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Singlet-Triplet Mechanistic Duality in the Photosubstitution of Nitrophenyl Ethers with Ethyl Glycinate. The Role of Single Electron Transfer.

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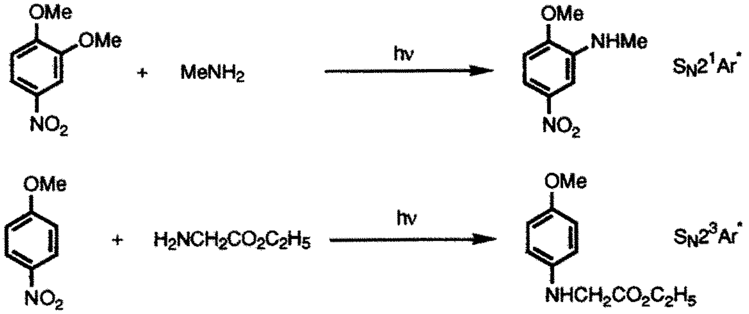
Abstract: Mechanistic studies show that 4-nitroveratrole and 4,5-dinitroveratrole undergo nucleophilic aromatic photosubstitution with ethyl glycinate through an S_N2Ar^* route. However, in the first case the photoreaction takes place through a singlet excited state whereas for 4,5-dinitroanisole a triplet excited state is involved. Electrochemical data for the present photoreactions reagents and for 4-nitroanisole, involved in a related photoreaction previously described by us, are reported. A mechanistic scheme, governed by a direct collapse - electron transfer competition in the singlet excited state stage, is proposed for the nucleophilic aromatic photosubstitution reactions of nitrophenyl ethers with amine nucleophiles.

INTRODUCTION

Photoinduced electron transfer plays a central role in the mechanistic interpretation of organic photoreactivity.[1] Nucleophilic aromatic photosubstitution is one of the photoreactions more intensively studied since its discovery in 1956.[2] In spite of this effort, mechanistic studies had been for years restricted almost to photohydrolysis reactions.[3] Van Riel et al.[4] pointed out the existence of three kinds of pathways leading to nucleophilic aromatic photosubstitutions: 1) direct displacement (S_N2Ar^*); 2) electron transfer from the "nucleophile" to the aromatic substrate; and 3) electron transfer from the aromatic compound to an acceptor followed by attack of the nucleophile on the aromatic radical-cation. In recent years several research groups have directed their attention to these reactions.[3-10] In the course of our investigation of the photosubstitution of 4-nitroveratrole and 4-nitroanisole with amines, we found[11] that the regioselectivity of these reactions depends on the ionization potential of the nucleophile. A mechanistic borderline between S_N2Ar^* reactions (for high ionization potential amines) and electron transfer from the amine to the substrate triplet excited state (for low ionization potential amines) was proposed on the basis of continuous irradiation[12] and laser flash photolysis[13] experiments. Some other related regioselectivity changes have been reported for photo-Smiles reactions[5] and for the photosubstitutions of 1-methoxy-1-nitronaphthalene with nucleophiles.[7]

The S_N2Ar^* type reactions of nitrophenyl ethers with primary amines previously studied by us[12] (Scheme 1) showed an interesting dichotomy. Photoreactions of 4-nitroveratrole occured from a singlet excited state[12a] whereas the photoreactions of 4-nitroanisole happened through a triplet excited state.[12c] However, different nucleophiles were involved (methylamine and n-hexylamine with 4-nitroveratrole, and ethyl glycinate with 4-nitroanisole), hampering any general rationalization.

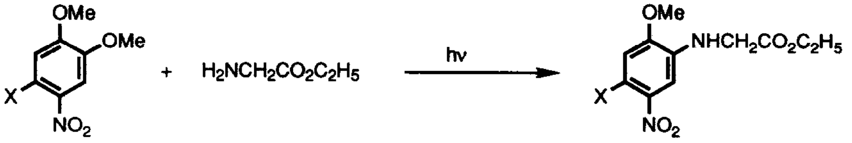


Scheme 1

All this considered, we wish to report here a mechanistic study (continuous irradiation) on the photoreactions of two nitrophenyl ethers with different electronic properties (4-nitroveratrole and 4,5-dinitroveratrole) with ethyl glycinate (high ionization potential amine, to ensure a S_N2Ar^* mechanism) as unique nucleophile (Scheme 2). These results are discussed in conexion with the corresponding one for 4-nitroanisole, already published by us[12c] (Scheme 1), and all of them complemented with electrochemical measurements. Several well established approaches can be found in the literature to analyze and discuss photochemical mechanistic data with the help of electrochemical measurements.[14] In the present work the use of the Weller ion-pair formation model[15] leads to a general reactivity scheme for nitrophenyl ethers photosubstitution reactions with amine nucleophiles.

RESULTS

The preparative photoreaction between 4-nitroveratrole and excess ethyl glycinate in MeOH-water (20:80 v.v) (90m irradiation with a 125W medium-pressure Hg lamp and pyrex filter) gave N-ethoxycarbonylmethyl-2-methoxy-5-nitroaniline,[16] **1**, in 48% yield based on unrecovered starting material. The ethyl glycinate was added as hydrochloride and liberated *in situ* using the stoichiometric amount of sodium hydroxide. The preparative photoreaction between 4,5-dinitroveratrole and excess ethyl glycinate hydrochloride was carried out in acetonitrile-water (38:62 v.v) at pH 8 (3h irradiation with a 400W medium-pressure Hg lamp and pyrex filter) affording 73% yield of N-ethoxycarbonylmethyl-2-methoxy-4,5-dinitroaniline,[18] **2**, based on consumed starting material (Scheme 2).



X=H **1**

X=NO$_2$ **2**

Scheme 2

Quantum yield measurements. Overall quantum yields for the production of **1**, and **2** were measured at different nucleophile concentrations (Tables I, and II). Quantum yields increase by increasing the nucleophile concentration in both cases. The multiplicity of the reactive excited states was investigated using potassium sorbate as selective triplet quencher[12] (Table III). There is a significant quenching effect due to potassium sorbate in the 4,5-dinitroveratrole photoreaction, but *no quenching effect* is observed for 4-nitroveratrole. Also, no photosensitization by benzophenone (able of photosensitize other 4-nitroveratrole photosubstitutions[12a]) could be observed. Addition of m-dinitrobenzene or methyl viologen, well known quenchers of processes that happen through single electron transfer from the nucleophile to the nitrophenyl ether triplet excited state[12a,13], has no effect in any case. This result confirm the operativity of S_N2Ar^* type mechanisms in both cases.

Table I. Overall Quantum Yield of Production of 1 in the Photoreaction of 4-Nitroveratrole (1 x 10^{-3} M) with Ethyl Glycinate (Nu) in Methanol/Water (20:80 v/v) at Different Nucleophile Concentrations

$[Nu]^a$	0.064	0.104	0.204	0.310	0.400	0.510	0.600	0.697
$\Phi^{366}\times10^3$	6.7	9.5	16.2	23.1	24.4	30.0	34.1	36.2

[a] Amine real concentrations once the amount of ammonium cation produced by hydrolysis is substracted.

Table II. Overall Quantum Yield of Production of 2 in the Photoreaction of 4,5-Dinitroveratrole (1.7×10^{-3} M) with Ethyl Glycinate (Nu) in Methanol/Water (20:80 v/v) at Different Nucleophile Concentrations

$[Nu]^a$	0.0021	0.0176	0.0315	0.0527	0.0702	0.1070	0.1210
$\Phi^{366} \times 10^3$	11.0	57.0	68.5	74.3	84.1	93.2	101.4

[a] Amine real concentrations once the amount of ammonium cation produced by hydrolysis is substracted.

Table III. Overall Quantum Yield of Production of 2 in the Photoreaction of 4,5-Dinitroveratrole (1.7×10^{-3} M) with Ethyl Glycinate (0.0702 M) in Methanol/Water (20:80 v/v) in the Presence of Different Concentrations of Potassium Sorbate Q

$[Q] \times 10^3$	0	3.4	7.9	10.0	18.1	21.8
$\Phi^{366} \times 10^3$	84.1	42.1	28.6	27.8	18.2	14.2

Electrochemical measurements. In the Table IV the ground state oxidation potentials of the donor (ethyl glycinate) and the reduction potential of the acceptors (4-nitroveratrole and 4,5-dinitroveratrole) involved in our photoreactions are reported. We have extended the measurements to 4-nitroanisole since its photoreaction with ethyl glycinate has been previously reported by us[12c] and it will be discussed toghether with the ones first described in the present work.

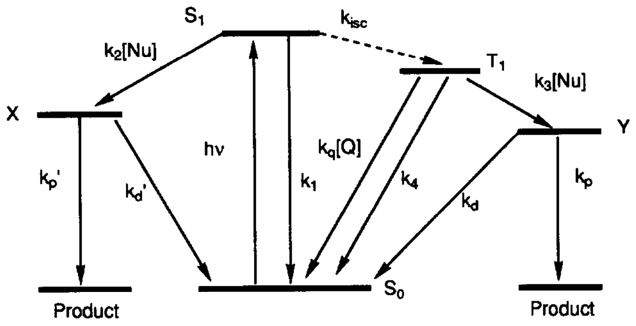
Table IV. Reduction potentials for several nitrophenyl ethers and oxidation potential for ethyl glycinate.

Substrate[a]	NVT	4-NA	4,5-DNVT	$GlyNH_2$
E_p/V(vs SCE)	-1.25	-1.32	-0.92	+1.60

[a] NVT = 4-nitroveratrole, 4-NA = 4-nitroanisole, 4,5-DNVT = 4,5-dinitroveratrole, $GlyNH_2$ = ethyl glycinate.

DISCUSSION

On the basis of the above results and others previously reported by us in related systems,[12] we suggest the overall kinetic scheme described in the Scheme 3 for the reactions considered in the present work. The species X and Y can be assigned to an ensemble of σ-complexes (Meisenheimer type), possibly in the ground state surface. Some of the σ-complexes will evolve to a final photosubstitution product by loosing a good leaving group (methoxy in the present cases or nitrite anion for 4-nitroanisole as previously reported[11b,12c]), the rest reverting to the original ground state. The different effects of the triplet quencher (and photosensitizers) on the photoreactions quantum yields confirm what has already been described for other primary amine (high ionization potential) nucleophiles[12a]. Thus, the complexes can be produced by interaction of the nucleophile with the substrate triplet (4,5-dinitroveratrole case, and also the already reported photoreaction of 4-nitroanisole with ethyl glycinate[12c], $S_N2^3Ar^*$ mechanism) or singlet excited state (4-nitroveratrole, $S_N2^1Ar^*$).



Scheme 3

The application of the steady-state approximation to Scheme 3 in the absence of quencher leads to equations 1 and 2 for the right (3-nitroanisole and 4,5-dinitroveratrole) and left parts (4-nitroveratrole) of the scheme respectively,

$$\Phi = \Phi_{isc}\,\frac{k_p}{k_p + k_d}\cdot\frac{k_3[Nu]}{k_4 + k_3[Nu]} \qquad \text{eq. 1} \qquad\qquad \Phi = \frac{k'_p}{k'_p + k'_d}\cdot\frac{k_2[Nu]}{k_{isc} + k_1 + k_2[Nu]} \qquad \text{eq. 2}$$

and from them:

$$\frac{1}{\Phi} = \frac{1}{\Phi_{isc}}\cdot\frac{k_p + k_d}{k_p}\left[1 + \frac{k_4}{k_3[Nu]}\right] \qquad \text{eq. 3} \qquad\qquad \frac{1}{\Phi} = \frac{k'_p + k'_d}{k'_p}\left[1 + \frac{k_1 + k_{isc}}{k_2[Nu]}\right] \qquad \text{eq. 4}$$

Therefore, if the scheme applies and the photosubstitution products come from unique origins, a linear relationship between Φ^{-1} and $[Nu]^{-1}$ should be observed. Indeed this is the case, and the representations for the studied photoreactions (Scheme 2) are shown in Fig. 1 and 2.

Regression analysis of the dependence of Φ^{-1} upon $[\text{ethyl glycinate}]^{-1}$ for the 4-nitroveratrole case (figure 1), using the values of the Table I gave a linear equation (c.c 0.9979).

$$\Phi^{-1} = (16.9 \pm 1.6) + (8.7 \pm 0.2)[Nu]^{-1}$$

From eq. 4 $(k_1 + k_{isc})/k_2 = 0.51$. As a limiting value $k_2 = k_{diff}$ and $k_{diff} = 9 \times 10^9\ M^{-1}s^{-1}$ at 30°C calculated by the Debye equation[19]. Then $(k_1 + k_{isc}) = 4.6 \times 10^9$. In spite of the high efficiency of the k_2 step, low quantum yields ($\Phi < 0.1$) are observed even extrapolating at infinite nucleophile concentration. This must be due to a low efficiency in the next branching point. Thus several Meisenheimer complexes can be formed and only those able to produce a methoxy leaving group will lead to the substitution product. Even in those cases a proton abstraction has to occur prior to the cleavage of the carbon-oxygen bond. This step is in direct competition with the carbon-nitrogen bond fragmentation which again would reduce the efficiency by producing the starting substrate.

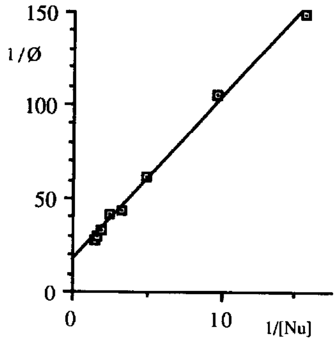


Fig. 1.- Plot of inverse quantum yield of photosubstitution product vs. inverse nucleophile (ethyl glycinate) concentration the photoreaction of 4-nitroveratrole with ethyl glycinate. Data from Table I.

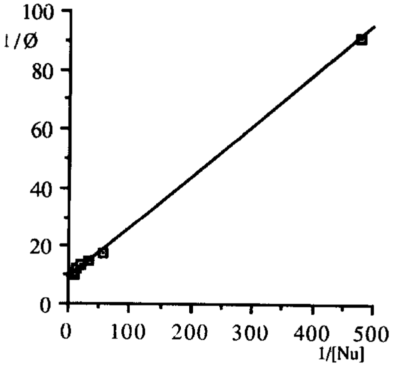


Fig. 2.- Plot of inverse quantum yield of photosubstitution product vs. inverse nucleophile (ethyl glycinate) concentration in the photoreaction of 4,5-dinitroveratrol with ethyl glycinate. Data from Table II.

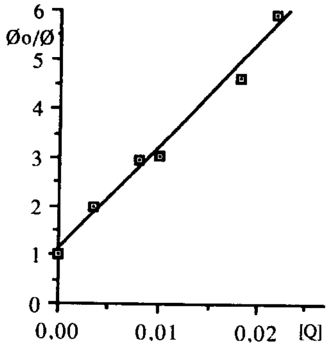


Fig. 3.- Plot of the relative inverse quantum yield of 4,5-dinitroveratrole photosubstitution with ethyl glycinate vs. quencher concentrations (potassium sorbate). Data from Table III.

A similar regression analysis (figure 2) for the 4,5-dinitroveratrole photoreaction, using the values of Table II gave a linear equation (c.c. 0.9996).

$$\Phi^{-1} = (9.03 \pm 0.38) + (0.172 \pm 0.002)[\mathrm{Nu}]^{-1}$$

From eq.3 we have k_4/k_3 equal to the slope to intercept ratio; therefore, $k_4/k_3 = 0.019$. In this case a relationship between quantum yield and triplet quencher concentration is observed. According to the Stern-Volmer analysis, the dependence of the relative reciprocal quantum yield on the quencher concentration is given by equation 5:

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q[Q]}{k_3[\mathrm{Nu}] + k_4} \qquad \text{eq. 5}$$

From the data of Table III (Figure 3) we find the following linear equation (c.c. 0.992):

$$\Phi_0/\Phi = (1.11 \pm 0.17) + (210.3 \pm 13.1)[Q]$$

and therefore from eq. 5, $k_q/k_3[\mathrm{Nu}] \simeq 210$. Assuming as a limiting value $k_q \simeq 9 \times 10^{-9}\ s^{-1}$ and since $[\mathrm{Nu}] = 0.07$ M, we obtain $k_3 \simeq 6.1 \times 10^{8}\ l\ M^{-1}s^{-1}$ and $k_4 \simeq 1.2 \times 10^{7}\ s^{-1}$ ($\tau \simeq 8.3 \times 10^{-8}$ s). The relatively low quantum yield values must be attributed again to a low efficiency in the next branching point (k_d vs k_p) as commented for the 4-nitroveratrole case. Summarizing, our kinetic studies indicate that only one excited state is directly involved in each studied photoreaction, and that in one case this is the singlet (4-

nitroveratrole case, $S_N2^1Ar^*$) and in the other the triplet excited states (4,5-dinitroveratrole case, $S_N2^3Ar^*$)

Tertiary and aromatic amines are good fluorescence quenchers for aromatic compounds. The quenching is normally attributed to enhanced decay through electron transfer to a geminate ion-pair and fast back electron transfer, and enhanced intersystem crossing to the substrate triplet excited state.[20] Our mechanistic changes can be discussed using the well established Weller model of radical ion pair formation.[15] The free energy change involved in electron transfer in an encounter complex to give a radical ion pair can be given by[1b]:

$$\Delta G_{et} = F[(E_D)^{ox} - (E_A)^{red}] - \Delta E_{exc} + \Delta E_{coul} \qquad \text{eq. 6}$$

$$\Delta E_{coul} = \frac{e^2 N}{4\pi \varepsilon_0 a}\left[\frac{1}{\varepsilon} - \frac{2}{37.5}\right] \qquad \text{eq. 7}$$

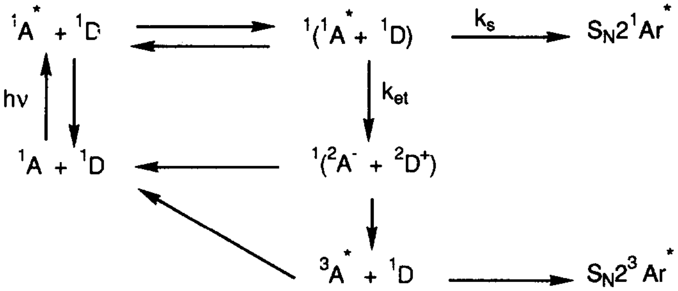
Table V. Free Energies of Electron Transfer from Ethyl Glycinate to Nitrophenyl Ether Acceptors in their Singlet Excited State Calculated from eq. 6 using the values of Table IV.

Acceptor	$[^1(\Delta E_{exc})]^a$	$[^1(\Delta G)_{et}]^a$	Mechanism
4-Nitroveratrole	290	-23	$(S_N2^1Ar^*)^b$
4-Nitroanisole	315	-41	$(S_N2^3Ar^*)^c$
4,5-Dinitroanisole	285	-50	$(S_N2^3Ar^*)^b$

[a] kJ/mol. [b] This work. [c] ref. 12c.

The redox potentials of the donor and acceptors involved in our photoreactions were measured and as previously commented are reported in Table IV. The excitation energy (ΔE_{exc}) can be approximated from the absorption spectrum, and the exact value of ΔE_{coul} can be obtained according to the Born equation, from eq. 7. In general, the distance a for a solvent-separated radical ion pair is taken as 0.7 nm[15a]. Using this value and $\varepsilon_0 = 8.854\times10^{-12}\ CV^{-1}m^{-1}$ one obtains $\Delta E_{coul} \simeq -8$ kJ/mol for a solvent with a $\varepsilon \simeq 70$. Using those data and eq. 6, values for $(\Delta G)_{et}$ in the different cases (4-nitroveratrole, 4-nitroanisole and 4,5-dinitroveratrole) are calculated (Table V).

Table V also reports the mechanism experimentally found in every case. Both theoretical treatments and experimental observations suggest that, as a rule, the rate of outer-sphere electron transfer is directly related to ΔG_{et}. Our results indicate that the competition (direct reaction)-(electron transfer) in the interaction donor(amine)-acceptor(nitrophenyl ether), in the singlet excited state, can be the key factor for their interpretation. On these bases, we propose a general mechanistic scheme to justify the singlet-triplet S_N2Ar^* reactivity of nitrophenyl ethers, summarized in Scheme 4. Thus, when the electron transfer process is highly exergonic $k_{et} >> k_s$ and no photosubstitution on the singlet excited state is observed (4-nitroanisole[12c] and 4,5-dinitroveratrole cases). On the other hand when the electron transfer process is poorly exergonic (4-nitroveratrole case) we are in the oposite situation, $k_s >> k_{et}$, and photosubstitution on the singlet excited state is the observed mechanistic pathway. Fast back electron transfer in the radical-ion pair stage leading to the ground state or to the substrate triplet excited state can justify the absence of any effect when the photoreactions are carried out in the presence of *m*-dinitrobenzene or methyl viologen.



Scheme 4

The proposed scheme (Scheme 4) has been developed from photoreactions of several nitrophenyl ethers with ethyl glycinate (amine nucleophile) but it should also explain the known features of related systems. Simple qualitative considerations of redox potentials can now be used to predict the photochemical reactivity of several nucleophiles in front of a particular nitrophenyl ether. Thus, for amine nucleophiles, the formation of the $^1(^1A^*\ {}^1D)$ complex will be very favourable (no return from the complex) and for low ΔG_{et} absolute values singlet reactivity will be observed (4-nitroveratrole *vs.* ethyl glycinate, methylamine or n-hexylamine[12a]). On the other hand when ΔG_{et} absolute values become larger (i.e. 4-nitroveratrole *vs.* piperidine[12a]), triplet reactivity is observed. With only a small tunning, the present model can also explain the results observed with nucleophiles other than amines. Among those, the most studied one is the hydroxide ion. For instance, the photohydrolysis of 4-nitroveratrole is known[1a,12a] to belong to the $S_N2^3Ar^*$ type. At first sight this result does not fit in the model. Hydroxide ion is a very poor reductant in water and therefore, a low ΔG_{et} absolute value is predicted and photoreaction through the singlet excited state should be observed ($S_N2^1Ar^*$). To get an explanation for this apparent deviation a second factor must be introduced, namely the coordinating ability (related in the particular case of aromatic photosubstitution with the softness) of the nucleophile. For the case of a hard (non coordinating) nucleophile like the hydroxide ion, the tendency to form the $^1(^1A^*\ {}^1D)$ complex will be very low. The return from it will efficiently compete with the substitution ($k_r >> k_s$), thus justifying the absence of singlet photochemistry in this case.

$$^{1}A^{*} + {}^{1}D \xleftarrow{k_r} {}^{1}({}^{1}A^{*}\ {}^{1}D) \xrightarrow{k_s} S_N2\,{}^{1}Ar^{*} \quad \text{Mechanism}$$

As a summary, the proposed model predicts, for a particular nitrophenyl ether, a change from triplet to singlet and again to triplet photoreactivity on going from hard and poorly reductant nucleophiles to soft and good reductant nucleophiles.

EXPERIMENTAL

All melting points are uncorrected, ^{1}H NMR and ^{13}C NMR spectra were recorded at 80 and 20 MHz using TMS as internal standard. The GC analysis were performed using a HP-Crosslinked Dimethylsilicone Gum 12m x 0.2mm x 0.33m film thickness capillary column. Quantum yield measurements were performed on a merry-go-round apparatus. The wavelenght of excitation was selected using a monochromator. The photoreaction of 4,5-dinitroveratrol with ethyl glycinate afforded N-ethoxycarbonylmethyl-2-methoxy-4,5-dinitroaniline **2** as described in reference 18.

N-Ethoxycarbonylmethyl-2-methoxy-5-nitroaniline, **1**. Irradiation of a solution of 4-nitroveratrole (0.218 g, 1.19 mmol), ethyl glycinate hydrochloride (1.918 g, 13.8 mmol), and sodium hydroxide (0.550 g, 13.8 mmol) in a mixture of 50 mL of methanol and 200 mL of water for 90 m in a Pyrex immersion well reactor using a 125-W medium-pressure Hg lamp as light source afforded starting material (4-nitroveratrole, 0.200 g) and 0.012 g of product **1** (48% yield based on the consumed starting material), mp 77-80 C (lit[16] 80-81 C), isolated by column chromatography through acid alumina using hexane/$CHCl_3$ (1:1) as eluent: IR (KBr) 3410, 1730, 1620, 1530, 1340 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.31 (t, J = 6.8 Hz, 3H), 3.91 (s, 3H), 3.95 (s, 2H), 4.2 (q, J = 6.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 2.9 Hz, 1H), 7.67 (dd, J = 8.8 Hz, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) 14.1, 45.1, 56.0, 61.5, 103.9, 108.1, 114.0, 137.3, 142.2, 151.7, 170.2; MS, m/e (relative intensity) 254 (M^{+} 24), 181 (100), 166 (19), 165 (12), 135 (22).

Quantum Yield measurements (Tables I to III). Quantum yields for the photoproducts were measured as previously reported[12c] using a merry-go-round apparatus. The irradiation source was a 250W medium pressure Hg lamp. The wavelength of excitation (366 nm) was selected using a monochromator. Product appearance was monitored, and the amount of photosubstitution product was determined by GC analysis. Actinometry was performed using potassium ferrioxalate[21], and conversion was kept around 5% in all the cases. Care was taken that >98% of the light were absorbed by the sample and the actinometer. The temperature was kept at 28 1 C in all cases. The concentration of reactants is given in the Tables. No precautions were taken to prevent the presence of oxygen. All the values are the result of five measurements, eliminating the two extremes and averaging the other three.

Electrochemical measurements (Table IV). Cyclic voltametry was carried out with a Tacussel GSTP4 function generator and a home-made potentiostat.[22] Measurements were performed employing a platinum disk (1mm diameter) and glassy carbon disk (2mm diameter) working electrodes. All potentials were referenced to aqueous saturated calomel (SCE). All measurements were made in acetonitrile and NEt_4BF_4 (puriss) and NBu_4BF_4 (puriss) 0.1M as supporting electrolites without any purification using a scan rate of 100 mV/s. All the experiments were conducted at 13 C.

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