# Photo-oxidative Decarboxylation of Phenylacetic Acids induced by Pyrimido[5,4-*g*]pteridine-10-oxide involving a Single-electron-transfer Process in Both Stages

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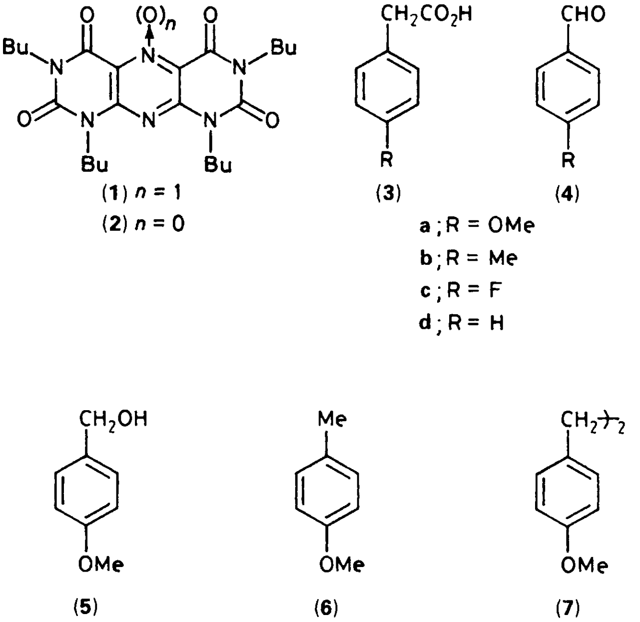
Irradiation of phenylacetic acid derivatives (**3a**—**d**) in the presence of pyrimido[5,4-*g*]pteridine-10-oxide (**1**) with UV visible light gives the corresponding benzaldehyde derivatives (**4a**—**d**) as the major product *via* a single-electron-transfer process in both stages.

There have been ample precedents for photochemical decarboxylation of arylacetic acids in the presence of various electron acceptors involving photo-induced single-electron transfer (SET) followed by decarboxylation to give arylmethanes, 1,2-diarylethanes, and adducts with the electron acceptors employed.[1]

We now report an intriguing example of photochemical oxidative decarboxylation of phenylacetic acids (**3a**—**d**) leading to the corresponding benzaldehydes (**4a**—**d**) by a novel heterocyclic *N*-oxide, pyrimido[5,4-*g*]pteridine-10-oxide (**1**).[2] The present result clearly demonstrates that the *N*-oxide (**1**) effectively functions as an electron acceptor [$E^{\text{red}}_{1/2} = -0.97$ V *vs.* standard calomel electrode (SCE) in MeCN] in its singlet-excited state and as agents for both oxygenation and dehydrogenation in both stages of the photoreaction. This type of the reaction has never been observed in the photochemistry of heterocyclic *N*-oxides, and its discovery originates from the special photochemical reactivity of (**1**); the *N*-oxide (**1**) efficiently oxidises various substrates[3] without an intramolecular rearrangement of the *N*-oxide function generally observed in the photoreaction of the heterocyclic *N*-oxides (Scheme 1).[4]

A mixture of *p*-methoxyphenylacetic acid (**3a**) (50 mM) and (**1**) (5 mM) in dry acetonitrile was irradiated with a 400 W high-pressure mercury arc lamp through a $BiCl_3$ solution filter (>355 nm) at ambient temperature under argon for 40 min.† During this period, 10% of (**1**) was consumed to give pyrimido[5,4-*g*]pteridine (**2**)‡ almost quantitatively, and *p*-methoxybenzaldehyde (**4a**) and *p*-methoxybenzyl alcohol (**5**) were produced in 42 and 8% yields [based on consumed



Scheme 1

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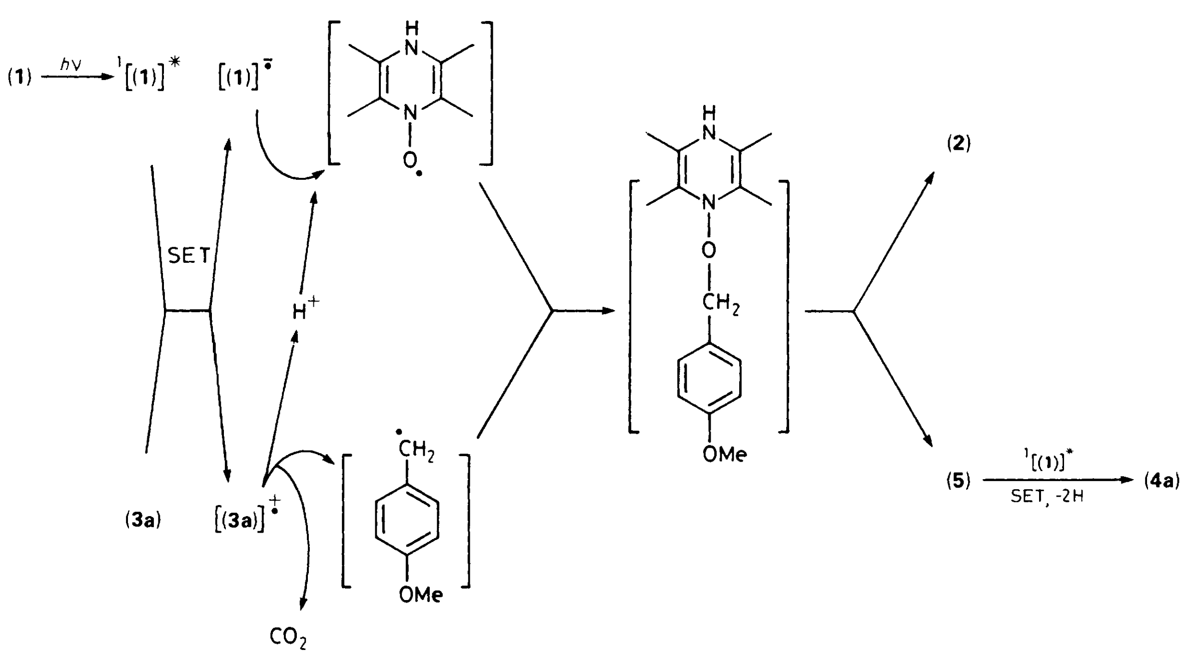
† The pyrimido[5,4-*g*]pteridine (**2**) induces the photochemical decarboxylation of (**3a**) to give (**6**) ($\phi = 0.64$) and (**7**) ($\phi = 0.01$). Thus, the irradiation time was limited to minimise the influence of (**2**) on the present photoreaction. Quantum yields were determined at 365 nm excitation by using potassium ferrioxalate actinometer in acetonitrile in the presence of (**1**) or (**2**) (5 mM) and substrates (250 mM).

‡ All compounds described here were assigned by comparison of GC retention times and the spectral data with either those of authentic samples or those of compounds reported in the literature.



Scheme 2

(1)], respectively, together with trace amounts of 4-methylanisole (**6**) and 1,2-di(*p*-methoxy)phenylethane (**7**).[5] The quantum yield for the formation of (**4a**) in this reaction was 0.01.† An independent experiment showed that analogous irradiation of (**5**) in the presence of (**1**) caused a smooth dehydrogenation ($\phi$ = 0.09) to give (**4a**) quantitatively. This fact suggests an intermediacy of (**5**) in the formation of the major product (**4a**). These reactions did not occur in the dark (*e.g.* reflux for 4 h) or in the absence of (**1**).

Analogously, *p*-methylphenylacetic acid (**3b**), *p*-fluorophenylacetic acid (**3c**), and phenylacetic acid (**3d**) underwent photo-oxidative decarboxylation to give the corresponding benzaldehydes (**4b—d**) as major products [78—80%, based on two equimolar amounts of the consumed (**1**)]. On the other hand, *p*-nitrophenylacetic acid and ethyl *p*-methoxyphenylacetate were not oxidised by (**1**) under the conditions employed and were recovered unchanged.

No formation of a charge-transfer complex between (**3a**) or (**5**) and (**1**) in a ground-state was observed in acetonitrile. Experiments for the wavelength dependence showed that the photo-oxidation of (**3a**) and (**5**) by (**1**) occurs most efficiently by irradiation with around 365 nm light which is near the longest UV absorption band of (**1**) [370 nm ($\varepsilon = 2.2 \times 10^4$)]. Stern–Volmer plots for the quenching of the fluorescence of (**1**) by (**3a**) and (**5**) were linear [$k_q\tau_s$ = 13.5 mol$^{-1}$ dm$^3$ for (**3a**) and 3.7 mol$^{-1}$ dm$^3$ for (**5**)]. The quenching rate constants ($k_q$) were estimated to be $4.6 \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ for (**3a**) and $1.3 \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ for (**5**)§ which are near the diffusion controlled limit in acetonitrile. The formation of (**4a**) from both (**3a**) and (**5**) was not significantly affected by the triplet sensitisation using acetone. The above facts indicate that a singlet-excited (**1**) is responsible for the photo-oxidation of (**3a**) and (**5**) by (**1**).

The addition of tetracyanoethylene, a strong electron acceptor, to the mixture of (**1**) and (**3a**) or (**5**) in acetonitrile markedly inhibited the formation of (**4a**) with a concentration dependence, accommodating involvement of the SET process in these photoreactions.[6]

The free energy changes [$\Delta G_{et}$, kcal mol$^{-1}$ (1 cal = 4.184 J)] calculated for the SET from (**3a—d**) and (**5**) to a singlet excited (**1**) according to the Rehm–Weller relationship[7] were −14.2 for (**3a**), −3.8 for (**3b**), −0.2 for (**3c**), 1.7 for (**3d**), and −16.3 for (**5**),¶ suggesting the possible occurrence of the SET processes. The calculated $\Delta G_{et}$ values for the cases of (**3a—d**) are in a linear relationship with the logarithm of the relative consumption rates of (**1**) in their respective photoreactions.

Taking the above facts into consideration, we concluded that the present photoreaction involves the SET process in both stages, *i.e.* the SET of the phenylacetic acids (*cf.* **3a**) and the intermediary benzyl alcohols (*cf.* **5**) in the ground state to a singlet excited (**1**). The reaction sequence is outlined in Scheme 2, using the case of (**3a**) as an example. The formation of the decarboxylated product (**6**) and the coupling product (**7**) most likely supports the intermediary generation of the *p*-methoxybenzyl radical in the reaction course from (**3a**) to (**5**).

It is worthwhile noting that the photo-oxidative decarboxylation of (**3a**) leading to (**4a**) did not take place by employment of 3-methylpyridazine-2-oxide, which has been considered to oxidise substrates by an active oxygen-atom (oxene) liberated in its excited state[8] in a different manner from the *N*-oxide (**1**).

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§ The life-time of the fluorescence ($\tau_s$ : 2.95 ns) was measured by the single photon counting method.

¶ The oxidation peak potentials of phenylacetic acids [$E_p^{ox}$, V *vs.* SCE: (**3a**), 1.71; (**3b**), 2.16; (**3c**), 2.32; (**3d**), 2.40] and *p*-methoxybenzyl alcohol (**5**) ($E_p^{ox}$ = 1.62 V *vs.* SCE) were measured by cyclic voltammetry in dry acetonitrile and used for the present discussion in place of the oxidation potential ($E^{ox}_{1/2}$). (*Cf.* J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968). For the Rehm–Weller treatment, the singlet excited energy ($\Delta E_s$ = 3.24 V) of the *N*-oxide (**1**) was roughly estimated on the basis of its UV spectrum (λ 370 nm) and the fluorescence spectrum (λ 394 nm).

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