

## Singlet Oxygen Photo-oxidation of some Triazapentalenes

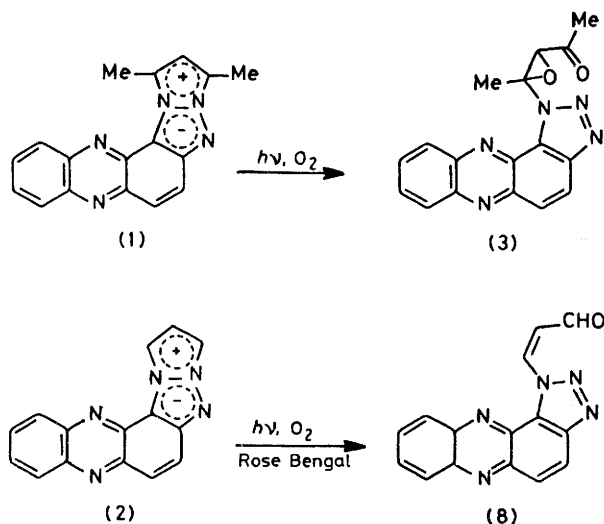
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The self-sensitized photo-oxidation of 1,3-dimethyl-5*H*-pyrazolo[1',2':1,2]-1,2,3-triazolo[3,2-*a*]phenazin-4-ium inner salt (1) leads to the cleavage of the triazapentalene moiety, yielding an epoxy-ketone. If the two methyl groups are absent, as in compound (2), the photo-oxidation takes place much better in the presence of dyes and yields an  $\alpha\beta$  unsaturated aldehyde. The first reaction is shown to involve singlet oxygen, the formation of which requires oxygen-promoted intersystem crossing from singlet to triplet (1), followed by energy transfer from the latter state. The rate of the singlet oxygen addition onto (1) was measured in some solvents, and showed no dependence on the polarity of the medium. The mechanism of the addition is discussed, taking into account also the results from the photo-oxidation of the 6,7-dihydro-derivatives of compounds (1) and (2).

NITROGEN-bridged pentalenes are betainic aromatic compounds which are isoelectronic with the pentalene dianion. Although several compounds containing polyazapentalene structures have been described,<sup>1</sup> no report on their photochemistry appears to have been published. Here we report on the photo-oxidation of the triazapentalenes (1) and (2),<sup>2</sup> which were recently obtained from phenazine derivatives.

## RESULTS AND DISCUSSION

**Preparative Photo-oxidations.**—1-(3,5-Dimethylpyrazolyl)phenazinyl-2-nitrene and 1-pyrazolyl-2-nitrene, formed from the corresponding azides or nitro-compounds, cyclize in high yield to yield 5*H*-pyrazolo-



[1',2':1,2]-1,2,3-triazolo[3,2-*a*]phenazin-4-ium inner salts (1) and (2). These triazapentalenes are remarkably stable both thermally and photochemically. However, both (1) and, more slowly, (2) are transformed on irradiation in the presence of oxygen.

In fact, the preparative irradiation of (1) in various solvents (MeCN, CHCl<sub>3</sub>, Me<sub>2</sub>CO) gave in high yield a single compound (3). This was shown by elemental analysis to have incorporated two atoms of oxygen, while spectroscopic properties showed the presence of a

carbonyl group and the occurrence of a modification of the pyrazole ring (higher field absorption of H-4 of the pyrazole moiety). Further information about the structure of this compound was given by quantitative form-

TABLE 1

Preparative photo-oxidations in acetonitrile

Starting material	Sensitizer	Product (yield %)
(1)	None	(3) (82)
(1)	Rose Bengal	(3) (80)
(2)	Rose Bengal	(8) (42)
(11)	Rose Bengal	(13) (42)
(12)	Rose Bengal	(14) (58)

ation of 1,2,3-triazolo[4,5-*a*]phenazine (4) by catalytic hydrogenation or reaction with piperidine at room temperature. By treatment of (3) with ethanolic hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine 3-hydroxy- and 3-ethoxy-pentane-2,4-dione trapped as 3,5-dimethyl-1-(2,4-dinitrophenyl)-4-hydroxy- (or ethoxy-) pyrazole were obtained in addition to (4).

This evidence showed the presence of the 2,3-epoxy-4-oxo-pentyl group bound to a nitrogen atom. The definitive choice of formula (3), excluding formula (7), was possible owing to the presence of a significant peak at  $m/e$  291 ( $M - N_2$ ) in the mass spectrum of this compound.

In comparable conditions (2) was only very slowly

TABLE 2

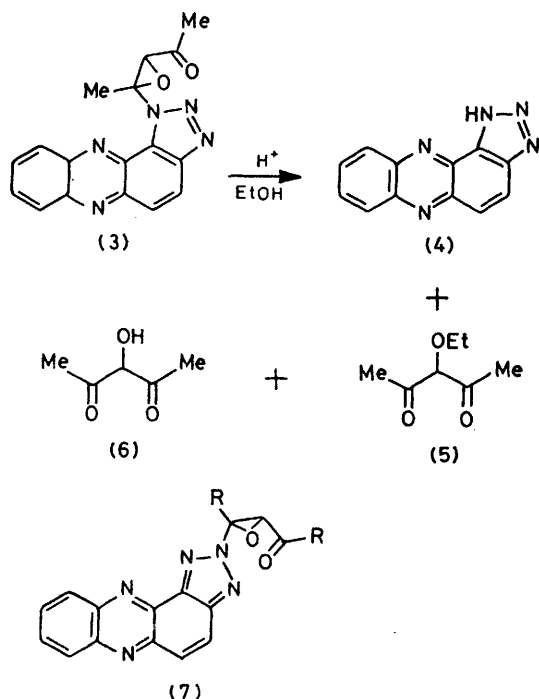
Relevant spectroscopic data of the photo-products

Product	<sup>1</sup> H N.m.r. <sup>a</sup>	Me groups	I.r. <sup>b</sup>
(3)	H-3 3.9s	2.12s 2.3s	1 710s
(13)	H-3 3.8s	2.2s	1 720s
(8)	6.1dd ( <i>J</i> 7.5, 11)	CHO 11d ( <i>J</i> 7.5)	1 670s, 1 640m
(14)	5.9dd ( <i>J</i> 7.5, 10)	11d ( <i>J</i> 7.5)	1 670s, 1 635m

<sup>a</sup> In CDCl<sub>3</sub>; chemical shifts in  $\delta$ ; coupling constants in Hz.  
<sup>b</sup> Nujol mull.

photo-oxidized, yielding a complex mixture. However (2) could be photo-oxidized in good chemical yield to a single compound (8) by sensitization with Rose Bengal. Elemental analysis showed that only one oxygen atom had been incorporated. The spectroscopic properties

of this compound showed the presence of an  $\alpha,\beta$  unsaturated aldehyde group. Formula (8) was definitively indicated by the formation of 1,2,3-triazole[4,5-*a*]-phenazine (4) on treatment with piperidine, and by the loss of  $N_2$  from the molecular ion in the mass spectrum.



Thus the photo-oxidation of (1) differs from that of (2) not only because different numbers of oxygen atoms are incorporated, but also because no sensitizer is required. We established that the photo-oxidation of (1) is a self-sensitized reaction occurring *via* singlet oxygen, on the basis of the following observations: (i) the rate of the photo-oxidation corrected for partial light absorption depends on the concentration of (1). Therefore compound (1) intervenes at least in two steps of the reaction: (ii) the photo-oxidation sensitized with Rose Bengal yields the same products as the unsensitized one: (iii) the rate of the photo-oxidation is strongly slowed down by adding small amounts of typical singlet oxygen physical quenchers, such as tertiary amines: and (iv) the photo-oxidation is quenched by diphenylisobenzofuran

TABLE 3  
Spectroscopic data of compound (1)

Solvent	$\lambda_{\text{max.}} (\epsilon)$		Fluorescence quantum yield (air saturated)
	First absorption band	Fluorescence	
Cyclohexane	596nm ( $8.3 \times 10^4$ )	603nm	.25
Chloroform	573 ( $7.4 \times 10^4$ )	665	.008
Chloroform-methanol	575 ( $7.6 \times 10^4$ )	670	.001

(DPIBF), a known chemical acceptor of singlet oxygen, which is in turn photo-oxidized under these conditions.

This conclusion is strongly supported by kinetic data (see below).

**Mechanistic Investigations.**—The self-sensitized photo-oxidation of (1) was examined in more detail for information on the energy transfer from excited (1) to oxygen and the reaction of singlet oxygen with ground-state

TABLE 4

Quantum yields in air saturated solvents

Solvent	$\phi_A$	$\phi_{(s)}^*$
Cyclohexane	.21	.064
Chloroform	.037	.013
Chloroform-methanol (8 : 2)	.053	.002

\* At  $[I] = 1 \times 10^{-6}M$ .

(1). Tables 3 and 4 gather the most significant spectroscopic characteristics of compound (1), as well as measurements of the efficiency of the oxygen sensitization from (1) in various solvents ( $\phi_A$ ).

The latter data were obtained measuring the photo-oxidation of DPIBF by sensitization with (1). As

TABLE 5

Quantum yield in various conditions relative to the yields in air saturated solvents

	Solvent	Air equilibrated	Degassed	Oxygen equilibrated	MeI added (5%)
		1	1.35	0.49	0.65
$\phi_F$	Cyclohexane	1	1.11	0.91	0.8
	Chloroform	1	1.11	0.91	0.8
$\phi_A$	Cyclohexane	1	2.45	1.35	1.35
	Chloroform	1	6.5	1.5	1.5
$\phi_{(s)}$	Cyclohexane	1	2.1	1.35	1.35
	Chloroform	1	4.4	1.5	1.5

DPIBF is known to react with singlet oxygen with no physical quenching and it was shown to be much more reactive than (1), the limiting value of the efficiency of DPIBF photo-oxidation obtained from measurements in the presence of growing amounts of this substrate

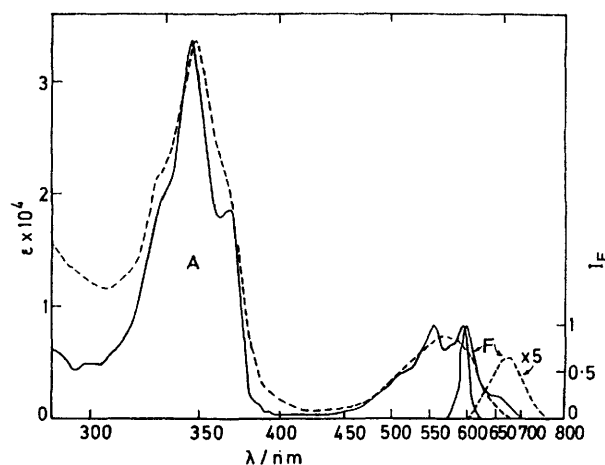
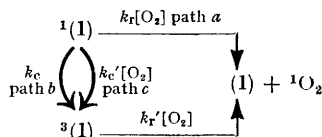


FIGURE 1 Absorption (A) and corrected fluorescence (F) spectra of compound (1) at room temperature; —, in cyclohexane; ----, in chloroform

coincides with  $\phi_A$ . Table 5 gathers the values, under various conditions (relative to the values obtained in air-saturated solvents, taken equal to 1), of the fluorescence quantum yield ( $\phi_F$ ), of the oxygen-sensitized quantum yield ( $\phi_A$ ), and of the rate of the self-sensitized photo-oxidation.

The polarity of the solvent strongly affects the nature of the singlet excited state of (1). In fact, in protic solvents  $\phi_F$  strongly decreases, while the fluorescence spectrum is altered and the Stoke's shift between absorption and emission spectra, which is negligible in non-polar solvents, becomes strong\* (see Table 2 and Figure 1). Thus, while in apolar solvents the singlet excited state has  $\pi, \pi^*$  character and the decay by fluorescence is important, in polar solvents the non-radiative internal conversion to the ground state is predominant, as the internal charge transfer, due to the betainic structure of compound (1), is facilitated.

About the mechanism of the energy transfer from excited (1) to oxygen, the following statements can be made. First, an efficient interaction between oxygen and singlet (1) is apparent.† In fact, a decrease of the fluorescence and a strong increase of  $\phi_A$  are observed in passing from air-saturated to oxygen-saturated solvents. The increase of  $\phi_A$  is consistent only with the hypothesis that the interaction between singlet (1) and oxygen is involved in the sensitization of the latter. In fact an increase in the oxygen concentration above the amount dissolved in air-saturated solvents would hardly affect the singlet oxygen yield,<sup>3a</sup> and thus  $\phi_A$ , unless the triplet lifetime is unreasonably short.‡ On the other hand, the increase of  $\phi_A$  by external heavy-atom effects shows that triplet (1) can sensitize oxygen. Therefore, rather than through a spin-forbidden direct energy transfer from the singlet state (path *a*), the sensitization implies oxygen-promoted intersystem crossing from singlet to triplet (1) (path *c*), and energy transfer from the latter state. In unperturbed conditions the intersystem crossing (path *b*) is negligible.§ This behaviour is reminiscent of that found for some aromatic hydrocarbons.<sup>3b</sup>



It may be seen in Table 4 that the higher values of  $\phi_A$  in non-polar solvents correspond to higher values of the photo-oxidation yield. The different efficiencies of the photo-oxidation in different solvents would thus

\* The same effect was also observed with other polar solvents.

† The ratio between the rate of reaction of the singlet excited state of (1) with oxygen and the rate of unimolecular decay of this state is *ca.* 260 : 1. Therefore, if the singlet lifetime is evaluated to be *ca.* 50 ns, from the absorbance spectrum, the rate of reaction with oxygen is *ca.*  $5 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$ .

‡ Indeed, the interaction of singlet (1) with oxygen leads in the end to sensitization of the latter in high yield. In fact, a value of 5 is obtained for the product

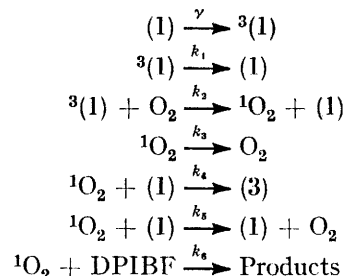
$$\frac{(\phi_A)_{\text{O}_2\text{-saturated}} \times (\phi_F)_{\text{air-saturated}}}{(\phi_A)_{\text{air-saturated}} \times (\phi_F)_{\text{O}_2\text{-saturated}}}$$

in cyclohexane. If the interaction of singlet (1) with oxygen were the only source of singlet oxygen, this product should equal the ratio between the concentrations of  $\text{O}_2$  in the two conditions, that is 5 : 1.

§ A direct proof that the energy transfer takes place from the triplet state could not be obtained, as no selective quencher could be found in this case, due to the low energy of singlet (1). This technique was used by Stevens for some aromatic hydrocarbons.<sup>3b</sup>

appear to depend rather on the efficiency of the oxygen sensitization than on the rate of reaction of singlet oxygen with ground-state (1). To have more quantitative information, the rate of the latter process was measured under different conditions.

The simplest kinetic scheme is:



where  $\gamma$  is the yield (depending on the oxygen concentration) of triplet (1). The quantum yield of the self-sensitized photo-oxidation is then:

$$\phi_{(3)}(\text{self-sens}) = \frac{\gamma k_2 [\text{O}_2] k_4 [1]}{(k_1 + k_2 [\text{O}_2]) \{k_3 + (k_4 + k_5) [1]\}} = \frac{\phi_A k_4 [1]}{k_3 + (k_4 + k_5) [1]}$$

If now the yield of the Rose Bengal-sensitized photo-oxidation is measured in conditions in which the light is only absorbed by the sensitizer (the experiments were done in  $\text{CHCl}_3$ -MeOH (8 : 2), due to the Rose Bengal solubility), the following expression is valid:

$$\phi_{(3)}(\text{sensitized}) = \frac{\phi_s k_4 [1]}{k_3 + (k_4 + k_5) [1]}$$

where  $\phi_s$  is the quantum yield of the energy transfer from the sensitizer to oxygen (which is known in the case of Rose Bengal). From the reciprocal plot in Figure 2,  $\beta = k_3/k_4$  can be obtained, which allows the determination of  $k_4$  from the known value of  $k_3$ . A reliable measurement of  $k_5$  is not possible, due to the low value of  $\phi_{(3)}$ . If now dependence of the quantum yield of the self-sensitized photo-oxidation of (1) on the substrate concentration is studied, the value  $\phi_A \beta$  is obtained:  $\phi_A$  being known from the previous experiments,  $\beta$ , and thus  $k_4$ , may be calculated also from this measure.

It may be seen that the two values for  $k_4$  are very near in the mixed solvent  $\text{CHCl}_3$ -MeOH. Still another independent check on  $k_4$  may be obtained by the method of Foote,<sup>8a</sup> studying the competition between (1) and DPIBF in the Rose Bengal-sensitized photo-oxidation, the rate of oxidation of DPIBF being known. The value thus obtained for  $k_4$  is lower; however, considering the difference of the approaches used, the concordance may be considered satisfying.

The self-sensitized photo-oxidation of (1) was studied also in pure  $\text{CHCl}_3$  and in cyclohexane (Figure 2). The values for  $k_4$  thus obtained show a limited variation in going from polar to non-polar solvents. This is what is usually observed in singlet oxygen reactions, and

TABLE 6  
Kinetic data on the photo-oxidation

Substrate	Sensitizer	Solvent	Measure	Calculated value	Notes
(1)	Rose Bengal	Chloroform-methanol (8 : 2)	$\beta\phi_s^{-1} = 1.2 \times 10^{-3}$	$k_4 = 6.3 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$	a
(1)	None		$\beta\phi_A^{-1} = 1.71 \times 10^{-2}$	$k_4 = 6.4 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$	b
(1), DPIBF	Rose Bengal		$k_6/k_4 = 19$	$k_4 = 4.2 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$	c
(1)	None	Chloroform	$\beta\phi_A^{-1} = 1.2 \times 10^{-2}$	$k_4 = 3.7 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$	d
(1)	None	Cyclohexane	$\beta\phi_A^{-1} = 6.2 \times 10^{-3}$	$k_4 = 4.5 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$	e

<sup>a</sup> Taking  $\phi_s = 0.76$  (ref. 4),  $k_3 = 5.8 \times 10^4 \text{ s}^{-1}$  (ref. 5, 6). <sup>b</sup>  $\phi_A$  From Table 4. <sup>c</sup> Taking  $k_6 = 8 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$  (ref. 7).  
<sup>d</sup> Taking  $k_3 = 1.66 \times 10^4 \text{ s}^{-1}$  (ref. 5),  $\phi_A$  from Table 4. <sup>e</sup> Taking  $k_3 = 5.9 \times 10^4 \text{ s}^{-1}$  (ref. 5),  $\phi_A$  from Table 4.

certainly is better suited to a concerted reaction than to a reaction occurring through intermediates more distinctly polar than the starting compound.

As for the mechanism of the singlet oxygen addition onto (1) to yield (3), the following considerations can be made. Cycloaddition to methyl acetylenedicarboxylate was observed to take place on the triazapentalenes (1) and (2), but it mainly occurred on the positions 1 and 13b ('azomethinylidic' site),<sup>8b</sup> while (3) and (8) cannot be formed from an initial adduct (9). On the contrary

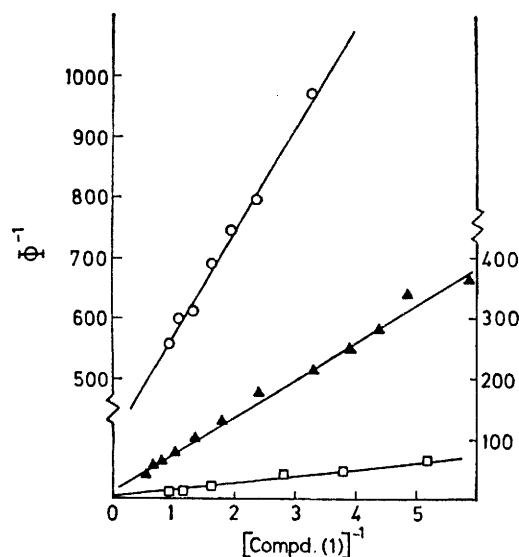
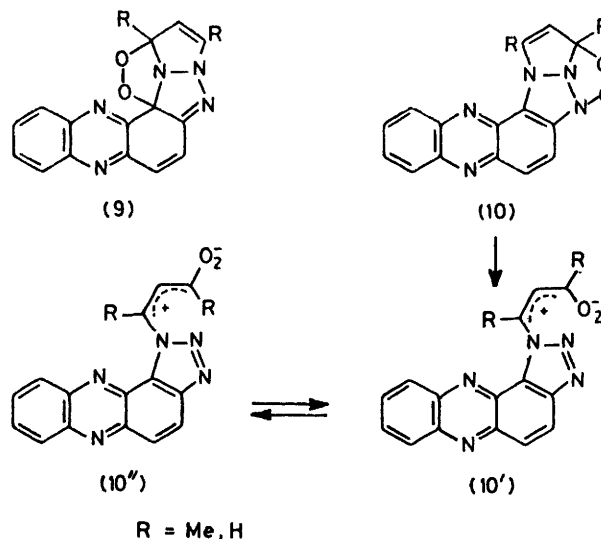


FIGURE 2 Reciprocal quantum yield of the photo-oxidation of (1) vs. the reciprocal of the concentration of the substrate (after correction for partial absorption); □, in cyclohexane; ▲, in chloroform; ○, in chloroform-methanol (8 : 2)

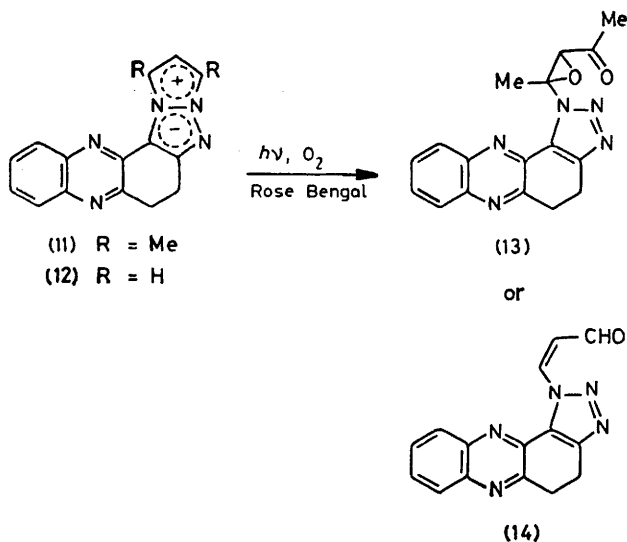
the formation of (7) from (9) would be conceivable. By analogy with a reaction observed in another case,<sup>9</sup> the photo-oxidation may be better envisaged as an addition of  $^1\text{O}_2$  on positions 3 and 5 (the 'azomethiniminic' site) leading to the carbonyl oxide (10')  $\rightleftharpoons$  (10''). In this intermediate, a double bond is present in the allylic position; therefore, a considerable rotation barrier is expected between the different conformers. If R = Me, the preferred conformation will be one such as (10'), due to the encumbrance of the methyl group, while if R = H a conformation such (10'') would be preferred. Thus, on this basis the intramolecular attack to yield an epoxyketone from (1) is understandable, as well as the formation of an  $\alpha\beta$ -unsaturated carbonyl compound in the case of (2).

To support our hypothesis on the role of the alkyl

group on the further reaction of the initial photo-oxide, the photo-oxidation of compounds (11) and (12), in which the structure characteristics of (1) and (2) are almost unchanged, was examined. As expected, the sensitized photo-oxidation of (11) yielded (13), while (14) was obtained from (12).



Thus, it may be inferred that in the case of the photo-oxidation of (2) and (12) one oxygen atom is ultimately transferred to the medium, the conformation of the carbonyl oxide being unsuitable to an intramolecular attack. This mechanism appears attractive, although different ones may be envisaged.





## EXPERIMENTAL

The triazapentalenes (1) and (2) were prepared as previously reported.<sup>2</sup> Compounds (11) and (12) were obtained by catalytic hydrogenation of (1) and (2) as described elsewhere.<sup>8b</sup> Commercial (Merck and Carlo Erba) spectroscopic grade solvents were used after distillation.

**Apparatus.** The u.v.-visible spectra were recorded on a Perkin-Elmer 200 spectrophotometer and the fluorescence spectra either on a Aminco-Bowman SPF or on a Perkin-Elmer MF 181 spectrofluorimeter. <sup>1</sup>H N.m.r. spectra were determined on a Perkin-Elmer R-12 instrument using SiMe<sub>4</sub> as internal standard; i.r. spectra on a Perkin-Elmer 257 spectrophotometer; and mass spectra on a Du Pont 492 spectrometer operating at a source temperature of 190 °C (75 eV).

**Preparative Photo-oxygenation.** A solution of the appropriate pentalene (100 mg) and Rose Bengal (30 mg), when required, in acetonitrile (150 ml) was irradiated at 18 °C by means of a medium-pressure mercury lamp (Philips HPK 125 W) through a yellow filter ( $\lambda_{\text{trans}} \geq 500$  nm) until complete conversion. The solution was evaporated under reduced pressure and the residue dissolved in a little chloroform. This solution was washed with water in order to eliminate the dye, dried, and chromatographed on silica gel (Merck 60 HR) eluting with benzene-ethyl acetate (7:3). The following products were obtained (the yields are reported in Table 1). From compound (1): 4-[1-(1,2,3-triazolo[4,5-a]phenazinyl)]-3,4-epoxypentan-2-one (3), as white needles, m.p. 193–195 °C (from ethanol) (Found: C, 63.8; H, 4.3; N, 22.1. C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub> requires C, 63.9; H, 4.1; N, 21.9%). From compound (2): 3-[1-(1,2,3-triazolo[4,5-a]phenazinyl)]propenal (8), as white needles, m.p. 238 °C (from nitroethane) (Found: C, 65.3; H, 3.3; N, 25.3. C<sub>15</sub>H<sub>9</sub>N<sub>5</sub>O requires C, 65.4; H, 3.3; N, 25.4%). From compound (11): 4-[1-(4,5-dihydro-1,2,3-triazolo[4,5-a]phenazinyl)]-3,4-epoxypentan-2-one (13) as white needles, m.p. 201–202 °C (from nitroethane) (Found: C, 63.4; H, 4.6; N, 21.8. C<sub>17</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub> requires C, 63.5; H, 4.7; N, 21.8%). From compound (12): 3-[1-(4,5-dihydro-1,2,3-triazolo[4,5-a]phenazinyl)]propenal (14) as ivory plates, m.p. 182 °C (from nitroethane) (Found: C, 64.7; H, 4.1; N, 25.2. C<sub>15</sub>H<sub>11</sub>N<sub>5</sub>O requires C, 65.0; H, 4.0; N, 25.2%).

**Catalytic Hydrogenation of Compound (3).**—Compound (3) (50 mg) in ethanol (10 ml) was hydrogenated at room temperature in the presence of 10% palladium-charcoal. The catalyst was filtered off, and the solvent evaporated to yield 1,2,3-triazolo[4,5-a]phenazine (4), (30 mg), melting above 300 °C, identical in its spectroscopic characteristics with an authentic sample.<sup>10</sup>

**Reaction of Compounds (3) and (8) with Piperidine.**—Compound (3) (50 mg) was dissolved in piperidine (1 ml). A dark red colour developed, and after 2 h the amine was evaporated at reduced pressure and the residue was washed with ethanol, yielding colourless (4) (28 mg). Compound (8) was dissolved in the same manner and the red solution was left at room temperature for 1 day. After evaporation of the amine the oily residue was chromatographed on silica gel eluting with benzene-ethyl acetate (7:3), yielding compound (4) (20 mg).

**Hydrolysis of Compound (3) in the Presence of 2,4-Dinitrophenylhydrazine.**—To a hot solution of 2,4-dinitrophenylhydrazine (200 mg, 2 mmol) in anhydrous ethanol (90 ml) (3) (320 mg, 1 mmol) and 3N HCl (6 ml) were added. The mixture was refluxed for 1 h and then left overnight. The

precipitate was filtered off and stirred with 5% aqueous Na<sub>2</sub>CO<sub>3</sub> (2 × 10 ml). The extracts were acidified with acetic acid, the cream-coloured precipitate was collected and recrystallized from dimethylformamide to yield 1,2,3-triazolo[4,5-a]phenazine (4) (160 mg). The original ethanolic solution was evaporated, the residue dissolved in ethyl acetate (35 ml) and washed with 5% aqueous Na<sub>2</sub>CO<sub>3</sub> (2 × 10 ml) and then with water. The organic layer was dried and the solvent distilled off. The residue was chromatographed on silica gel (Merck 60 HR) eluting with benzene-ethyl acetate (9:1 to 7:3), to yield 1-(2,4-dinitrophenyl)-2,4-dimethyl-3-ethoxypyrazole (60 mg) as yellow plates, m.p. 106–107 °C (from cyclohexane) (Found: C, 51.3; H, 4.8; N, 18.2. C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O<sub>5</sub> requires C, 51.0; H, 4.6; N, 18.3%), and 1-(2,4-dinitrophenyl)-2,4-dimethyl-3-hydroxypyrazole (130 mg) as orange needles m.p. 188–189 °C (from ethanol) (Found: C, 47.6; H, 3.7; N, 19.9. C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>O<sub>5</sub> requires C, 47.5; H, 3.6; N, 20.1%).

**Measurements.**—For the measurement of the reaction quantum yield, 3-ml samples were irradiated in spectrophotometric cells (1 cm) by means of a super-high-pressure mercury lamp (Osram HBO 200W/4) equipped with a Splinder and Hoyer interference filter ( $\lambda_{\text{max}}$  543 nm,  $\Delta\lambda_{\frac{1}{2}}$  9 nm) or a liquid NiSO<sub>4</sub> filter, determining the chemical transformation by spectrophotometric measurements.

In experiments with solutions containing both DPIBF and (1) the disappearance of the former was determined by measuring the optical density at 420 nm [where (1) absorbs very little, see Figure 1], and the disappearance of the latter by measurements at 550–600 nm, according to the solvent employed. The light intensity was monitored by potassium Reineckate actinometry.<sup>11</sup> Fluorescence quantum yields were determined relative to Rhodamine B.<sup>12</sup> Samples for measurements in the absence of oxygen were prepared using four freeze-pump (10<sup>−4</sup> Torr)-thaw cycles. Oxygen was then admitted for measurements in oxygen-saturated solutions.

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