



Photoelectron Transfer Induced Decarboxylation of Substituted Carboxylic Acids Across a Liquid/Liquid Interface

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Abstract: Methylene blue photocatalyzed electron transfer reactions of some phenoxyacetic acid derivatives and N-phenylglycine across a liquid/liquid interface led to their efficient decarboxylation. Nanosecond laser flash photolysis studies of this process, in a reverse micellar system of Aerosol-OT (AOT)-benzene-water indicated that the liquid/liquid interface acts as a barrier in controlling the energy wasting back electron transfer. Intramolecular C-C bond forming reactions of these radicals were utilized for the synthesis of various chroman derivatives. © 1997 Elsevier Science Ltd.

Photoinduced electron transfer processes are being increasingly utilized for developing newer synthetic methodologies in organic chemistry.²⁻⁶ However, the efficiencies of such processes are often limited by facile back electron transfer between the radical ion pairs produced in such processes. Due to the importance of photoinduced electron transfer processes in a number of naturally occurring as well as technological processes such as photosynthesis, artificial solar energy conversion and imaging, methods of controlling back electron transfer processes have been actively pursued.⁷ Among these methods, the use of interfaces has been found to be highly effective. For example, the solid/liquid interface has been used in heterogeneous systems such as in suspensions of semiconductors in various solvents.⁸ Although the study of such systems for conversion of light energy to chemical energy has received a lot of attention, studies on the use of semiconductors to bring about synthetically useful modifications in organic molecules are limited.^{9,10} Several microheterogeneous systems have also been effectively used for the control of back electron transfer.⁹ Such systems essentially consist of particles much smaller than the wavelength of light and therefore form optically clear or translucent solutions. Some of the microheterogeneous systems which have been extensively studied, include semiconductor colloids, organized assemblies of surfactant or lipid molecules such as micelles, vesicles or LB films as well as non organized systems such as solutions of organic and inorganic polymers. Various aspects of the use of such assemblies for the control of back electron transfer have been reviewed extensively.¹¹ Most of the studies on control of back electron transfer processes using heterogeneous and microheterogeneous systems have dealt with the mechanistic aspects and very few studies involving the exploitation of such systems for synthetic applications have been reported.

An interface that has not been well investigated for such applications is the liquid/liquid interface.¹² We have earlier reported that the use of photoinduced electron transfer catalyzed decarboxylation of several carboxylic acids using a liquid/liquid membrane, consisting of benzene and water as a means of controlling back electron transfer.¹³ There is considerable interest in the development of new methods for decarboxylating organic acids due to the synthetic importance of such transformations.¹⁴⁻²¹ Irradiation of solutions containing the carboxylic acids in benzene and methylene blue in water, led to the

decarboxylation of these acids, generating alkyl radicals. Efforts were made to utilize these radicals for synthetically useful intramolecular C-C bond forming reactions. In order to obtain further insight into the mechanism of methylene blue sensitized decarboxylation across the liquid/liquid membrane we have carried out comparative laser flash photolysis studies of this reaction in homogeneous and heterogeneous media. The heterogeneous medium used was a reverse micellar solution consisting of Aerosol-OT (AOT)-benzene-water. These aspects as well the study of methylene blue photosensitized decarboxylation of some phenoxyacetic acid derivatives and N-phenylglycine across a liquid/liquid membrane which indicates that apart from enhancement in efficiency of charge separation the liquid/liquid interface also plays a role in determining the nature of the product formed, are discussed in this paper.

RESULTS AND DISCUSSION

Photodecarboxylation of Aryloxyacetic Acid Derivatives. Irradiation of acetonitrile solutions of N-arylglycines in the presence of methylene blue (MB^+) has been reported to lead to the photodecarboxylation of these acids and the proposed mechanism involves electron transfer from the acid to the excited triplet state of methylene blue, followed by decarboxylation of the acid radical cation.¹⁵ In the present study, we have reinvestigated the photodecarboxylation in such systems by examining the methylene blue photosensitized decarboxylation of N-phenylglycine and observed efficient photodecarboxylation as reported earlier for this system. However, when acetonitrile solutions of the acids listed in Table 3, containing methylene blue were irradiated, photodecarboxylation was not observed. Similar results were obtained when acetonitrile/water and acetonitrile/benzene were used as solvents for the reaction.¹³

The primary process in the sensitized photodecarboxylation reaction is proposed to involve an electron transfer from the acid to the excited state of the sensitizer. The efficiency of this electron transfer between 2-allylphenoxyacetic acid **1** and the excited triplet state of methylene blue ($^3\text{MB}^{+*}$) was probed by laser flash photolysis. Figure 1 shows the spectrum of $^3\text{MB}^{+*}$ generated by 532 nm laser excitation of a solution of methylene blue, in acetonitrile/water (2:1 v/v). The transient absorption spectrum with a broad band in the 700-900 nm region could be attributed to the excited triplet state of methylene blue, by comparison with the spectra reported earlier.²² The triplet state decayed with a rate constant of $1.2 \times 10^5 \text{ s}^{-1}$. Addition of 2-allylphenoxyacetic acid in the millimolar range led to quenching of $^3\text{MB}^{+*}$ and Figure 2 shows the dependence of the triplet decay rate constant on the acid concentration. From the slope of the plot, a quenching rate constant of $1.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ was obtained using the Stern-Volmer equation (1). This rate

$$k_{\text{obs}} = k_0 + k_q [\text{Q}] \quad (1)$$

constant is typical of electron transfer reactions between various donors with the triplet state of methylene blue.²³ The lack of a strong residual absorption (inset, Figure 2) indicates that the initial electron transfer does not lead to charge separated species and this can be attributed to efficient back electron transfer between the initially formed radical ion pairs.

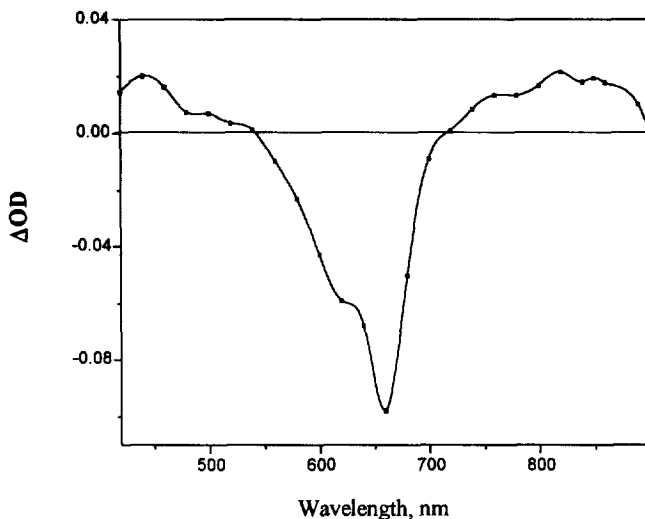


Figure 1. Transient absorption spectrum recorded immediately following the laser pulse (532-nm) excitation of methylene blue in acetonitrile/water (2:1 v/v). OD of the solution at the excitation wavelength was 0.1

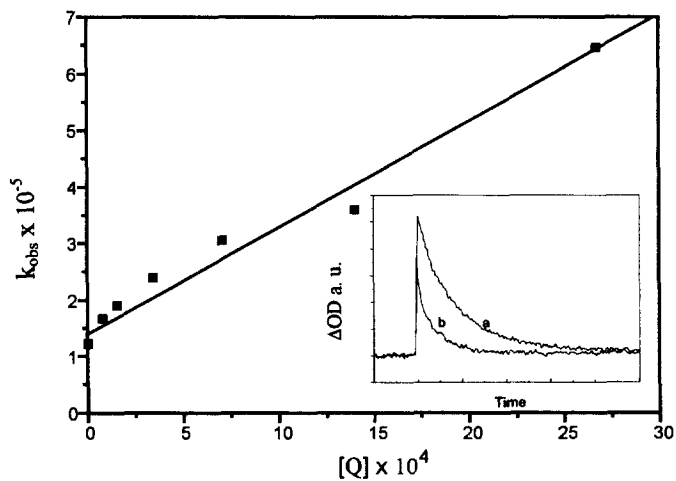
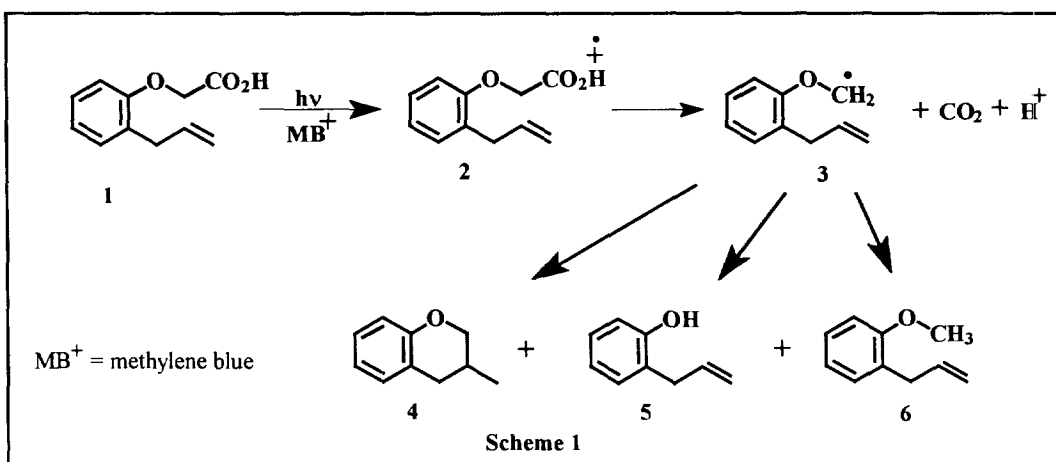


Figure 2. Effect of 2-allylphenoxyacetic acid concentration $[Q]$, on the decay rate constant (k_{obs}) of triplet methylene blue in acetonitrile/water (2:1 v/v). Excitation was carried out using 532-nm laser pulses. The decay was monitored at 840 nm. OD of the solution at the excitation wavelength was 0.1. Inset shows the decay of triplet methylene blue (a) in the absence of the acid and (b) in presence of 2.7×10^{-3} M the acid. Each division on the time axis corresponds to 10 μ s

When photodecarboxylation of 2-allylphenoxyacetic acid was carried out at a liquid/liquid interface using a heterogeneous solvent mixture of benzene and water efficient decarboxylation was observed. Irradiation of a mixture of 2-allylphenoxyacetic acid (380 mg, 2 mmol) dissolved in benzene (200 mL) and methylene blue (70 mg, 0.2 mmol) dissolved in water (100 mL) under vigorous stirring and argon atmosphere led to a 86 % decarboxylation as indicated by the CO₂ generated. CO₂ formed was estimated by bubbling the effluent gas from the reaction mixture through saturated barium hydroxide solution and measuring the amount of barium carbonate produced. After irradiation, the benzene layer was separated and concentrated and analysis of this mixture on a GC/MS indicated the formation of 3-methylchroman (4, 50 %) as the major product along with 2-allylphenol (5, 20 %) and 2-allylanisole (6, 16 %) (Scheme 1).



The enhancement in efficiency of photosensitized decarboxylation on using the liquid/liquid interface could arise due to a phase transfer catalysis involving partial solubilization of the solutes into the different liquid phases, namely benzene and water. Alternatively, the enhancement in efficiency could be attributed to the liquid/liquid interface acting as a barrier, preventing back electron transfer. In order to probe the role of the liquid/liquid interface, laser flash photolysis studies of methylene blue and the acid dissolved in a reverse micellar system of Aerosol OT (AOT)-benzene-water was carried out. To prepare the reverse micellar system of AOT-benzene-water, first a solution of AOT (1.34 g, 3 mmol) in benzene (30 mL) was prepared. To this solution, water (500 μ L) was added slowly under vigorous stirring. This microheterogeneous system can closely mimic the liquid/liquid interface effectively without compromising the optical quality of the medium since the droplets of water are too small (10-200 nm) to scatter light.

In a reverse micellar solution of methylene blue and 2-allylphenoxyacetic acid, methylene blue will be located in the water pool inside the micellar core due to its highly hydrophilic nature. The location of the acid molecules will be mainly in the bulk benzene phase with the ability to diffuse toward the core of the reverse micelle. Excitation with the 532-nm output of the ND:YAG laser resulted in the population of the triplet excited state of methylene blue, as observed by the transient triplet absorption spectrum. The triplet state decays with a rate constant of 1.2×10^5 which is not different from that observed in

homogeneous solution. On gradual addition of 2-allylphenoxyacetic acid to this system, quenching of triplet methylene blue was observed. Normally, kinetic analysis in any micellar medium is carried out assuming a Poisson distribution of the solutes over the micelles and a single micelle may contain more than one excited state species and several quencher molecules. In the present study, however, very dilute solutions of methylene blue (3×10^{-5} M) were used ensuring that number of sensitizer molecules present in a micellar unit was not more than one. Also, the quencher molecules (carboxylic acid) will reside outside the micelles, being hydrophobic and highly soluble in benzene. The rate constant for this quenching was calculated using the normal Stern-Volmer equation 1 and a linear dependence of rate constant for triplet decay (k_{obs}) versus quencher concentration was observed (Figure 3). From the slope of the plot obtained, the rate constant for quenching k_q was found to be $9 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. The slightly reduced rate in this case compared to quenching in homogeneous medium can be attributed to the enhanced microviscosity of the micellar medium.

On complete quenching of the triplet excited state, a new long lived species was formed ($\tau = 1 \text{ ms}$) and its absorption spectrum showing a peak with the maximum centred around 850 nm is shown in Figure 4. This species was assigned as the protonated methylene blue radical, by comparison with the absorption spectrum of the same species generated from electron transfer between methylene blue and diphenylamine.²⁴

The efficiency of charge separation in micellar and homogeneous media has been compared by following the yield of the protonated form of the methylene blue radical at 840 nm, employing nano-second laser flash photolysis experiments. Figure 5 shows the change in the absorbance at 840 nm, on 532-nm laser flash photolysis of the methylene blue/2-allylphenoxyacetic acid system in the reverse micellar (trace a) and homogeneous media (trace b). The solutions had been optically matched at 532 nm ($OD = 0.1$) to ensure that equal number of photons were absorbed in each case. A five fold enhancement in the yield of the protonated methylene blue radical in the micellar medium, as compared to that in the homogeneous medium, indicated a much better charge separation in the former. These studies strongly support the view that the liquid/liquid interface plays a significant role in preventing back electron transfer. The efficiency of charge separation across the benzene/water layer could be expected to be higher than in the micellar system since the liquid/liquid interface will be better defined in such mixtures.

Further support for the electron transfer across the liquid/liquid interface was provided by comparison of the efficiency of decarboxylation and the solubilities of the different acids in water (Table 1). If the process takes place across the interface and back electron transfer really decreases the efficiency, acids which partition more into water would be expected to undergo decarboxylation less efficiently. This was indeed the case. For phenoxyacetic acid and 2-allylphenoxyacetic acid the electronic factors, which control decarboxylation, are similar, whereas their solubilities in water are substantially different (Table 2). Due to preferential solubilization of phenoxyacetic acid in water, photoinduced electron transfer for this acid will occur within the water layer itself where rapid back electron transfer would prevent the decarboxylation process, whereas, due to the limited solubility of 2-allylphenoxyacetic acid in water, the decarboxylation process is expected to be more efficient. The results in Table 3 indicate that this is

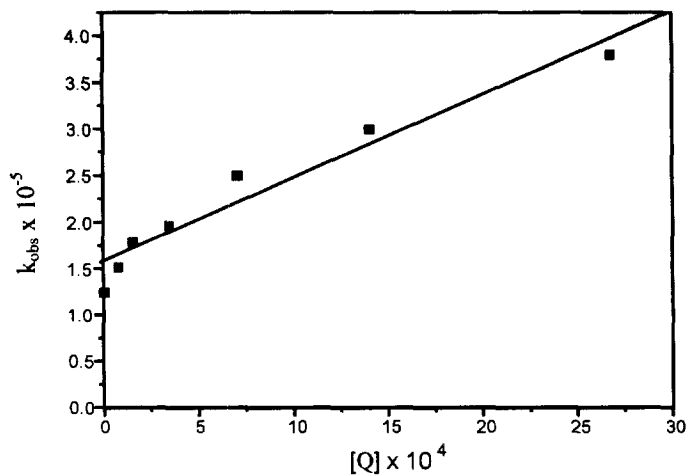


Figure 3. Effect of 2-allylphenoxyacetic acid concentration $[Q]$, on the decay rate constant (k_{obs}) of triplet methylene blue, in AOT-benzene-water reverse micelles. Excitation was carried out using 532-nm laser pulses. The decay was monitored at 840 nm. OD of the solution at the excitation wavelength was 0.1.

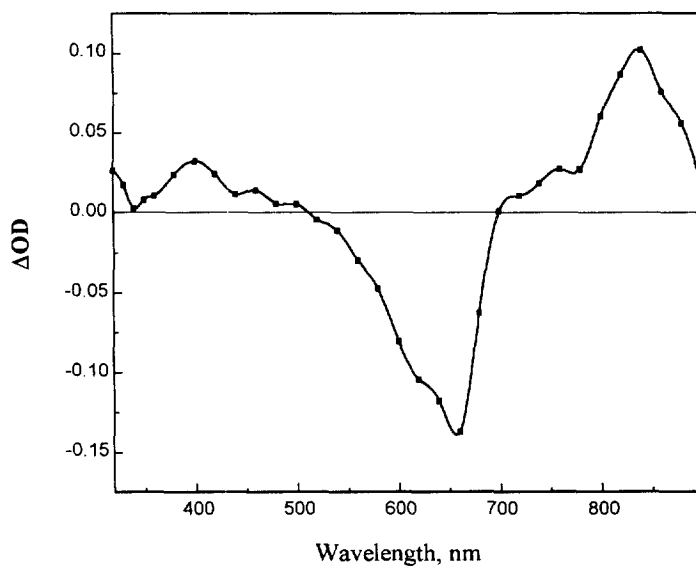


Figure 4. Transient absorption spectrum recorded immediately following the laser pulse (532-nm) excitation of methylene blue, in the presence of 2-allylphenoxyacetic acid, in AOT-benzene-water reverse micelles. OD of the solution at the excitation wavelength was 0.1.

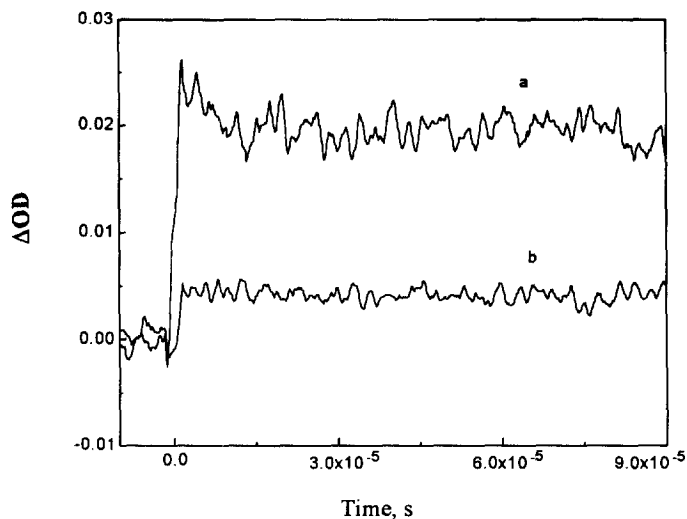


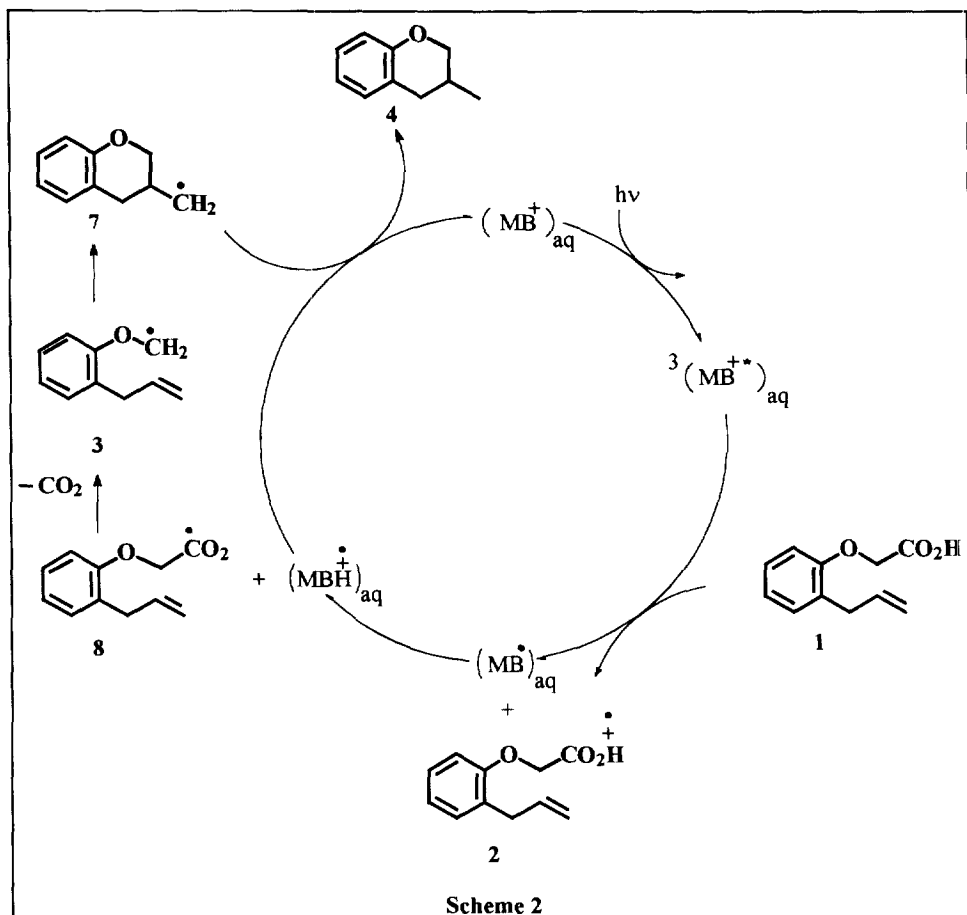
Figure 5. Transient absorption of the protonated form of methylene blue radical at 840 nm, formed on excitation of a deaerated solution containing methylene blue and 2-allylphenoxyacetic acid (10^{-2} M) in (a) AOT-benzene-water reverse micelles (b) acetonitrile/water (2:1 v/v). Excitation was carried out using a 532-nm laser pulse. OD of the solution at the excitation wavelength was 0.1

Table 1. Partitioning of the Acids in Benzene Water Mixture and the %age Decarboxylation under Methylene Blue Photosensitization, for a few Aryloxyacetic Acid Derivatives

Sl. No.	Acid used	Partitioning of acid in water (%)	Decarboxylation (%)
1.	1-Allyl-2-naphthoxyacetic acid	1.0	73
2.	2-Naphthoxyacetic acid	1.2	36
3.	2-Allyl-4-chlorophenoxyacetic acid	1.8	43
4.	2-Allylphenoxyacetic acid	3.2	86
5.	2-(Prop-1-enyl)phenoxyacetic acid	4.7	50
6.	Phenoxyacetic acid	47.8	24

indeed the case. A similar trend was also observed for the other acids, in the relationship between the efficiency of partitioning in water and the efficiency of photodecarboxylation. These results confirm that the liquid/liquid interface plays an important role in the control of back electron transfer.

Based on these results the mechanism shown in Scheme 2 indicating formation of the major products can be proposed for the MB^+ photocatalyzed decarboxylation across the liquid/liquid interface.



On excitation by Pyrex-filtered light, MB^+ will be selectively excited, leading to the formation of its triplet state ($\phi^3\text{MB}^{+\ast} = 0.52$).²⁵ Electron transfer from the ground state of the acid in the benzene layer to $^3\text{MB}^{+\ast}$ dissolved in the aqueous phase will lead to the formation of the acid radical cation **2** and the methylene blue radical. This process will be followed by a rapid proton exchange from the acid radical cation to methylene blue, in order to maintain the charge balance between the two solvent layers. This leads to the formation of the protonated form of the methylene blue radical. The carboxyl radical **8** formed in the process can undergo rapid decarboxylation,¹⁶ to give the alkyl radical **3** which can subsequently undergo cyclization followed by hydrogen abstraction, to yield the chroman **4**. Some of **3** can undergo dealkylation to eventually form the phenol **5** or abstract a hydrogen atom to give the anisole **6** (Scheme 1). Since only catalytic amounts of the sensitizer dye (10 % of the acid concentration) was used and efficient decarboxylation was observed it is indicated that the dye is being recycled. This can probably occur via the oxidation of the protonated methylene blue radical, by the alkyl radical **7**, to give back the dye.

Table 2 shows the yields of CO₂ and 3-methylchroman on photodecarboxylation of 2-allylphenoxyacetic acid using methylene blue and other sensitizers. The best yields were obtained when catalytic amounts of MB⁺ in water/benzene were used. At higher concentrations of MB⁺, a slight decrease in the extent of photodecarboxylation was observed and this may be attributed to self quenching of the triplet excited state of MB⁺ by ground state dye. Sensitizers like anthraquinone and quinoline are known to bring about

Table 2. Yields of CO₂ and 3-Methylchroman in the Photodecarboxylation of 2-Allylphenoxyacetic Acid, using Various Sensitizers

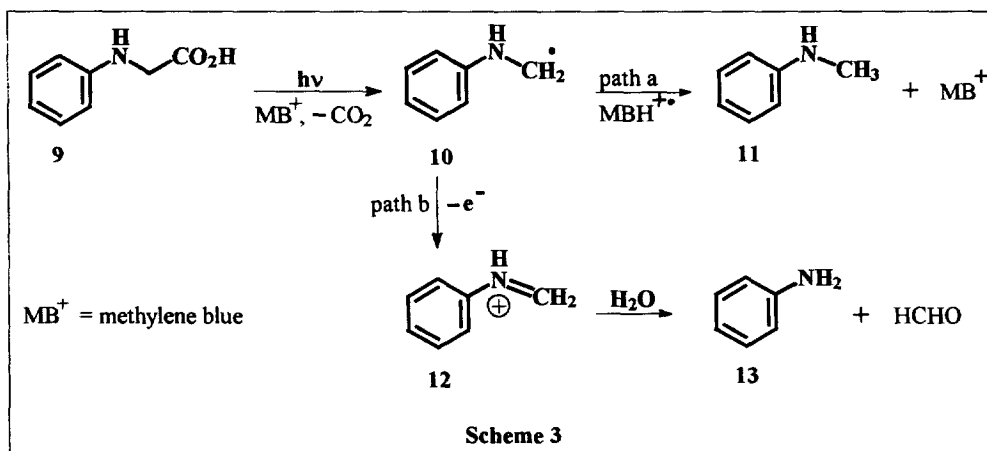
Sensitizer	Acid (mmol)	Sensitizer (mmol)	Solvent (300 mL)	Time (h)	Yield of CO ₂ (%)	Yield of 4 (%) [*]
Methylene blue	2	0.2	CH ₃ CN/H ₂ O	5	<1	<1
Methylene blue	2	2	C ₆ H ₆ / H ₂ O	2.5	40	35
Methylene blue	2	0.2	C ₆ H ₆ / H ₂ O	2.5	60	50
Methylene blue	2	0.2	C ₆ H ₆ / H ₂ O	5	86	55
Anthraquinone	2	2	C ₆ H ₆	2.5	90	10
Quinoline	2	2	C ₆ H ₆	2.5	30	5

* Yields are based on the amount of the acid decarboxylated

efficient decarboxylation of phenoxyacetic acid derivatives. In the present study when these sensitizers were used, the efficiency of formation of the intramolecularly cyclized product was not high. For example, on irradiation of a benzene solution of 2-allylphenoxyacetic acid using quinoline as sensitizer, 30 % decarboxylation, with only a 5 % yield of the chroman was observed. With anthraquinone as sensitizer, although 90 % decarboxylation was observed, only 10 % yield of the cyclized product was obtained. Earlier studies of photodecarboxylation in homogeneous media have indicated that complex reaction mixtures containing adducts formed between sensitizer and alkyl radicals are formed in such cases.¹⁵

Photodecarboxylation of N-Phenylglycine. Sensitizers such as acridine and methylene blue have been shown to photodecarboxylate N-phenylglycine with high efficiency in aerated acetonitrile solution leading to the formation of aniline as the major photoproduct.¹⁶ Similarly acridine photosensitized decarboxylation of N-phenylglycine in deaerated acetonitrile solution led to aniline as the major amine derived photoproduct.²¹ Formation of N-methylaniline has not been observed in these studies. In the present study also aniline was the major photoproduct observed on sensitized photodecarboxylation of N-phenylglycine in argon saturated acetonitrile solutions. When the photodecarboxylation was carried out in a

heterogeneous solvent mixture of benzene/water, however, the major photoproduct formed was N-methylaniline (54 %) along with some amount of aniline (20 %). Scheme 3 shows the proposed mechanism for the formation of the two products. The alkylamino radical is known to undergo further oxidation to yield iminium ion (path b), which may hydrolyze to form the aldehyde and amine. For homogeneous solutions this process is favoured. In the heterogeneous solvent mixture of water/benzene, however, formation of N-methylaniline, probably via H-atom transfer from $\text{MBH}^{+\bullet}$ (path a) appears to be the favoured pathway.

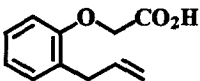
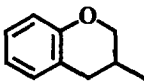
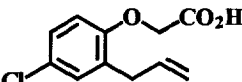
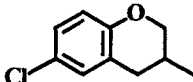
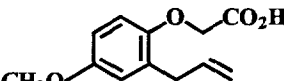
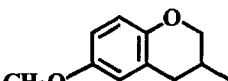
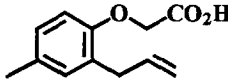
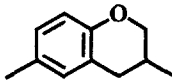
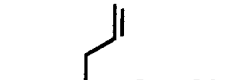
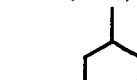
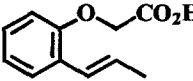
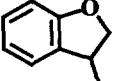


Comparison of the photosensitized decarboxylation reactions of phenoxyacetic acid and N-phenylglycine in homogeneous media with those across the liquid/liquid interface suggests that apart from enhancement in efficiency of photodecarboxylation, the liquid/liquid membrane also plays a role in product selectivity. Secondary oxidations of the alkyl radical generated as well as coupling reactions between the sensitizer and alkyl radicals appears to be less favoured in the heterogeneous photocatalyzed reactions.

Intramolecular C-C Bond Forming Reactions. In order to demonstrate the synthetic utility of the efficient electron transfer across the liquid/liquid interfaces, benzene solutions of several aryloxyacetic acid derivatives and aqueous solutions of methylene blue were irradiated using the Pyrex filtered output of a Hanovia medium pressure mercury lamp under vigorous stirring and argon atmosphere. The major products formed by the intramolecular cyclization of the corresponding alkyl radicals are shown in Table 3.

Acknowledgements. We thank the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India for financial support of this work. This is document No. RRLT-PRU-90 from the Regional Research Laboratory, Trivandrum.

Table 3. Major Products from the Photodecarboxylation of 2-Allylaryloxyacetic acids in Benzene, Using Methylene Blue in Water as Sensitizer

Sl. No.	Acid used	Photoproduct *	Yield of CO ₂ (%)
1			86
	1	4 (50 %)	
2			43
	14	15 (70 %)	
3			67
	16	17 (64 %)	
4			78
	18	19 (74 %)	
5			73
	20	21 (55 %)	
6			74
	22	23 (55 %)	

* Yields are based on the amount of the acid reacted

EXPERIMENTAL SECTION

The IR spectra were recorded on a Perkin Elmer model 882 Infrared Spectrometer. ^1H (90 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded on a JEOL EX 90 NMR Spectrometer using tetramethylsilane (TMS) as internal standard. The mass spectra were recorded either on a Finnigan MAT model 8430 or JEOL JMS AX 505 HA mass spectrometer or 5890 series II Hewlett Packard GC-MS. GC data were obtained on OV 101 (25 m length, 0.2 mm ID) or on HP-FFAP (25 m length, 0.2 mm ID) capillary column, using FID detector. The products were identified by comparing their gas chromatographic retention times and their mass spectra, with those of authentic samples. Yields were estimated gas chromatographically using suitable internal standards. UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer. HPLC analyses were carried out using a Shimadzu LC-6AD instrument, employing a CLC-ODS analytical column using a mixture (1:3) of water and methanol. All the melting points are uncorrected and were determined using a MEL-TEMP II melting point apparatus.

Preparative photochemical reactions across the liquid/liquid interface were carried out using a 450 W Hanovia medium pressure mercury lamp in a Pyrex-jacketed, water cooled immersion well in a heterogeneous solvent mixture of benzene (200 mL) and water (100 mL) under vigorous stirring. Yields reported are based on the amount of the carboxylic acid reacted. During irradiations, the solvent mixture was continuously and vigorously purged with argon. The effluent gases were passed through a saturated solution of barium hydroxide. The extent of decarboxylation was monitored from the amount of barium carbonate precipitated.

The partitioning of acids between benzene and water layer was determined in each case by measuring the absorbance of the corresponding acid in the benzene layer in a mixture of benzene and water. This solvent mixture with the acid was thoroughly mixed before any absorbance measurement.

Laser flash photolysis studies were carried out by exciting the solutions using the 532-nm output (2nd harmonic) of a Nd:YAG laser (pulse width, ~8 ns, energy 150 mJ). Solutions were deaerated by bubbling with argon. A reverse micellar solution of Aerosol OT (AOT) in benzene was prepared by dissolving AOT (1.3 g, 3 mmol) in benzene (30 mL) and adding 500 μL of water to it. This solution was kept overnight before using it for any experiment. Reverse micellar solution of methylene blue was prepared by the addition of methylene blue to the above solution to get an OD of 0.1. Laser flash photolysis experiments in homogeneous media were carried out using a mixture (2:1) of acetonitrile and water.

A general procedure for the preparation of the allylphenoxyacetic acid derivatives involves the reaction of chloroacetic acid with 2-allylphenols in the presence of sodium hydroxide in water.²⁶ Allylphenoxyacetic acids formed were purified by recrystallization from benzene. 2-Allyl ethers were prepared from the corresponding 2-allylphenols using reported procedures.²⁶ 2-Propenylphenoxyacetic acid was prepared from chloroacetic acid and 2-propenylphenol.²⁶

Preparation of 2-Allylphenoxyacetic Acid (1). Reaction of 2-allylphenol (10 g, 75 mmol) with chloroacetic acid (7 g, 75 mmol) yielded 2-allylphenoxyacetic acid (**1**) (7 g, 50 %).

1: mp: 143-144 °C.

IR spectrum ν_{\max} (KBr): 3000 (broad, OH), 2600 (CH), 1750 (C=O) cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 3.4-3.6 (2 H, d), 4.6-4.7 (2 H, s), 4.9-5.2 (2 H, m), 5.7-6.3 (1 H, m), 6.7-7.4 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 29.20, 66.50, 114.41, 115.20, 122.11, 125.15, 126.80, 127.20, 127.62, 127.71, 154.12, 174.98.

Mass spectrum m/z (relative intensity): 192 (M^+ , 70), 145 (14), 131 (62), 115 (85), 105 (98), 91 (100), 77 (95), 63 (47), 51 (60). Molecular weight calculated for $\text{C}_{11}\text{H}_{12}\text{O}_3$: 192.0786. Found: 192.0799 (high-resolution mass spectrometry).

Preparation of 2-Allyl-4-chlorophenoxyacetic Acid (14). Reaction of 2-allyl-4-chlorophenol (13 g, 75 mmol) with chloroacetic acid (7 g, 75 mmol) yielded 2-allyl-4-chlorophenoxyacetic acid (**14**) (10 g, 60 %).

14: mp 107-108 $^\circ\text{C}$.

IR spectrum ν_{\max} (KBr): 2950 (broad, OH), 2600 (CH), 1750 (C=O) cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 3.3-3.5 (2 H, d), 4.6-4.7 (2 H, s), 4.9-5.2 (2 H, m), 5.7-6.3 (1 H, m), 6.4-7.4 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 33.92, 65.25, 112.65, 116.41, 126.91, 130.14, 131.24, 135.71, 153.86, 174.68.

Mass spectrum m/z (relative intensity): 226 (M^+ , 85), 165 (50), 139 (51), 132 (60), 115 (73), 103 (100), 89 (31), 77 (80), 51 (37). Molecular weight calculated for $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Cl}$: 226.0397. Found: 226.0412 (high-resolution mass spectrometry).

Preparation of 2-Allyl-4-methoxyphenoxyacetic Acid (16). Reaction of 2-allyl-4-methoxyphenol (12.3 g, 75 mmol) with chloroacetic acid (7 g, 75 mmol) yielded 2-allyl-4-methoxyphenoxyacetic acid (**16**) (9.1 g, 55 %).

16: mp 83-84 $^\circ\text{C}$.

IR spectrum ν_{\max} (KBr): 2950 (broad, OH), 2600 (CH), 1750 (C=O) cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 3.3-3.5 (2 H, d), 3.6-3.7 (3 H, s), 4.5-4.6 (2 H, s), 4.9-5.2 (2 H, m), 5.7-6.3 (1 H, m), 6.6-7.8 (3 H, m).

^{13}C NMR spectrum (CDCl_3): δ 34.00, 55.20, 65.50, 110.15, 113.00, 116.00, 116.30, 130.52, 136.92, 149.05, 154.50, 170.40.

Mass spectrum m/z (relative intensity): 222 (M^+ , 100), 163 (60), 147 (18), 135 (50), 120 (15), 103 (60), 91 (50), 77 (30), 65 (20). Molecular weight calculated for $\text{C}_{12}\text{H}_{14}\text{O}_4$: 222.0892. Found: 222.0897 (high-resolution mass spectrometry).

Preparation of 2-Allyl-4-methylphenoxyacetic Acid (18). Reaction of 2-allyl-4-methylphenol (11g, 75 mmol) with chloroacetic acid (7 g, 75 mmol) yielded 2-allyl-4-methylphenoxyacetic acid (**18**) (7.6 g, 50 %).

18: mp: 99-100 $^\circ\text{C}$.

IR spectrum ν_{\max} (KBr): 2900 (broad, OH), 2550 (CH), 1750 (C=O) cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 2.0-2.1 (3 H, s), 3.3-3.5 (2 H, d), 4.6-4.7 (2 H, s), 4.9-5.2 (2H, m), 5.7-6.3 (1 H, m), 6.5-7.2 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 20.43, 34.25, 65.42, 111.67, 115.49, 127.57, 128.97, 131.06, 131.36, 136.94, 153.23, 174.47.

Mass spectrum m/z (relative intensity): 206 (M^+ , 100), 145 (55), 131 (30), 119 (45), 105 (17), 91 (42), 77 (17), 63 (8), 51 (7). Molecular weight calculated for $\text{C}_{12}\text{H}_{14}\text{O}_3$: 206.0943. Found: 206.0955 (high-resolution mass spectrometry).

Preparation of 1-Allylnaphthoxyacetic Acid (20). Reaction of 1-allylnaphthol (13.8 g, 75 mmol) with chloroacetic acid (7 g, 75 mmol) yielded 2-allylnaphthoxyacetic acid (**20**) (11 g, 60 %).

20: mp 97-98 °C.

IR spectrum ν_{max} (KBr): 2900 (broad, OH), 2600 (CH), 1750 (C=O) cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 3.8-3.0 (2 H, d), 4.7-4.8 (2 H, s), 4.8-5.1 (2 H, m), 5.8-6.3 (1 H, m), 6.8-8.0 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 29.23, 66.49, 114.41, 115.21, 122.53, 123.78, 123.96, 126.50, 128.23, 128.41, 129.96, 133.12, 136.49, 152.51, 174.99.

Mass spectrum m/z (relative intensity): 242 (M^+ , 75), 181 (70), 165 (100), 153 (50), 128 (40), 115 (30), 102 (7), 89 (6), 77 (10). Molecular weight calculated for $\text{C}_{15}\text{H}_{14}\text{O}_3$: 242.0943. Found: 242.0941 (high-resolution mass spectrometry).

Preparation of 2-Prop-1-enylphenoxyacetic Acid (22). 2-Prop-1-enylphenol (5 g, 37 mmol) was reacted with chloroacetic acid (3.5 g, 37 mmol) to give 2-prop-1-enylphenoxyacetic acid (**22**) (3 g, 55 %).

22: mp: 113-115 °C.

IR spectrum ν_{max} (KBr): 2950 (broad, OH), 2600 (CH), 1700 (C=O) cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 1.8-2.0 (3 H, d), 4.6-4.7 (2 H, s), 6.0-6.5 (2 H, m), 6.6-7.5 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 18.82, 65.31, 112.24, 125.15, 126.82, 127.24, 127.60, 127.75, 154.12, 174.95.

Mass spectrum m/z (relative intensity): 192 (M^+ , 57), 145 (10), 131 (72), 115 (59), 105 (100), 91 (99), 77 (73), 63 (20), 51 (47). Molecular weight calculated for $\text{C}_{11}\text{H}_{12}\text{O}_3$: 192.0786. Found: 192.0786 (high-resolution mass spectrometry).

Photodecarboxylation of 2-Allylphenoxyacetic Acid. 2-Allylphenoxyacetic acid (**1**) (380 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene (200 mL) and water (100 mL) under argon purging and vigorous stirring. In this case, 86 % decarboxylation was observed. Analysis of the benzene layer on a gas chromatograph, using suitable internal standard showed the formation of 3-methylchroman (**4**) (129 mg, 50 %), 2-allylphenol (**5**) (47 mg, 20 %) and 2-allylanisole (**6**) (48 mg, 18 %). 2-Allylphenol and 2-allylanisole were characterized by comparison of their mass spectra and retention times on a GC column, with authentic samples.

4: IR spectrum ν_{max} (neat): 2900 (CH), 1400 cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 0.9-1.1 (3 H, s), 2.0-3.0 (4 H, m), 3.5-4.3 (2 H, m), 6.7-7.2 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 16.94, 27.03, 33.23, 71.72, 116.35, 120.11, 121.75, 127.09, 129.72, 154.39.

Mass spectrum m/z (relative intensity): 148 (M^+ , 100), 133 (75), 119 (15), 105 (25), 91 (22), 78 (35), 51 (8).

Photodecarboxylation of 2-Allyl-4-chlorophenoxyacetic Acid. 2-Allyl-4-chlorophenoxyacetic acid (**14**) (452 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene and water under argon purging and vigorous stirring. In this case, 43 % decarboxylation was observed. Analysis of the product mixture on a gas chromatograph, with suitable internal standard showed 3-methyl-6-chlorochroman (**15**) (150 mg, 70 %) as the major photoproduct.

15: IR spectrum ν_{max} (neat): 2900 (CH), 1400 cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 0.9-1.1 (3 H, s), 1.8-3.0 (4 H, m), 3.4-4.2 (2 H, m), 6.5-7.3 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 17.10, 26.00, 32.90, 71.10, 116.35, 120.50, 124.00, 126.50, 129.10, 154.00.

Mass spectrum m/z (relative intensity): 182 (M^+ , 100), 167 (55), 141 (71), 112 (47), 77 (77), 51 (50). Molecular weight calculated for $\text{C}_{10}\text{H}_{11}\text{OCl}$: 182.0498. Found: 182.0485 (high-resolution mass spectrometry).

Photodecarboxylation of 2-Allyl-4-methoxyphenoxyacetic Acid. 2-Allyl-4-methoxyphenoxyacetic acid (**16**) (444 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene (200 mL) and water (100 mL) under argon purging and vigorous stirring. In this case 67 % decarboxylation was observed. Analysis of the product mixture on a gas chromatograph, with suitable internal standard showed 3-methyl-6-methoxychroman (**17**) (153 mg, 64 %) as the major photoproduct.

17: IR spectrum ν_{max} (neat): 2900 (CH), 1400 cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 0.8-1.1 (3 H, s), 1.8-3.0 (4 H, m), 3.4-4.2 (2 H, m), 3.6-3.7 (3 H, s), 6.5-7.3 (4 H, m).

^{13}C NMR spectrum (CDCl_3): δ 16.88, 27.06, 33.47, 55.58, 71.66, 113.10, 114.29, 116.80, 122.32, 148.43, 153.23.

Mass spectrum m/z (relative intensity): 178 (M^+ , 100), 163 (35), 136 (40), 108 (25), 77 (17), 51(15). Molecular weight calculated for $\text{C}_{11}\text{H}_{14}\text{O}_2$: 178.0994. Found: 178.1003 (high-resolution mass spectrometry).

Photodecarboxylation of 2-Allyl-4-methylphenoxyacetic Acid. 2-Allyl-4-methylphenoxyacetic acid (**18**) (412 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene (200 mL) and water (100 mL) under argon purging and vigorous stirring. In this case, 78 % decarboxylation was observed. Analysis of the product mixture on a gas chromatograph, with suitable internal standard showed 3,6-dimethylchroman (**19**) (140 mg, 74 %) as the major photoproduct.

19: IR spectrum ν_{max} (neat): 2900 (CH), 1400 cm^{-1} .

^1H NMR spectrum (CDCl_3): δ 0.9-1.1 (3 H, s), 1.8-3.0 (4 H, m), 2.1-2.3 (3 H, s) 3.4-4.3 (2 H, m)

6.5-7.3 (4 H, m).

¹³C NMR spectrum (CDCl₃): δ 16.97, 20.43, 27.15, 33.26, 71.75, 114.23, 116.08, 121.42, 127.72, 130.08, 152.18.

Mass spectrum m/z (relative intensity): 162 (M⁺, 100), 147 (65), 133 (15), 121 (35), 105 (17), 91 (65), 77 (20), 65 (17), 51 (17).

Photodecarboxylation of 1-Allylnaphthoxyacetic Acid. 1-Allylnaphthoxyacetic acid (**20**) (484 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene (200 mL) and water (100 mL) under argon purging and vigorous stirring. In this case, 73 % decarboxylation was observed. Analysis of the product mixture on a gas chromatograph, with suitable internal standard showed 3-methylnaphthochroman (**21**) (130 mg, 55 %) as the major photoproduct.

21: IR spectrum ν_{\max} (neat): 2900 (CH), 1400 cm⁻¹.

¹H NMR spectrum (CDCl₃): δ 1.0-1.2 (3 H, s), 2.0-3.4 (3 H, m), 3.6-4.4 (2 H, m) 6.9-7.9 (6 H, m).

¹³C NMR spectrum (CDCl₃): δ 17.27, 26.94, 29.71, 71.42, 113.34, 118.77, 121.72, 123.10, 126.20, 127.48, 128.35, 128.94, 133.15, 152.01.

Mass spectrum m/z (relative intensity): 198 (M⁺, 95), 183 (17), 165 (16), 156 (45), 128 (100), 115 (12), 76 (10). Molecular weight calculated for C₁₂H₁₄O: 198.1045 Found: 198.1003 (high-resolution mass spectrometry).

Photodecarboxylation of 2-Prop-1-enylphenoxyacetic Acid. 2-Prop-1-enylphenoxyacetic acid (**22**) (384 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene (200 mL) and water (100 mL) under argon purging and vigorous stirring. In this case, 50 % decarboxylation was observed. Analysis of the product mixture on a gas chromatograph, with suitable internal standard showed 3-ethylbenzofuran (**23**) (74 %) as the major photoproduct.

23: IR spectrum ν_{\max} (neat): 2900 (CH), 1400 cm⁻¹.

¹H NMR spectrum (CDCl₃): δ 0.8-1.1 (3 H, t), 1.3-2.0 (2 H, m), 3.2-3.4 (1 H, m) 4.1-4.8 (2 H, m) 6.7-7.4 (4 H, m).

¹³C NMR spectrum (CDCl₃): δ 11.24, 27.56, 43.29, 76.43, 109.37, 120.17, 124.23, 127.99, 130.79, 159.94.

Mass spectrum m/z (relative intensity): 148 (M⁺, 47), 119 (100), 105 (2), 91 (74), 77 (5), 65 (8), 51 (4).

Photodecarboxylation of N-phenylglycine. N-Phenylglycine (302 mg, 2 mmol) was irradiated in the presence of methylene blue (70 mg, 0.2 mmol) for 5 h in a heterogeneous mixture of benzene (200 mL) and water (100 mL) under argon purging and vigorous stirring. In this case, 80 % decarboxylation was observed. HPLC analysis of the product mixture indicated the formation of N-methylaniline (54 %) and aniline (20 %) as the major photoproducts.

Photodecarboxylation of N-phenylglycine in acetonitrile. N-Phenylglycine (302 mg, 2 mmol) was irradiated in acetonitrile (300 mL) for 5 h in the presence of methylene blue (70 mg, 0.2 mmol). The reaction mixture was continuously purged with argon during the irradiation. HPLC analysis of the product mixture indicated the formation of aniline (58 %) and N-methylaniline (3 %). In this case 70 % decarboxylation was observed.

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