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DICYANOBENZENE SENSITIZED CARBON-CARBON BOND CLEAVAGE IN METHOXYBICUMENES. PRODUCTS AND MECHANISTIC STUDIES.

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Radical cations of p-methoxy-p-X-bicumenes generated by ET to excited-state dicyanobenzene undergo rapid irreversible C-C bond scission giving cumyl cations and radicals. The photoefficiency of the process ($\Phi = 0.13$ *for* $X = MeO$, $\Phi < 0.005$ *for* $X = CN$) *and the fate of the radicals produced depends strongly on substitution.*

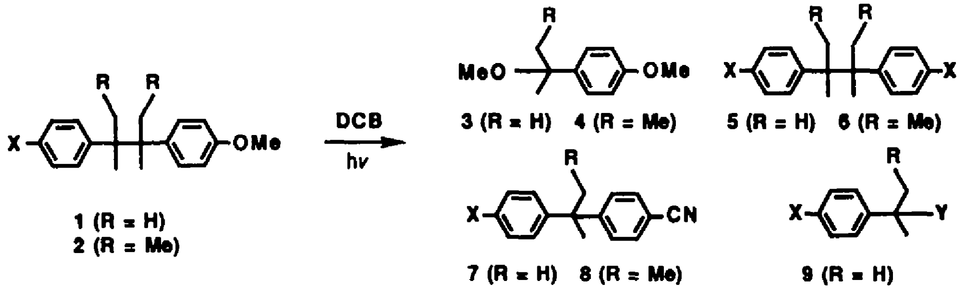
Cleavage of carbon-carbon bonds in radical cations results in the formation of carbocations and carbon centered-radicals as primary products[1-3]. The radical cations may be conveniently generated by photoinduced electron transfer[1,4]. Photoefficiency of such processes and reactivity patterns of the intermediates generated are important factors determining the utility of radical cation fragmentations in mechanistic and synthetic studies. For example, the fate of the radicals and cations is often decided by electron-transfer, proton transfer or another reaction between the primary products and the counterion[1]. These secondary reactions may consume the sensitizer, affecting the catalytic nature of the photoprocess.

Our interest in mesolytic[5] C-C bond scission[3,6] lead us to explore some of these aspects in the 1,4-dicyanobenzene (DCB) sensitized fragmentation of 4-methoxybicumenes (**1** and **2**, Table 1 and Scheme 1). The electron transfer between DCB* or other excited-state cyanoaromatics and electron rich compounds, such as anisole derivatives, is well documented[1,4,7]. Indeed, the fluorescence of DCB is quenched by **1a**, **1d** or **10** (a model compound for **1c**)[8] with similar rate constants ($2.0 \pm 0.5 \cdot 10^{10}$ M^{-1} s^{-1} in acetonitrile). The magnitude of the rate constants and the fact that **1d** is as efficient[8] as **1c** or **2c** in quenching DCB* indicate that the process is diffusion limited. Such a rapid rate would be expected for exergonic (by 23 kcal/mole) electron-transfer (ET) quenching of DCB*, as predicted by the Weller equation[9].

The products formed in these reactions are consistent with the transient formation of radical cations, $1^{\cdot+}$ or $2^{\cdot+}$, which undergo rapid scission of the central C-C bond (Scheme 1). The cleavage leads to the formation of p-methoxycumyl cation and X-substituted cumyl radical[10]. The cations are trapped by methanol, yielding methyl

Table 1.

Products of Photoinduced C-C Bond Cleavage in the 4-Methoxybicumenes/Dicyanobenzene System[a]

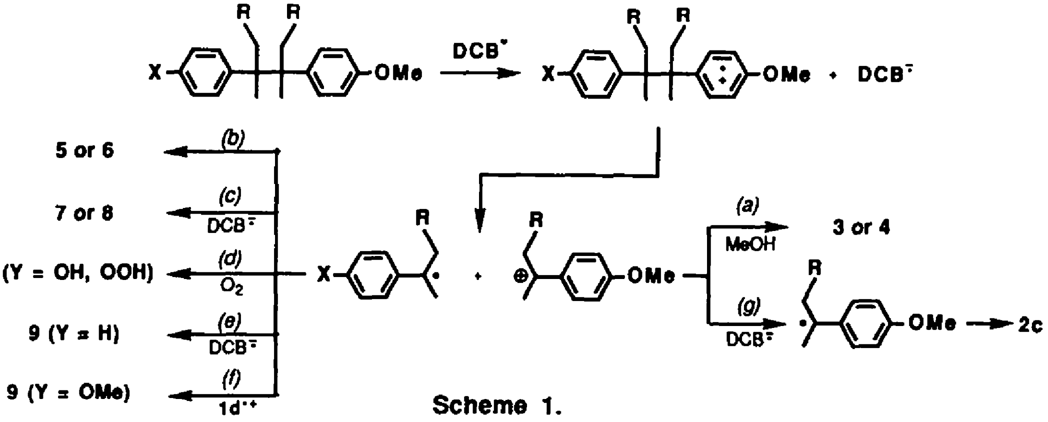


Compound	X	Relative[b] Efficiency	3 or 4	5 or 6	Yield (%)[c] 7 or 8	9 (Y)
1a	H	1.0	100	40	44	–
1a[d]	H	—	100	e	–	78 (OH) 20 (OOH)
1b	Me	3.2	100	72	36	–
1c	MeO	24.3	79	–	16	–
1d	CN	<0.05	100	36	–	36 (H) 14 (OMe)
2a[f]	H	3.8	100	44	40	–
2c[g]	MeO	22.4	86	–	14	–

(a) At 22°C under argon atmosphere, unless indicated otherwise. (b) Efficiency of the consumption of 1 or 2 $[\ln(X/X_0)/\ln(1a/1a_0)]$ measured in a competition experiment with two bicumenes in a common reaction mixture. (c) Measured by NMR or GC with an internal standard. The yields are based on consumed bicumenes at *ca.* 50-60% conversion. (d) Reaction run under oxygen. DCB consumption was less than 5%. (e) Trace. (f) Mixture (1 : 1) of *erythro* and *threo* isomers. (g) Mixture (11 : 1) of *meso* and *dl* isomers.

ethers 3 or 4 in excellent yields (Scheme 1, path *a*). The fate of the radicals depends on the substitution. All cumyl radicals couple to form symmetrical bicumenes 5 or 6 (path *b*). In the case of p-methoxy substituted radicals this reaction regenerates the starting bicumenes (1c and 2c), resulting in underestimation of the cleavage efficiency.

This process is evident in the case of **2c**. The isomerization of *meso*-**2c** to the *dl*-isomer is observed during the photoinduced fragmentation of this compound. Thus, the mixture initially containing *meso* and *dl* isomers in 11.8 : 1 ratio is converted to mixtures containing *meso*/*dl* isomers in *ca.* 5.7 : 1 and 3.9 : 1 ratios at 11% and 32% conversion of **2c**, respectively. This observation is not quite consistent with stereo-random coupling of p-methoxy-β-methylcumyl radicals. After correction for formation of **8c**, the random coupling requires the *meso*/*dl* ratio of *ca.* 7.7 and 4.4 at the specified degrees of conversion. A small fraction of the observed isomerization is, therefore, due to some other process. This is especially evident in the reaction of **2c** run under oxygen atmosphere. Oxygen is able to efficiently intercept the cumyl radicals as shown in experiments with **1a** (see below). Under these conditions the *meso*/*dl* ratio should remain unchanged; however, at 22% conversion the measured ratio was only 7.8. The observed small excess of isomerization over that expected from random coupling of radicals and isomerization of **2** under O_2 is apparently *not due* to the reversibility of C-C bond scission in radical cations. The irreversibility of the bond scission is convincingly demonstrated in experiments performed with *erythro*-**2a**. At 50% conversion the recovered **2a** shows no isomerization (<1%).



Scheme 1.

The reduction potentials of the cumyl radicals[11] with electron donating groups are higher than -1.7 V. Their reduction by $DCB^{\bullet-}$ is highly unlikely. Instead, the reaction between these two reactive species leads to unsymmetrical coupling products **7** or **8** (path *c*). This is in contrast to the results reported[1a-c] by Arnold *et al.*, who in similar studies involving diphenylmethyl radicals (E_{red} = -1.14 V)[11] detected only the products of radical reduction. In agreement with these observations, in case of **1** or **2** the reaction is no longer catalytic in DCB. The sensitizer is consumed during the reaction with a rate slightly less than half of that for disappearance of **1** or **2**. Thus, the reduction potential of the radical produced in the cleavage step sets a limit for the catalytic process. The consumption of DCB can, however, be minimized if the reaction is run under oxygen. For example, in case of **1a** less than 3% of DCB is consumed but the photoefficiency of the reaction is diminished *ca.* threefold. In this case (path *d*), the cumyl radical yields peroxide **9a** (Y=OOH), alcohol **9a** (Y=OH) and trace amounts of **5a**, but no **7a** is detected.

The products observed for **1d** are more complex. The reduction potential[11] for the p-cyanocumyl radicals is less than - 1.3 V. Under our conditions, $DCB^{\bullet-}$ is able to reduce a fraction of these radicals. Thus, in addition to the coupling product **5d**, the corresponding cumene **9d** (Y=H) is detected (path *e*). Also, small amounts of ether **9d** (Y=MeO) are observed. We attribute its formation to one-electron oxidation of the p-cyanocumyl radical by $\mathbf{1d}^{\bullet+}$ followed by reaction of the cation produced with MeOH (path *f*). Apparently, the longer lifetime of $\mathbf{1}^{\bullet+}$ – as compared to other radical cations (see below) – significantly increases its probability of collision with the radical.

The results of product studies provide a unifying mechanism for the follow up reactions of fragments resulting from the C-C bond cleavage. The p-methoxycumyl cations are rapidly trapped by methanol. It is interesting, however, that the exergonic ET between the p-methoxycumyl cation (E_{red} = -0.14 V)[11] and $DCB^{\bullet-}$ (E_{ox} = -1.60 V)[4b] is not observed in the majority of cases. The p-methoxycumyl radicals produced by this reaction should lead to the generation of bismethoxybicumene (**1c** or **2c**) and to regeneration of the starting unsymmetrical bicumene. With the exception of **2c** (see below) these processes are not detected. Although, it might be argued that the **1c** (or **2c**) formed is consumed faster than it is produced, the relative efficiencies of cleavage exclude such a possibility, at least in the case of **1b** and **2a**. This argument is significantly strengthened by the lack of isomerization of **2a** during the reaction. The excess isomerization observed in the case of **2c** (see above) can, however, be accounted for by such a reduction process. The important difference between **2c** and other bicumenes (**1a,b,d** or **2a**) is the rate of fragmentation of their radical cations (see below). Apparently, the fragmentation of $\mathbf{2c}^{\bullet+}$ takes place faster than radical ion separation, producing the cumyl cation in the vicinity of $DCB^{\bullet-}$. The reduction of p-methoxy-β-methylcumyl cations by $DCB^{\bullet-}$ produces the corresponding radical (path *g*) which can couple with the radical produced directly by the radical cation cleavage, in a process equivalent to in-cage-recombination. This reaction results in isomerization of **2c**, even in the presence of oxygen. The slower fragmenting radical cations of **1a,b,d** and **2a** have a chance to diffusionally separate from $DCB^{\bullet-}$ before the C-C scission takes place. In such a situation, methanol trapping of the formed cations is the dominant process. This trapping prevents the reduction of cations, and possibly contributes to the cleavage irreversibility.

The fate of the radicals is determined mostly by their redox potentials. In absence of oxygen, the radicals couple to form symmetrical dimers. They also react with $DCB^{\bullet-}$. We propose that for electron rich radicals (high reduction potential) this reaction involves radical/radical anion coupling followed by loss of CN^- (path *c*). The rate of this coupling reaction should depend on the electronic demand of the substituted cumyl radical. Indeed, the most nucleophilic p-methoxycumyl radical adds more slowly than p-methylcumyl radical, which in turn is slower than the less nucleophilic cumyl radical. This trend in reactivity is evident from the relative yields of **7** (or **8**) observed in these reactions (Table 1). However, if the electron withdrawing group is attached to the ring, the preferred reaction is exergonic electron transfer between $DCB^{\bullet-}$ and the radical (path *e*), rather than the coupling reaction. This is the case for diphenylmethyl radical[1a-c], p-cyanocumyl radical.

An alternative way to produce **7** or **8** may involve loss of the CN^- from the $DCB^{\bullet-}$ prior to coupling. We were unable, however, to detect any 4,4'-dicyanobiphenyl or cyanobenzene in the reaction mixture. These products would be expected if p-cyanophenyl radicals were produced in the reaction mixture. Also the effect of substituent on the yield of **7** or **8** would be difficult to explain using a radical/radical coupling mechanism. The radical/radical anion mechanism is, therefore, the preferred alternative.

In the presence of oxygen, the radicals are trapped by O_2 giving alcohols and hydroperoxides (path *c*). Under these conditions, $DCB^{\bullet-}$ is also intercepted, apparently *via* exergonic electron transfer resulting in production of superoxide ion, which probably reacts rapidly with the solvent. The oxygen serves as a secondary electron acceptor, and although the absolute efficiency of the reaction is diminished under these conditions, the reaction is catalytic in DCB.

The efficiency of the cleavage is mostly determined by the relative rates of radical cation fragmentation and back-electron transfer (BET) between the radical cation and $DCB^{\bullet-}$. The radical cations are electronically very similar. The remote substituent is not expected to strongly perturb the p-methoxyphenyl moiety common to all radical ions. Thus, the differences in photoefficiency reflect mainly the differences in rates of the C-C bond cleavage. The relative efficiencies indicate that electron donating groups (X = MeO, Me) increase the rate of fragmentation while electron withdrawing substituents (X = CN) retard it significantly. This trend implies that considerable positive charge is transferred across the scissile bond in the transition state (TS) for this reaction[12]. Steric crowding[13] accelerates the fragmentation in the X = H series (**1a** *vs*. **2a**), but has no effect in bismethoxybicumenes (**1c** *vs.* **2c**). This observation is consistent with an earlier TS in compounds with electron-donating groups (X = MeO) than with hydrogen (X = H), since an earlier TS leads to a smaller strain release.

The reaction is efficient on an absolute scale. The quantum yield (Φ) of disappearance of **2c** measured at 305 nm is *ca.* 0.13. The rate of C-C bond cleavage in the radical cations is apparently[10] faster than 10^9 s^{-1}. Assuming that the measured quantum yield ($k_f/k_{BET} = \Phi/(1 - \Phi)$) reflects only the relative rates of BET (k_{BET}) and C-C bond scission (k_f), the estimated rate constant (k_{BET}) for ET between $DCB^{\bullet -}$ and $\mathbf{1}^{\bullet +}$ (or $\mathbf{2}^{\bullet +}$) is on the order of 10^9 - 10^{10} s^{-1}. This estimate is in good agreement with the data of Farid and Gould[14] from which it can be estimated that BET with a driving force[9] of *ca.* 3.2 eV (inverted region) should have a rate constant in that range.

EXPERIMENTAL SECTION.

General. ^1H NMR spectra were recorded on either a Bruker WM360 or WM200, and are reported in ppm in reference to TMS. Absorption measurements were made with a HP 8450 UV/vis spectrophotometer. Gas chromatography was performed on a Varian 3700 with FI detector using a 50 cm by 1/8'' column packed with 5% OV101 on 80\100 Supelcoport. Hexadecane or octadecane were used as internal standards. The temperature programming consisted of a one minute isothermal (160°C) period followed by heating at 15°C/min to 250°C. The flow of helium was set at 30 mL/min. Error in all GC measurements was determined through reproducibility (four injections per sample). Mass spectra were obtained on a Kratos MS 9\50 double focusing spectrometer in Electron Impact (EI) mode. Peaks reported were either considered structurally significant or had an intensity greater than 10% of the base peak. IR spectra were recorded on a Perkin-Elmer 281B spectrophotometer. Films were cast from chloroform onto NaCl plates.

Syntheses of methoxybicumenes **1** - **2** has been described previously[12]. Other materials were purchased from Aldrich and used as received unless indicated otherwise. Solvents used for all reactions were spectrophotometric or HPLC grade. THF was distilled from potassium/benzophenone under argon. Preparative flash chromatography was carried out using Merck silica gel 60 (230-400 mesh). Preparative and analytical TLC was run on Merck precoated plates with layer thicknesses of 0.5 and 0.25 mm, respectively. Methylene chloride-hexane mixtures (listed as volume by volume ratios, *r*) were used as eluents in analytical and preparative chromatography.

Identification and quantification of products. Bicumene (8 - 12 mg or 50 - 100 mg) and DCB (1 - 2 molar equivalents) were weighed into a 5 mm NMR-tube or a larger test tube and the tube was sealed with a septum. The tube was purged with argon and the contents were dissolved in a deoxygenated mixture of THF/MeOH (4:1 v/v) to give 30 - 60 mM solution of **1** or **2**. Deuterated solvents, with methyl *t*-butyl ether (10 µL) as an internal standard, were used in NMR experiments. A carefully integrated ^{1}H NMR spectrum was then recorded, and/or a GC analysis was performed. The sample was irradiated at 25°C with a 400 W Hanovia medium-pressure Hg-vapor lamp through a pyrex filter for 2 - 24 h. Under these conditions light is absorbed by DCB. If DCB is absent, irradiation of the solution containing **1a** or **2c** does not lead to any measurable reaction. Direct irradiation of **1** or **2** ($\lambda < 300$ nm) gives different products. After irradiation, the mixtures were quantified by NMR, GC or GC/MS. The products were identified by comparison with authentic samples within the mixtures and/or after separation.

Authentic samples of methyl ethers **3**, **4** and **9d** (X = MeO), and bicumenes **5** and **6** were obtained as described previously[12]. Cumyl alcohol and peroxide (**9a** X = OH, X = OOH) are commercially available. Independent samples of **7a,c** were prepared by a Friedel-Crafts reaction of the 4-cyanocumyl bromide with benzene and anisole, respectively. Remaining adducts (**7b** and **2a,c**) were identified from their spectral data.

2-(4'-Cyanophenyl)-2-phenylpropane (**7a**): Rf = 0.27 (*r* = 0.43), retention time 1.97 min. ^{1}H NMR ($CDCl_3$): 1.69 (s, 6 H), 7.17 -7.23 (m, 2 H), 7.25 - 7.31 (m, 3 H), 7.33 (d, J = 9 Hz, 2 H), 7.55 (d, J = 9 Hz, 2 H). IR (film): 2940, 2180, 1600, 1480, 1430, 1390, 1350, 1050, 1000, 810, 740, 680 cm^{-1}. MS (relative intensity): 221 (25), 206 (100), 190 (8), 128 (7).

2-(4'-Cyanophenyl)-2-(4''-methylphenyl)propane (**7b**): ^{1}H NMR ($CDCl_3$): 1.66 (s, 6 H), 2.31 (s, 3 H), 7.07 (m, 4 H), 7.31 (d, J = 8 Hz, 2 H), 7.54 (d, J = 8 Hz, 2 H). IR (film): 2940, 2180, 1720, 1600, 1490, 1450, 1270, 1060, 1000, 820, 790 cm^{-1}.

2-(4'-Cyanophenyl)-2-(4''-methoxyphenyl)propane (**7c**): Retention time 3.43. ^{1}H NMR ($CDCl_3$): 1.68 (s, 6 H), 3.80 (s, 3 H), 6.82 (d, J = 9 Hz, 2 H), 7.10 (d, J = 9 Hz, 2 H), 7.33 (d, J = 9 Hz, 2 H), 7.55 (d, J = 9 Hz, 2 H). IR (film): 2950, 2180, 1600, 1500, 1450, 1280, 1240, 1170, 1010, 810 cm^{-1}.

2-(4'-Cyanophenyl)-2-phenylbutane (**8a**): Rf = 0.27 (*r* = 0.43), retention time 2.17 min. ^{1}H NMR ($CDCl_3$): 0.73 (t, J = 7 Hz, 3 H), 1.61 (s, 6 H), 2.14 (q, J = 7 Hz, 2 H), 7.10 - 7.30 (m, 5 H), 7.30 (d, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H). IR (film): 2950, 2180, 1730, 1600, 1490, 1460, 1430, 1370, 1050, 1000, 810, 740, 680 cm^{-1}.

2-(4'-Cyanophenyl)-2-(4''-methoxyphenyl)butane (**8b**): Retention time 3.59. ^{1}H NMR ($CDCl_3$): 0.73 (t, J = 7 Hz, 3 H), 1.61 (s, 6 H), 2.1 (q, J = 7 Hz, 2H), 3.80 (s, 3 H), 6.82 (d, J = 9 Hz, 2 H), 7.08 (d, J = 9 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 7.56 (d, J = 8 Hz, 2 H). IR (film): 2940, 2180, 1720, 1600, 1500, 1450, 1230, 1160, 1010, 810 cm^{-1}.

Testing of cleavage reversibility. The reversibilty of C-C bond scission in radical cations was tested using sterochemically enriched *meso*-**2c** (*meso*/*dl* = 11 :1) and *erythro*-**2a** (no detectable *threo*-isomer). The bicumenes (*ca.* 100 mg) and DCB were irradiated as described in the product study section. The degree of conversion was tested using GC analysis *vs.* a standard, non-irradiated sample (GC conditions do not lead to isomer separation). After the desired conversion was reached, the unreacted bicumenes were isolated by column chromatography (no separation of isomers) and analyzed by NMR. The methylene protons of the two diastereomeric forms of **2a,c** are easily distinguishable[12]. For comparison purposes, equimolar mixtures of both isomers of **2a,c** were available from radical coupling[12]. In a test performed with **2c**, where the sample without DCB was irradiated for 4 or 8 hours, no consumption of **2c** was observed by GC and the starting material recovered after column chromatography showed no change in the *meso/dl* ratio.

Quenching studies. DCB (200 - 250 mg) was weighed into a 50 mL volumetric flask and dissolved in spectrophotometric grade CH_3CN to yield 31 - 39 mM solution. This solution (3 mL) was transferred to a 1 x 1 cm fluorimetric cuvette. The fluorescence spectrum was recorded using a Perkin-Elmer MPF-44A instrument (excitation wavelength 301 ± 10 nm, λ_{max} = 315 nm; 310 nm cut-off filter was used with the detector). The solution of the appropriate bicumene (0.13 - 0.15 M) was then added in 10 μL portions and the intensity of the fluorescence at 315 nm was measured. At least eight data points per mesurement were obtained. The usual Stern-Volmer analysis gave $k_q\tau$ values. The lifetime of DCB* in CH_3CN is 9.7 ns[1c]. Thus, the quenching rate constants could be evaluated. The data obtained were as follows: **1a** $1.49 \cdot 10^{10}$ s^{-1}; **1b** $2.62 \cdot 10^{10}$ s^{-1}; **1d** $2.42 \cdot 10^{10}$ s^{-1}; **1c** was not sufficiently soluble in CH_3CN. Data obtained with 3,4-diethyl-3,4-bis-(4'-methoxyphenyl)hexane (**10**) gave value of $1.39 \cdot 10^{10}$ s^{-1}.

Competition studies. The relative efficiencies of bicumene consumption were measured at 25°C. The samples were irradiated with a 450 W Hanovia lamp fitted with pyrex filter. The bicumenes (5 - 10 mg each) and DCB (10 -15 mg) were dissolved in 0.5 mL of THF/MeOH (4:1 v/v) in 5 mm NMR tubes and sealed with septa. The appropriate internal standard was added, and the samples were deoxygenated by bubbling argon. A 0.1 mL sample was withdrawn to serve as a reference. The remaining solution was irradiated for 1 - 6 hours. The samples were analyzed by GC by multiple injection of the reference sample and the irradiated sample. The relative efficiency of the consumption of **1** or **2** was defined as $\ln(X/X_0)/\ln(\mathbf{1a}/\mathbf{1a}_0)$, where X equals concentration of the tested bicumene.

Quantum yield measurements. DCB (188.7 mg) was weighed into a 10 mL volumetric flask and dissolved in THF/MeOH (4:1 v/v). The bicumene (**2c**, 8.0 mg) and octadecane (7.6 mg) were weighed into a 2 mL volumetric flask and dissolved in the DCB solution. The ratio of the fluorescence intensity of the DCB solution and the DCB/**2c** solution was determined to be 1.71 (λ_{exc} = 307 ± 10 nm, λ_{max} = 350 nm). The DCB/**2c** solution (0.2 mL) was transferred to a small volume 1-cm-path cuvette and irradiated with a focused, calibrated (iron oxalate actinometry[15]; $1.84 \cdot 10^{-6}$ einsteins/hour) beam of light from a 150 W Xe/Hg arc lamp fitted with monochromator (Spectral Energy GM100) set to 304 ± 8.5 nm. The degree of conversion of **2c** was measured using GC by multiple alternating injections of the reference sample (no irradiation) and the irradiated sample. The measurement was repeated twice giving $\Phi = 0.13 \pm 0.02$, after correction for incomplete quenching and regeneration of the starting material due to radical coupling (see text).

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(8) For solubility reasons **10** (see experimental part) was used as a model for **1c** or **2c**. These compounds have two quenching "sites" (methoxyphenyl moieties) as compared to **1d** which has only one.

(9) The reduction potential of DCB is -1.60 V (ref 4b); the oxidation potential of p-methylanisole, a model for **1** and **2**, is 1.67 V (Sankararaman, S.; Haney, W. A. Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824, all potentials *vs*. SCE). Energy of the singlet excited state of DCB is 4.27 eV (ref 4b). The Weller equation predicts that electron transfer between **1** or **2** and DCB* is exergonic by *ca.* 1 eV.

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