic anions and from excited states.

The concerted/stepwise dichotomy is reflected in the present photochemical reactions in the dual mechanism proposed (Scheme 2), with in-cage or out-of-cage fragmentation. Thus,
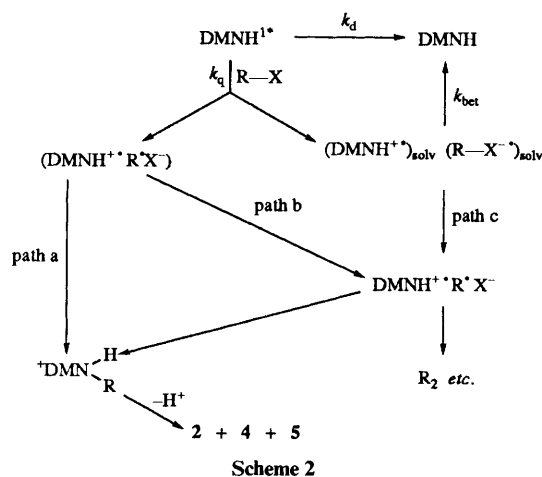
Scheme 2

quenching of DMNH¹* by **1a** occurs efficiently with a quenching constant (k_q) of 1.05×10^9 mol⁻¹ s⁻¹ ($k_q = K_{fluorescence}/\tau$; $\tau = 8.1 \times 10^{-9}$ s); *i.e.*, k_q is <10% of the rate of diffusion ($k_{diff} = 1.91 \times 10^{10}$ mol⁻¹ s⁻¹ in acetonitrile)[19]

and involves fragmentation of the C–Cl bond concerted with electron transfer. Diffusion out-of-cage produces free DMNH$^{\cdot+}$ (detected by flash photolysis) and free benzyl radicals (as shown by the formation of small amounts of bibenzyls). However this pathway (path b in Scheme 2) makes only a minor contribution to DMNH alkylation, which rather occurs by in-cage benzyl radical/radical cation coupling (path a). Accordingly, this reaction for **1a** is largely insensitive to radical traps.

The reaction with **1a** is also relatively insensitive to medium polarity ($\phi_{MeCN}/\phi_{PhH} \approx 3$) despite the fact that the overall ease of formation of separated ion pairs is much greater in a polar solvent than in a non-polar solvent, the Coulombic barrier to separation being greatly reduced by the operation of much more effective solvation in the more polar solvent. Though photoinduced electron transfer reactions have typically been carried out in polar solvents, non-polar solvents have been used in many cases for product-forming reactions. It has recently been pointed out[20] that the Coulombic interaction energy available for stabilisation of an ion pair is much larger in a solvent of low relative permittivity than in a solvent of high relative permittivity. When this difference is taken into account it follows that the overall energetics of electron transfer to form an initial in-cage ion pair may be largely independent of solvent polarity. The difference in product distribution (benzylation in position 2 vs. benzylation in the unsubstituted ring changing from 4:1 in acetonitrile to 16:1 in benzene) probably reflects a small effect of solvent polarity on the preferred conformation of the complex initially formed between DMNH^{1*} and **1a**.

With a more effective acceptor such as **1c**, quenching is more efficient ($k_q = 0.5\ k_{diff}$) and, by analogy with the electrochemical reduction process, the photoinduced process is believed to occur mainly by path a.

The mechanism changes for **1d**. The 4-nitrobenzyl radical anion is a relatively stabilised species [calculated $E_d(\mathbf{1d}^{\cdot-}) = -4\ \text{kcal mol}^{-1}$,[12] much less negative than in the case of **1a**, and cyclic voltammetry at high scan rates suggests that the radical anion is a true intermediate and undergoes slow cleavage with a rate constant of $4 \times 10^{-6}\ \text{s}^{-1}$ in DMF].[13] Thus, **1d**$^{\cdot-}$ is formed by photoinduced electron transfer from DMNH^{1*} and diffuses out-of-cage to yield the free solvated species prior to loss of chloride and formation of the 4-nitrobenzyl radical (path c). Furthermore, formation of the observed products implies re-encounter between DMNH$^{\cdot+}$ and 4-nitrobenzyl radicals. Although this leads to no difference in the regiochemistry of substitution when compared to the in-cage coupling processes for **1a**, **1b** and **1c** in acetonitrile, the radicals formed from **1d**$^{\cdot-}$ are now susceptible to trapping by dodecylthiol, alkylation of DMNH being quenched in the presence of this effective radical trap. This out-of-cage mechanism is also consistent with a decrease in quantum yield by two orders of magnitude for the change from acetonitrile to benzene as solvent, the energy barrier to formation of the free solvated radical anion being so substantially greater in the less polar solvent. The reaction is quite inefficient, apparently because the radical anion cleavage is, as seen above, relatively slow and competes poorly with back electron transfer between the solvated radical ions [$\gg 10^8\ \text{mol}^{-1}$ s^{-1}; notice that k_{bet} is expected to be larger for the more stable DMNH$^{\cdot+}$/**1d**$^{\cdot-}$ radical ion pair than with **1a**, since we are here in the inverted Marcus region].[21]

In conclusion, this work provides new examples of aromatic alkylations achieved through photoinduced electron transfer, and which occur via benzyl radical/arene radical cation combination instead of the known benzyl radical/arene radical anion interaction. Where SET is exothermic or moderately endothermic, the photocleavage of benzyl chlorides occurs in a way quite similar to that observed in electrochemistry, viz. SET followed by radical anion cleavage in the case of **1d** and concerted electron transfer/fragmentation in the other cases. A

characteristic of photoinduced reactions is that only the latter process is efficient, since it occurs directly upon encounter of ^{1}DMNH with the halides. On the contrary, when free solvated radical ions are formed under the photochemical conditions, the fact that they are formed in pairs makes very inefficient any process which is insufficiently fast to compete with back electron transfer.

Experimental

1,4-Dimethoxynaphthalene (DMNH)[22] and 4-cyanobenzyl chloride[23] were prepared and purified according to published procedures. The other materials and solvents were of commercial origin (Carlo Erba and Aldrich). ^{1}H NMR spectra were measured in CDCl$_3$ and are reported in ppm vs. SiMe$_4$ as the internal standard.

Preparative irradiations

A solution of DMNH (250 mg, 1.33 mmol) and benzyl chloride (**1a**, 500 mg, 3.95 mmol) in MeCN (130 cm^3) in a Pyrex vessel was flushed with argon for 15 min and then irradiated by means of six 20 W phosphor coated lamps (centre of emission, 350 nm) for 12 h. The solution was concentrated under reduced pressure, and the residue chromatographed on a silica gel column eluting with a benzene–cyclohexane 1:3 mixture. The major fractions obtained were unreacted DMNH (54 mg) and 2-benzyl-1,4-dimethoxynaphthalene (**2a**, 105 mg, 36% based on reacted DMNH), slightly brown oil (Found: C, 82.1; H, 6.7. Calc. for C$_{19}$H$_{18}$O$_2$: C, 81.98; H, 6.52%); δ_H 3.85 (s, 3 H), 3.88 (s, 3 H), 4.2 (s, 2 H), 5.55 (s, 1 H), 7.15–7.35 (m, 5 H), 7.4–7.6 and 7.95–8.3 (AA'BB' system, 4 H).

The other reactions were similarly carried out and the product yields obtained are detailed in Table 1. The following products were isolated and characterised.

2-(4-Chlorobenzyl)-1,4-dimethoxynaphthalene (2b). Light yellow crystals, mp 45–48 °C (cyclohexane) (Found: C, 73.2; H, 5.8. Calc. for C$_{19}$H$_{17}$ClO$_2$: C, 72.95; H, 5.48%); δ_H 3.83 (s, 3 H), 3.88 (s, 3 H), 4.13 (s, 2 H), 6.48 (s, 1 H), 7.15–7.3 (AA'BB' system, 4 H), 7.4–7.6 and 7.9–8.3 (AA'BB' system, 4 H).

2,6- (or 2,7-) bis(4-Chlorobenzyl)-1,4-dimethoxynaphthalene (3b). Colourless crystals, mp 138–140 °C (cyclohexane) (Found: C, 71.1; H, 5.0. Calc. for C$_{26}$H$_{22}$Cl$_2$O$_2$: C, 71.40; H, 5.07%); δ_H 3.83 (s, 3 H), 3.89 (s, 3 H), 4.05–4.2 (m, 4 H), 6.48 (s, 1 H), 7.1–7.4 (m, 8 H), 7.88 (d, 1 H, $J = 7$ Hz), 8.03 (s, 1 H) and 8.15 (d, 1 H, $J = 7$ Hz).

2-(4-Cyanobenzyl)-1,4-dimethoxynaphthalene (2c). Colourless crystals, mp 88 °C (cyclohexane) (Found: C, 79.2; H, 5.7; N, 4.6. Calc. for C$_{20}$H$_{17}$NO$_2$: C, 79.18; H, 5.65; N, 4.62%); δ_H 3.86 (s, 3 H), 3.96 (s, 3 H), 4.24 (s, 2 H), 6.50 (s, 1 H), 7.25–7.70 (m, 6 H) and 8.0–8.35 (m, 2 H).

Mixture of 2,5-, 2,6-, 2,7- and 2,8-bis(4-cyanobenzyl)-1,4-dimethoxynaphthalene (3c). Oil which solidifies on standing (Found: C, 80.8; H, 5.6; N, 6.3. Calc. for C$_{28}$H$_{22}$N$_2$O$_2$: C, 80.36; H, 5.30; N, 6.69%); δ_H 3.55–4.40 (eight s), 4.1–4.9 (eight s), 6.4–6.55 (four s), 7.05–7.8 (m) and 7.8–8.35 (m).

5-(4-Cyanobenzyl)-1,4-dimethoxynaphthalene (4c). Colourless crystals, mp 65–69 °C (cyclohexane) (Found: C, 78.9; H, 5.7; N, 4.3%); δ_H 3.58 (s, 3 H), 4.0 (s, 3 H), 4.73 (s, 2 H), 6.65 and 6.72 (AB system, 2 H), 7.1 and 7.45 (AA'BB' system, 4 H), 7.3 (d, 1 H, $J = 7$ Hz), 7.45 (dd, 1 H, $J = 7$ and 8 Hz) and 8.25 (d, 1 H, $J = 8$ Hz).

6-(4-Cyanobenzyl)-1,4-dimethoxynaphthalene (5c). Colourless crystals, mp 97–99 °C (cyclohexane) (Found: C, 79.3; H, 5.8; N, 4.5%); δ_H 3.95 (s, 3 H), 4.2 (s, 2 H), 6.68 and 6.72 (AB system, 2 H), 7.27 (d, 1 H, $J = 8$ Hz), 7.3 and 7.55 (AA'BB' system, 4 H), 8.02 (s, 1 H) and 8.15 (d, 1 H, $J = 8$ Hz).

2-(4-Nitrobenzyl)-1,4-dimethoxynaphthalene (2d). Orange crystals, mp 110–111 °C (benzene) (Found: C, 70.7; H, 5.2; N,

4.1. Calc. for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33%); δ_H 3.88 (s, 3 H), 3.93 (s, 3 H), 4.28 (s, 2 H), 6.50 (s, 1 H), 7.4 and 8.15 (AA'BB' system, 4 H), 7.5 and 8.2 (AA'BB' system, 4 H).

5-(4-Nitrobenzyl)-1,4-dimethoxynaphthalene (4d). Light yellow crystals, mp 123–124 °C (benzene) (Found: C, 70.7; H, 5.2; N, 4.1%); δ_H 3.6 (s, 3 H), 4.0 (s, 3 H), 4.68 (s, 2 H), 6.7 and 6.82 (AB system, 2 H), 7.35 and 8.1 (AA'BB' system, 4 H), 7.1–7.65 (m, 2 H) and 8.25–8.45 (m, 1 H).

6-(4-Nitrobenzyl)-1,4-dimethoxynaphthalene (5d). Light yellow crystals, mp 121–122 °C (benzene) (Found: C, 70.1; H, 5.0; N, 4.2%); δ_H 3.9 (s, 3 H), 4.0 (s, 3 H), 4.28 (s, 2 H), 6.68 and 6.75 (AB system, 2 H), 7.3 (d, 1 H, J = 8 Hz), 8.15 (d, 1 H, J = 8 Hz), 7.35 and 8.15 (AA'BB' system, 4 H), 8.03 (s, 1 H).

Steady-state measurements

Aliquots (3 cm³) of 1 × 10^{-3} mol dm⁻³ solutions of DMNH containing the appropriate amount of the donors (1) in Pyrex tubes were degassed by flushing with argon, septum-capped and irradiated in a merry-go-round system by means of six phosphor-coated lamps as above. The irradiation was discontinued at a DMNH conversion < 20%. DMNH conversion and product formation were determined by GLC with dodecane as an internal standard. Under these conditions the only significant products were the monobenzylated derivatives **2**, **3** and **4** (confirmed in each case by GC–MS). The light flux was measured by benzophenone–benzhydrol actinometry.

Fluorescence intensities were measured on an Aminco-Bowman SPF instrument on 1 × 10^{-4} mol dm⁻³ DMNH solutions in spectrophotometric quartz cells after degassing by argon flushing.

Flash photolysis

The laser pulse photolysis apparatus used in these experiments and operated at 355 nm has recently been described.[24] 1,4-Dimethoxynaphthalene (DMNH) was used at a concentration of 10^{-2} mol dm⁻³ and photophysical measurements were carried out at room temperature in degassed solutions of acetonitrile (hplc grade, dried over molecular sieves). Degassing was achieved by bubbling a stream of acetonitrile-saturated argon through the solution for 20 min. Substrate concentrations were such that DMNH was essentially the only species absorbing at the excitation wavelength. The UV–VIS spectrum of each sample solution was monitored throughout the experiments to ensure sample stability.

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