

Photo-oxygenation of Benzene Derivatives by a Novel Derivative of the Heterocyclic *N*-Oxide, Pyrimido[5,4-*g*]pteridine 5-Oxide, involving a Single-electron-transfer Process

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1,3,7,9-Tetrabutylpyrimido[5,4-*g*]pteridine-2,4,6,8(1*H*,3*H*,7*H*,9*H*)-tetrone 5-oxide (1) efficiently oxygenates benzene (4a), toluene (4b), and anisole (4c) under photochemical conditions in a reaction mode different from that of 3-methylpyridazine 2-oxide (3) to give the corresponding phenols (5a-c) as major products. Experimental results clearly indicate that the photochemical oxygenation of (4a-c) by (1) involves a single-electron-transfer process followed by oxygen-atom transfer rather than interception of atomic oxygen generated from (1) in an excited state.

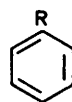
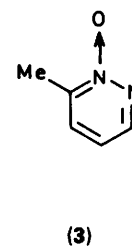
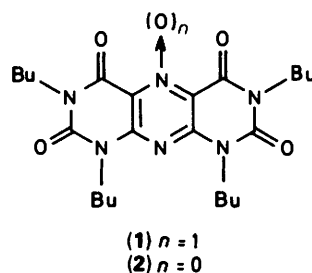
The photochemistry of heterocyclic *N*-oxides has been extensively studied, but some details remain equivocal.¹ The known photochemical reactions of heterocyclic *N*-oxides are classified as intramolecular rearrangement of the *N*-oxide function or intermolecular oxygen-atom transfer (deoxygenation). Although the latter reaction can be considered to be a simple chemical model for biological mono-oxygenation, an understanding of the mechanism for this photoreaction is less advanced than for the former reaction, because it is usually not the predominant process in the photochemistry of heterocyclic *N*-oxides. Two interpretations have been given for the photochemical oxygen-atom transfer reaction of the *N*-oxides; (i) it occurs by interception of oxygen atoms generated in their triplet excited state (the oxene mechanism), while the intramolecular rearrangement takes place *via* the intermediacy of an oxaziridine formed in the singlet excited state; (ii) both reactions occur in the singlet excited states and involve the same oxaziridine intermediate which can transfer the oxygen atom to the substrates and rearrange intramolecularly.

During our search for heterocyclic *N*-oxides which could serve as efficient oxygen-atom transfer agents, without accompanying photochemical intramolecular rearrangements, we found that 1,3,7,9-tetrabutylpyrimido[5,4-*g*]pteridine-2,4,6,8(1*H*,3*H*,7*H*,9*H*)tetrone 5-oxide (1)² is suitable for this purpose.

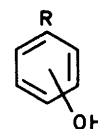
This paper³ describes the results of a detailed study of the photochemical oxygenation of the benzene derivatives (4a-c) by the *N*-oxide (1), showing its high efficiency and rationalising a new mechanistic aspect which involves the oxygen-atom transfer process initiated by a single-electron transfer (SET) from (4a-c) to singlet excited (1). The present results depend largely on comparative experiments with the photo-oxygenation of (4a-c) by 3-methylpyridazine 2-oxide (3), which has been proposed to oxygenate substrates such as alkenes and aromatic compounds by the oxene mechanism.^{4,5}

Results

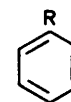
(a) *Photo-oxygenation of Benzene (4a) by the N-Oxides (1) and (3)*.—A mixture of (4a) (2.0M) and (1) (5.0mM) in dry acetonitrile was irradiated externally with a 400 W high-pressure mercury arc lamp through a Pyrex filter at ambient temperature under argon. After irradiation for 140 min, phenol (5a) was obtained in 51% yield based on the consumed (1). Longer irradiation times led to lower yields of (5a). This observation clearly indicates the occurrence of further photoreactions between the product (5a) and the *N*-oxide (1).



a; R = H
b; R = Me
c; R = OMe



a; R = H
b; R = Me
c; R = OMe



An independent experiment demonstrated that irradiation of a mixture of (5a) and (1) under analogous conditions caused smooth consumption of (1) and led to the formation of oxidised products including *o*- and *p*-catechols.†

Thus, when the photoreaction was carried out with irradiation for a short time (within 1 h) so that a significant amount of (1) was recovered, (5a) was obtained almost quantitatively based on (1) consumed. In the photoreaction the *N*-oxide (1) was converted into the pyrimido[5,4-*g*]pteridine (2) in high yield without the formation of detectable amounts of other photoproducts originating from (1), indicating that (1) behaves efficiently as an oxidant under the conditions employed. The oxygenation of (4a) did not proceed in the dark (*e.g.*, reflux for 8 h) or in the absence of (1).

Analogous irradiation of a mixture of (4a) (2.0M) and the pyridazine *N*-oxide (3) (5.0mM) in dry acetonitrile caused rapid consumption of (3) and gave phenol (5a) in 34% yield based on the consumed (3). In this photoreaction, deoxygen-

† Details of the photochemical oxidation of phenols and benzyl alcohols by the *N*-oxide (1) *via* the SET process will be reported in forthcoming papers.

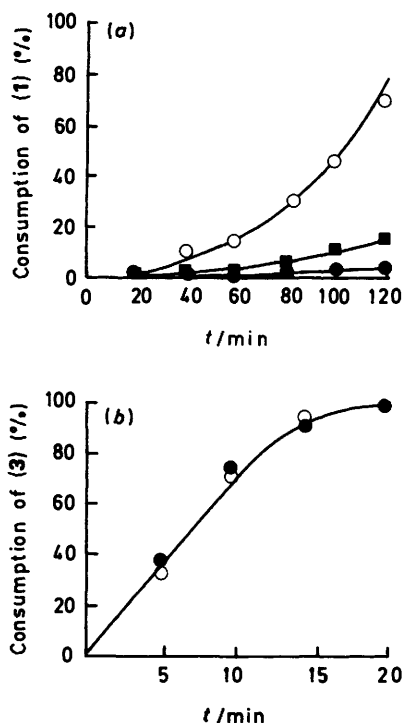


Figure 1. Consumption of the *N*-oxides (1) and (3) in dry acetonitrile in the absence or presence of anisole (4c) as a function of irradiation time. ●: without (4c), ■: with 10 equiv. of (4c), ○: with 100 equiv. of (4c).

ated pyridazine was obtained only in low yield (44% even after the irradiation for 20 min). This fact reflects the occurrence of other photoreactions of (3), e.g. intramolecular rearrangement, in agreement with the observations previously reported.⁴

(b) *Photo-oxygenation of Toluene (4b) by the N-Oxides (1) and (3).*—Under conditions similar to those in the foregoing experiments, a mixture of (4b) (2.0M) and (1) (5.0mM) in dry acetonitrile was irradiated for 1 h. The formation of cresol (5b) (*ortho:para*, 57:43) (46%), benzyl alcohol (6) (9%), benzaldehyde (7) (6%), and 1,2-diphenylethane (8) (3%) was confirmed on the basis of careful analysis by gas chromatography–mass spectroscopy (GC–MS) [yields are based on (1) consumed].* In this reaction *m*-cresol was not observed. An independent experiment showed that photochemical dehydrogenation of the alcohol (6) by (1) occurred quite readily under the conditions employed to give (7) in high yield.†

When a mixture of (4b) (2.0M) and the pyridazine *N*-oxide (3) (5.0mM) in dry acetonitrile was irradiated, (3) was completely consumed after 20 min and cresol (5b) was obtained (*ortho:meta + para*, 57:43) in 40% yield. Although the *meta:para*-isomer ratio could not be estimated accurately because of their close GC retention times under the conditions employed, the formation of the *meta*-isomer was proved by inspection of the fragmentation pattern in the mass spectra of *meta*-isomer-rich fractions. In this case, the side chain-oxidised

products (6), (7), and (8) were not detected. This discrepancy in products indicates that the photo-oxygenation of (4b) by (1) must proceed *via* a reaction mode different from that when (3) is used.

(c) *Photo-oxygenation of Anisole (4c) by the N-Oxides (1) and (3).*—Irradiation of a mixture of (4c) (0.5M) and (1) (5.0 mM) in dry acetonitrile for 40 min gave methoxyphenol (5c) (*ortho:para*, 60:40) and phenol (5a) in 42 and 14% yields [based on (1) consumed], respectively.* GC analysis of the reaction mixture showed no formation of *m*-methoxyphenol. The quantum yield for the formation of (5c) was 0.007.

With (3) as an oxidant, only (5c) was obtained in 42% yield (*ortho:meta:para*, 53:11:36) after complete consumption of (3) (20 min). As with (4b), the formation of the *meta*-isomer is characteristic of the photo-oxygenation using (3).

In the photo-oxidation of (4c) by pyridine *N*-oxide, it has been observed that the *O*-demethylation leading to (5a) occurs only in aqueous solution.⁶ Addition of a small amount of water to the reaction medium containing (4c) and (1) did not significantly affect the yield of (5a), however. Thus the formation of (5a) from (4c) can be ascribed to the primary nature of (1) itself as an oxidant.

The *N*-oxide (1) is very stable to UV irradiation in dry acetonitrile. Addition of (4c) to a solution of (1) in dry acetonitrile and irradiation resulted in the smooth consumption of (1) with the concentration dependence shown in Figure 1(a). In sharp contrast, the *N*-oxide (3) is highly sensitive to irradiation and the consumption of (3) is independent of the presence of (4c) [see Figure 1(b)]. This observation also is a clear indication of the different reaction mode for (1) and (3).

Discussion

As mentioned above, the pyrimido[5,4-*g*] pteridine *N*-oxide (1) oxygenated the benzene derivatives (4a–c) more slowly than did the pyridazine *N*-oxide (3). The deoxygenation of (1) to (2), however, occurred almost quantitatively without the formation of rearranged photoproducts, indicating that in the photochemistry of (1) oxygen-atom transfer to the substrates predominates over intramolecular rearrangements. The different product distributions in the photo-oxidations of the benzene derivatives (4a–c) by (1) and (3) suggest the possible operation of alternative oxidation mechanisms for the reactions.

Iwasaki *et al.*⁵ have claimed that atomic oxygen is liberated directly from the excited *N*-oxide (3) and oxygenates cyclohexene (oxene mechanism), on the basis of the fact that the consumption rate of (3) under irradiation in dichloromethane is not affected by the presence of cyclohexene. An analogous result was obtained in the photo-oxygenation of anisole (4c) with (3) when acetonitrile was used as solvent as shown in Figure 1(b).

In sharp contrast to the case of (3), (1) was stable in acetonitrile under irradiation and the consumption rate of (1) depended distinctly upon the concentration of (4c) as shown in Figure 1(a), implicating an appreciable interaction between (1) and (4c) in the photo-oxygenation. However, charge-transfer complex formation between (1) and (4c) in the ground state was not observed in acetonitrile.

Wavelength-dependence experiments showed that the consumption of (1) in the photoreaction with (4c) occurs most efficiently on irradiation at *ca.* 365 nm, which is near the longest UV absorption band of (1) (λ_{\max} 370 nm; ϵ 2.2×10^4) and excites (1) exclusively. Irradiation of a solution of (4c) and (1) in acetonitrile with a low-pressure mercury arc lamp (254 nm) through a quartz filter did not cause the consumption of (1).

The fluorescence of (1) in dry acetonitrile was effectively

* In the preliminary paper (ref. 3), we reported that the products (6), (7), (8), and (5a), were not formed, and *ortho:para* ratios for the isomeric phenols of 7:9 for (5b) and 1:10 for (5c), in the photo-oxidation of (4b) and (4c) with (1). After detailed reinvestigations, we concluded that previous results were erroneous.

† Details of the photochemical oxidation of phenols and benzyl alcohols by the *N*-oxide (1) *via* the SET process will be reported in forthcoming papers.

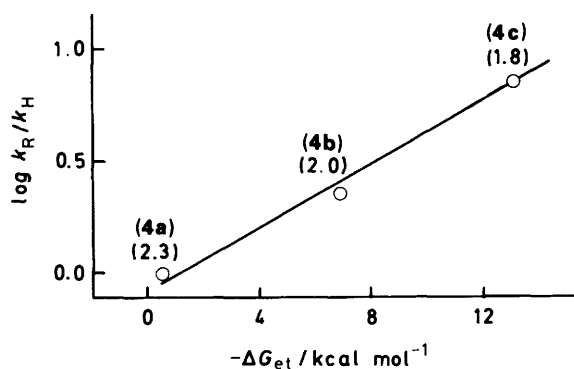


Figure 2. Correlation between relative consumption rates of the *N*-oxide (1) in the photo-oxygenation of the benzene derivatives (4a–c) by (1) and free energy changes (ΔG_{et}) calculated for the single-electron transfer from (4a–c) to singlet excited (1) on irradiation of solutions of (4a–c) (10.0mM) and (1) (1.0mM) in dry acetonitrile.

For calculations according to the Rehm–Weller equation, $\Delta G_{et} = 23.06 (E_{ox}^{\ddagger} - E_{red}^{\ddagger} - \Delta E_s) - e^2/\epsilon a$, the following values were used: singlet-excited energy (ΔE_s) of (1): 3.24 V (based on the UV spectrum: λ 370 nm and fluorescence spectrum: λ 394 nm); reduction potential (E_{red}^{\ddagger}) of (1): -0.97 V vs. standard calomel electrode (SCE) in dry acetonitrile (cyclic voltammetry); oxidation potentials (E_{ox}^{\ddagger}) of (4a–c) are shown in parentheses (cf. ref. 9); coulombic component ($e^2/\epsilon a$): 1.3 kcal mol $^{-1}$ (cf. A. J. Maroulis, Y. Shigemitsu, and D. A. Arnold, *J. Am. Chem. Soc.*, 1978, 100, 535).

quenched by the addition of (4c). Stern–Volmer plots for the quenching of the fluorescence of (1) (λ_{max} 394 nm) by (4c) were linear ($k_q\tau_s = 6.2 \text{ dm}^3 \text{ mol}^{-1}$). The quenching rate constant (k_q) was estimated* to be $2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is near the diffusion-controlled limit in acetonitrile.

The photo-oxygenation of (4c) by (1) was not affected by the addition of a triplet sensitizer such as acetone, acetophenone, or benzophenone, or a triplet quencher such as biacetyl.

These results indicate that singlet excited (1) is responsible for the present photo-oxygenations.

The addition of tetracyanoethylene or tetracyanoquinodimethane, strong electron acceptors, to the reaction medium containing (4c) and (1) markedly inhibited the formation of (5c), even in a low concentration. According to the Rehm–Weller treatment,⁷ the free energy changes (ΔG_{et}) for the SET from (4a–c) to singlet excited (1) were roughly calculated to be $-0.6 \text{ kcal mol}^{-1}$ for (4a), -7.5 for (4b), and -12.1 for (4c) (1 cal = 4.184 J), which are in a linear relationship with the relative consumption rates of (1) in the respective reactions as shown in Figure 2.

These results accommodate the involvement of the SET process^{8,9} from (4a–c) to the excited (1) in the initial stage of the photoreaction.

The formation of the oxidation products (6), (7), and (8) from toluene (4b) is characteristic of photochemical oxidation

using (1) and suggests the generation of an intermediate benzyl radical (E) during the reaction. The occurrence of the *O*-demethylation in the photoreaction of anisole (4c) with (1) appears to result from the intermediacy of the cation radical (A) (R = OMe) (see Scheme).

Taking the foregoing facts into consideration, the reaction sequence in the Scheme is a reasonable rationalisation of the photo-oxygenation of the benzene derivatives (4a–c) by (1). The photo-oxygenation of the benzene ring by (1) proceeds via the formation of a zwitterionic intermediate (C) by coupling of the radical ions (A) and (B),[†] generated as a result of the SET from (4) to singlet excited (1).

The photochemical formation of phenol (5a) from (4a) by (1) was efficiently accelerated by addition of trifluoroacetic acid (TFA) to the reaction medium; e.g., addition of TFA (15 mM) to a solution of (4a) (2.0M) and (1) (5.0mM) in dry acetonitrile increased the yield of (5a) sevenfold after irradiation for 2 h. The catalytic role of TFA is most likely explained in terms of suppression of the back electron transfer taking place between the radical ions (A) and (B), and stabilisation of the zwitterionic intermediate (C) by protonation.^{9–11}

Fragmentation of the intermediate (C) gives phenols (5) and (2) accompanied by direct proton loss (route a). 1,2-Hydrogen shift, namely the 'NIH shift,' in (C) leads to a transient intermediate (D) which collapses to give (5) and (2) (route b).^{1,12} (see *i* in the Scheme) In fact, the photochemical oxygenation of [4-²H]toluene and [4-²H]anisole by (1) resulted in the formation of *p*-cresol and *p*-methoxyphenol with deuterium contents of 38 and 18%, respectively.

In the case of toluene (4b), the proton transfer from the methyl group in the cation radical (A) (R = Me) to (B)^{9,13} generates a benzyl radical (E) and an imino-oxyl radical (F). Self-coupling of (E) produces 1,2-diphenylethane (8) and coupling of (E) with (F) could give benzyl alcohol (6) and (2) via fragmentation of the resulting intermediate (G). The alcohol (6) thus formed can be dehydrogenated by a singlet-excited (1) to give benzaldehyde (7) via the SET process[‡] (see *ii* in the Scheme).

In the case of anisole (4c), proton abstraction from the cation radical (A) (R = OMe) by (B) generates the radicals (H) and (F), which couple to give the intermediate (J). Fragmentation of (J) to the intermediate (K) and (2) and subsequent release of formaldehyde from (K) could give rise to (5a) (see *iii* in the Scheme). This type of oxygenative demethylation has been observed in the photoreaction of dimethylaniline with the *N*-oxide (1).¹⁴

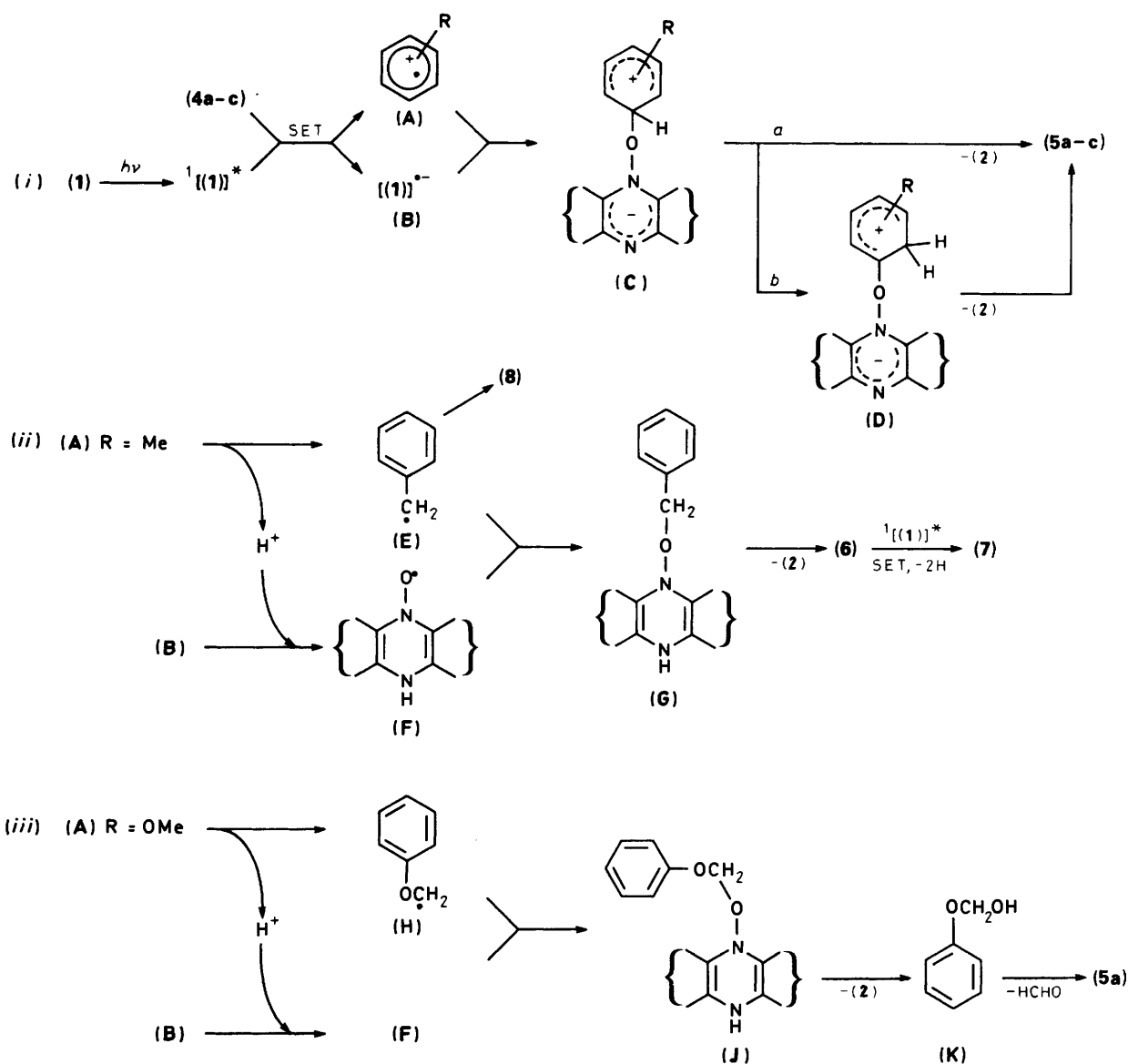
The present mechanism involving SET followed by oxygen-atom transfer is an alternative to the atomic oxygen (oxene) and oxaziridine mechanisms proposed previously for the photochemical oxygenation of aromatic hydrocarbons by heterocyclic *N*-oxides.¹ At present, we consider that this type of the photo-oxygenation originates from the special and characteristic photochemical properties of pyrimido[5,4-*g*]pteridine *N*-oxide systems such as (1).

Recent investigations^{15,16} of the mechanism of the biological oxidation of xenobiotic substances by cytochrome P450 have suggested that the oxidation occurs in most cases possibly via an initial SET from the substrates to the active oxygen species, the oxo-iron(IV) porphyrin cation radical, and subsequent oxygen-atom transfer. Accordingly, the present mechanism for the photo-oxygenation of the benzene derivatives (4a–c) by (1) formally parallels that proposed for the biological oxygenation catalysed by cytochrome P450 in that it involves an initial SET process. Thus, the photo-oxygenation by the *N*-oxide (1) can be regarded as a functional chemical model for the cytochrome P450-catalysed oxygenation of aromatic hydrocarbons.

* The lifetime of fluorescence of (1) (τ_s , 2.95 ns) was measured by a single-photon counting method.

† The anion radical (B) generated during controlled-potential electrolysis of the *N*-oxide (1) in dry acetonitrile showed a hyperfine splitting signal with $a_{N(5)} = 14.05 \text{ G}$ (1 G = 10^{-4} T) in its ESR spectrum. HMO calculations indicated the high localisation of spin density in the N(5)–O position of (B). The physical properties of (1) will be discussed in a separate paper.

‡ Details of the photochemical oxidation of phenols and benzyl alcohols by the *N*-oxide (1) via the SET process will be reported in forthcoming papers.



Scheme.

Experimental

Irradiations were carried out by using a 400 W high-pressure mercury arc lamp (Riko Kagaku Sangyo) through a Pyrex filter at ambient temperature under an argon atmosphere. A JASCO CRM-FA spectroirradiator (2 kW Xe lamp) was used for the wavelength-dependence experiments and for the measurement of quantum yields. M.p.s (uncorrected) were determined on a Yanagimoto micro-hot-stage apparatus. The spectroscopic measurements were performed with the following instruments: UV absorption spectra with Shimadzu-260 spectrophotometer; IR spectra with Hitachi Model 215 spectrometer; ¹H NMR spectra with a JEOL JNX270 (270 MHz) spectrometer using tetramethylsilane as an internal standard; mass spectra with a JEOL JMS-D 300 machine operating at 70 eV; fluorescence spectra with a Hitachi 650-60 spectrometer. GLC analyses were performed with a Shimadzu GC-8APF instrument with 1.2 m columns (PEG 5% on Uniport HP). TLC analyses were performed on silica gel 60 plates (Merck, art. 5721) using benzene-ethyl acetate (5:2). TLC scanning was performed on a Shimadzu CS-9000 dual-

wavelength flying-spot scanner [detector: 370 nm for (1) and (2)].

Synthesis of 1,3,7,9-Tetrabutylpyrimido[5,4-g]pteridine-2,4,6,8(1H,3H,7H,9H)-tetrone (2).—To a suspension of the *N*-oxide (1)² (489 mg, 1.0 mmol) in ethanol-water (7:3; 30 ml), sodium dithionite (80% purity; 326 mg, 1.5 mmol) was added and the mixture was stirred at room temperature for 2 h. After dilution of the mixture with water (50 ml), the resulting precipitate was filtered off and recrystallised from ethanol-water to give compound (2) (425 mg, 90%), m.p. 113–116 °C (Found: C, 60.1; H, 7.7; N, 17.5. C₂₄H₃₆N₆O₄·0.5H₂O requires C, 60.1; H, 7.8; N, 17.5%); *m/z* 472 (*M*⁺, 100%), 430 (*M*⁺ - 42), and 417 (*M*⁺ - 55); *v*_{max}(KBr) 1725 (C=O) and 1680 (C=O) cm⁻¹; *λ*_{max} (ε) (MeCN) 371 (1.7 × 10⁴), 364 (1.9 × 10⁴), 357 (1.7 × 10⁴), 272 (8.3 × 10³), 236 (3.1 × 10³), and 207 (5.8 × 10³) nm; *δ*_H(CDCl₃) 0.96 (6 H, t, Me), 1.00 (6 H, t, Me), 1.33–1.52 (4 H, m, -CH₂-), 1.63–1.80 (4 H, m, -CH₂-), 4.11 (4 H, br t, NCH₂-), and 4.29 (4 H, br t, NCH₂-).

Photo-oxygenation of Benzene (4a), Toluene (4b), and Anisole (4c) by 1,3,7,9-Tetrabutylpyrimido[5,4-g]pteridine-2,4,6,8-(1H,3H,7H,9H)-tetrone 5-Oxide (1) or 3-Methylpyridazine 2-Oxide (3).—(a) *Photoreaction of (4a–c) with (1).* A solution of (4a) (0.89 ml, 10 mmol), (4b) (1.06 ml, 10 mmol), or (4c) (0.27 ml, 2.5 mmol) in dry acetonitrile (5.0 ml) containing (1) (12.2 mg, 0.025 mmol) was irradiated externally. The reaction mixture was sampled every 10 min for 3 h. TLC and GC analyses of the mixtures showed the smooth consumption of (1) (by TLC densitometry, R_F 0.27) and the formation of the pyrimido[5,4-g]pteridine (2) (R_F 0.35) and the corresponding phenols, i.e., phenol (5a), cresol (5b), or methoxyphenol (5c). The maximum yields of the phenols (5a–c) and ratios of their regioisomers (by GC) were as follows: 51% (after 140 min) for (5a); 46% (after 1 h) for (5b) (*ortho:para*, 57:43); 42% (after 40 min) for (5c) (*ortho:para*, 60:40).

In the photoreaction of (4b) with (1), the formation of benzyl alcohol (6) (9%), benzaldehyde (7) (6%), and 1,2-diphenylethane (8) (3%) was observed. In the case of (4c), phenol (5a) (14%) was detected. The structures of the products (5a–c), (6), (7), and (8) were confirmed by comparison of their GC retention times and GC–mass spectral data with those of authentic samples. Their yields are based on the amount of (1) consumed.

(b) *Photoreaction of (4a–c) with (3).* Under analogous conditions a solution of (4a) (2.0M), (4b) (2.0M), or (4c) (0.5M) in dry acetonitrile containing (3) (5.0mM) was irradiated for 20 min. TLC and GC analyses of the reaction mixtures showed the complete consumption of (3) and the formation of (5a) (34%), (5b) (40%; *ortho:meta + para*, 57:43), and (5c) (42%; *ortho:meta:para*, 53:11:36). The absence of (6), (7), (8), and (5a) in the photoreaction of (4b) or (4c) with (3) was confirmed by GC analysis of the reaction mixtures.

Inhibitory Effect of Electron-transfer Quenchers on the Photo-oxygenation of (4c) by (1).—To a solution of (4c) (0.5M) and (1) (5.0mM) in dry acetonitrile, tetracyanoethylene or tetracyanoquinodimethane (0.5mM) was added and the mixture was irradiated for 3 h. The oxygenated product (5c) was not detected by GC analysis, and the starting materials (4c) and (1) were recovered. In control experiments, reaction of (4c) with the quenchers under the photochemical conditions employed was not observed to a detectable extent.

Effects of Triplet Sensitisers on the Photo-oxygenation of (4c) by (1).—(a) *With acetone.* A solution of (4c) (10.9 ml, 0.1 mol) and (1) (489 mg, 1.0 mmol) in dry acetone (189 ml) was irradiated with a 160 W low-pressure mercury arc lamp through a quartz filter at ambient temperature under argon for 5 h. TLC and GC analyses of the reaction mixture showed no appreciable reactions under the conditions employed. Irradiation of the above solution with a 400 W high-pressure mercury arc lamp through a Pyrex filter resulted in the formation of methoxyphenol (5c) in almost the same yield as in the non-sensitized experiment.

(b) *With acetophenone or benzophenone.* To a solution of (4c) (0.5M) and (1) (5.0mM) in dry acetonitrile, acetophenone or benzophenone (0.5 mol) was added and the mixture irradiated for 2 h. TLC and GC analyses of the reaction mixtures showed that the photo-oxygenation of (4c) by (1) leading to (5a) and (5c) was not accelerated by the addition of these sensitizers.

Effect of the Triplet Quencher Biacetyl on the Photo-oxygenation of (4c) by (1).—A solution of (4c) (0.5M) and (1) (5.0mM) in dry acetonitrile containing biacetyl (50mM) was irradiated for 80 min. TLC and GC analyses of the

reaction mixture showed that the photo-oxygenation of (4c) by (1) was not suppressed by the addition of this triplet quencher.

Quenching of the Fluorescence of (1).—Five samples of (1) (5.0mM) in dry acetonitrile containing (4c) (0.092, 0.184, 0.276, 0.368, and 0.460M) were prepared. The fluorescence intensities of these samples obtained by excitation at 365 nm were measured at the emission wavelength of (1) (394 nm). Stern–Volmer plots for quenching of the fluorescence of (1) by (4c) were linear and the quenching rate constant (k_q) was estimated to be ca. $2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (at room temperature) from the slope ($k_q \tau_s = 6.2 \text{ dm}^3 \text{ mol}^{-1}$) and the measured lifetime of the fluorescence (τ_s , 2.95 ns) of the *N*-oxide (1).

Determination of NIH Shift Values.—[4-²H]Toluene (deuterium content 88.9%) and [4-²H]anisole (deuterium content 91.2%) were prepared from the corresponding *para*-bromo-derivatives according to the procedure previously reported.⁵ A solution of [4-²H]toluene (2.0M) or [4-²H]anisole (0.5M) in dry acetonitrile containing (1) (5.0mM) was irradiated for 2 h. The deuterium retention (NIH shift value) in the isolated *para*-isomers of (5b) and (5c) was determined by GC–mass spectrometry: 38% for the *para*-isomer of (5b) and 18% for the *para*-isomer of (5c).

Effect of Trifluoroacetic Acid on the Photo-oxygenation of (4a) by (1).—To a solution of (4a) (0.5M) and (1) (5.0mM) in dry acetonitrile, trifluoroacetic acid (TFA) (5.0 or 15.0mM) was added and the mixtures were irradiated for 2 h. TLC and GC analyses of the reaction mixtures showed that the photo-oxygenation of (4a) by (1) was significantly accelerated by the addition of TFA, the acceleration depending on the concentration of TFA. The yields of (5a) were as follows: 4% (1.0 equiv. of TFA); 14% (3.0 equiv.), and 2% (no TFA) based on (1).

Quantum Yields for the Formation of (5a) and (5c) in the Photo-oxygenation of (4c) by (1).—The quantum yields were measured at 20 °C using potassium ferrioxalate actinometry at 365 nm. A solution of (4c) (5.0M) and (1) (5.0mM) in dry acetonitrile was purged well with argon. After irradiation for 7 min, the formation of (5a) and (5c) was assayed by GC. The quantum yields were estimated to be 0.002 for formation of (5a) and 0.007 for (5c).

Wavelength Dependence for the Photochemical Formation of (5c) from (4c) by (1).—A solution of (4c) (2.0M) and (1) (5.0mM) in dry acetonitrile was degassed carefully and irradiated with light of various wavelengths for 1 h (ca. $5.4 \times 10^8 \text{ erg/cm}^2$; $1 \text{ erg} = 10^{-7} \text{ J}$). The yields of (5c) were determined by GC analysis: 2.6% (354 nm), 3.4 (366), 2.6 (375), 0.9 (387), and 0.3 (395). A charge-transfer band was not observed in the difference UV spectrum of a mixture of (1) (5.0 mM) and (4c) (2.0M) vs. (1) (5.0mM) in dry acetonitrile.

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