($CDCl_3$) δ 3.05 (br t, 2 H, Ar CH_2), 3.79, 3.97, and 4.05 (3 s, 3 H each, OCH_3), 3.7-4.3 (masked signal, 2 H, NCH_2), 6.57 (s, 1 H, Ar H), 8.81 (d, J = 8 Hz, 1 H, =CH).

Run 2. Keto ester **22** (0.12 g, 0.30 mmol) was combined with LiCl (0.02 g, 0.47 mmol), H_2O (0.2 g, 11.1 mmol), and Me_2SO (2 mL). The mixture was heated at 100 °C for 4 h. After the usual workup[24] 50 mg (80%) of **25** was obtained.

Run 3. A mixture of **22** (0.21 g, 0.53 mmol), $Ba(OH)_2 \cdot 8H_2O$ (0.42 g, 1.40 mmol), EtOH (3 mL), and H_2O (4 mL) was refluxed for 14 h. The solvent was removed, and the residue was taken up in cold 6 N HCl (10 mL). The solution was washed with Et_2O, basified with cold 2 N NaOH solution, and extracted with Et_2O. Evaporation of the dried extracts gave 85 mg (70%) of **25**.

Registry No. **1**, 84752-50-1; **2**, 84752-35-2; **3**, 84752-36-3; **4**, 84752-37-4; **5**, 84752-38-5; **6**, 79314-67-3; **8**, 84752-39-6; **8**·HCl, 84752-52-3; **9**, 84774-87-8; **9**·HCl, 84752-51-2; **10**, 84752-40-9; **10**·HCl, 84752-54-5; **11**, 84752-41-0; **12**, 84774-88-9; **13**, 84752-53-4; **14**, 84752-42-1; **15**, 84752-44-3; **17**, 84752-43-2; **18**, 84752-45-4; **19**, 84752-46-5; **20**, 84752-47-6; **20**·HCl, 84786-78-7; **21**, 84752-48-7; **22**, 84752-49-8; **25**, 13338-60-8; **25**·HCl, 84786-79-8; ethyl 2,2-dimethylacetoacetate, 597-04-6; mescaline, 54-04-6; ethyl 2-(chloroformyl)-2-methylpropionate, 64244-87-7; ethyl chloride, 75-00-3; ethyl acrylate, 140-88-5.

Photooxidation of Some Triaza- and Tetraazabenzopentalenes

Angelo Albini, Gian Franco Bettinetti,* and Giovanna Minoli

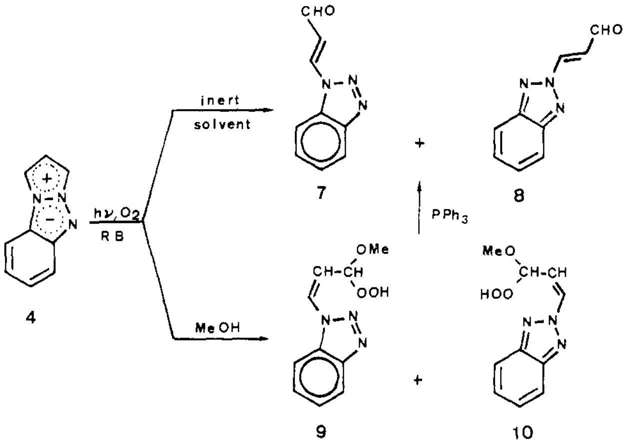
Istituto di Chimica Organica dell'Università, 27100 Pavia, Italy

Received July 22, 1982

The dye-sensitized photooxidation of some tri- and tetraazabenzopentalenes is reported. The pyrazolobenzotriazole **4** is converted to a mixture of 3-(1-benzotriazolyl)- and 3-(2-benzotriazolyl)propenals (**7** and **8**) in inert solvents, while in methanol the corresponding methoxy hydroperoxides **9** and **10** are formed. The products from 1,2,3-triazolo[1,2-*a*]benzotriazole (**5**) are the diazabutadiene derivative **11** and *cis,cis*-mucononitrile; it is suggested that these arise from the intermediate 2-benzotriazolyl nitrene. These reactions of **4** and **5** are rationalized by assuming the formation of intermediate carbonyl oxides. 1,2,3-Triazolo[2,1-*a*]benzotriazole (**6**) does not react under these conditions. The rates of reaction of azapentalenes **1a**, **2**, **4**, and **5** with singlet oxygen have been determined.

Information on the question of the intermediates involved in the addition of singlet oxygen to organic substrates can in principle be obtained by study of reactions of dipolar substrates. Although singlet oxygen should add to 1,3 dipoles in the same way as to dienes, on the basis of similarities between their MO correlation diagrams,[1] the former processes are poorly documented. Diazo derivatives,[1-5] nitrones,[6] sulfur and pyridinium ylides,[7] and azomethinimines[8] have been shown to undergo photooxidation. However, in every case the photoreaction results in fragmentation, providing only indirect understanding of the primary addition step. Some heterocyclic betaines, namely, sydnones and related compounds,[9-13] have also been studied, and here too the reactions resulted in extensive fragmentation.

Scheme I



Another class of stable heterocyclic betaines that can be considered in studies of addition of singlet oxygen is the azapentalene mesoionic betaines, which have not been extensively investigated despite the relatively easy accessibility of several members.[14] We have previously shown that some triazapentalene derivatives such as 5*H*-pyrazolo[1′,2′:1,2]1,2,3-triazolo[5,4-*a*]phenazin-4-ium inner salts (**1a,b**)[15] and 1,3-dimethylpyrazolo[1,2-*a*]benzotriazole

---

(1) Bethell, D.; Mc Keivor, R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 327.

(2) Highley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 3330.

(3) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1980**, *21*, 359.

(4) Ando, W.; Miyazaki, H.; Kohmoto, S. *Tetrahedron Lett.* **1979**, 1317.

(5) Sekiguchi, A.; Kabe, Y.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1979**, 233, 343.

(6) Ching, T. Y.; Foote, C. S. *Tetrahedron Lett.* **1975**, 3771.

(7) Ando, W.; Kohmoto, S.; Nishikawa, K. *J. Chem. Soc., Chem. Commun.* **1978**, 894.

(8) Schulz, M.; Grossmann, N. *J. Prakt. Chem.* **1976**, *318*, 575.

(9) Bhat, V.; Dixit, V. M.; Ugarker, B. G.; Trozzolo, A. M.; George, M. V. *J. Org. Chem.* **1979**, *44*, 2957.

(10) Dixit, V. M.; Bhat, V.; Trozzolo, A. M.; George, M. V. *J. Org. Chem.* **1979**, *44*, 4169.

(11) Toubro, N. H.; Hauser, B.; Harrit, N.; Holm, A.; Patts, V. T. *Tetrahedron* **1979**, *35*, 229.

(12) Kato, H.; Tani, K.; Kummisawa, Y.; Tamura, Y. *Chem. Lett.* **1980**, 721.

(13) Gotthard, H.; Hun, O. M.; Sohay-Tribbensee, S. *Chem. Ber.* **1981**, *114*, 285.

(14) Ramsden, C. *Tetrahedron* **1977**, *33*, 3203.

(15) Albini, A.; Bettinetti, G. F.; Minoli, G.; Pietra, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, *21*, 2904.

Table I. Photooxidation of Polyazapentalenes 4-6

substrate	solvent	dye^{a,b}	irradiation time	% conversion	products (% yield)
4	MeCN	RB	10 min	60	**7** (40), **8** (18)
	MeOH	RB	10 min	63	**9** (65), **10** (35)^{c}
	MeOH	RB	10 min	63	**7** (52), **8** (19)^{d}
5	MeCN	RB	1 h	40	**11** (18), **12** (18)
	CH_2Cl_2	TPP	1 h	8	**11** (30), **12** (60)
	CH_2Cl_2	TPP	4 h	50	**11** (8), **12** (25)
6	MeCN	RB	1 h	2	*e*
	CH_2Cl_2	TPP	1 h	1	*e*

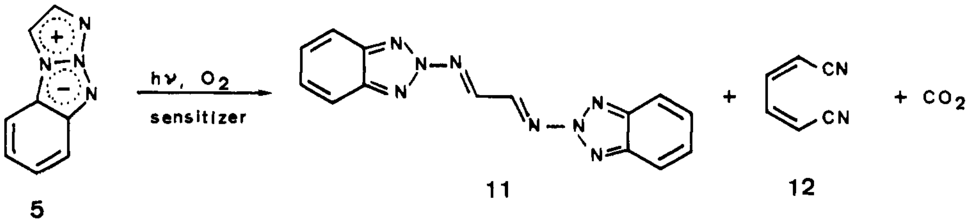
^{a} Rose Bengal, 0.1 mg/mL. ^{b} Tetraphenylporphyrin, 0.1 mg/mL. ^{c} NMR evaluation of the irradiation mixture. ^{d} After treatment with triphenylphosphine (equimolecular amount) at room temperature. ^{e} No evidence for the formation of new products by TLC.

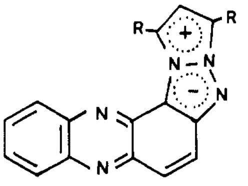
Table II. ^{1}H NMR and IR Spectral Data for New Compounds

compd	NMR^{a} H(1)	H(2)	H(3)	MeO	IR^{b}
7	9.9 (d, 8)	7 (dd, 8, 17)	8.5 (d, 17)		1675 (s), 1635 (m)
8	9.95 (d, 8)	7.3 (dd, 8, 16)	8.3 (d, 16)		1685 (s), 1635 (m)
9	6.3 (d, 8)	5.95 (dd, 8, 10)	7.2 (d, 10)	3.6 (s)	3400 (br)
10	6.7 (d, 7)	4.1 (dd, 7, 8)	7.9 (d, 8)	3.65 (s)	3400 (br)
11	9.4 (s, CH=N)				1580 (s)

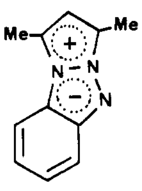
^{a} In $CDCl_3$ with chemical shift values in parts per million (δ) vs. internal Me_4Si; multiplicity and coupling constants in hertz are given in parentheses. ^{b} Nujol mull; values given in reciprocal centimeters.

Scheme II

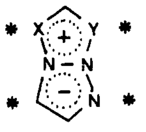




1a R = Me
b R = H



2



3 X,Y = CH,N

(**2**)[16] are useful models for study of the reaction of singlet oxygen with dipolar systems, as they give well-characterized products of photooxidation without fragmentation.

Since the chemical properties of heteropentalenes are determined by a nonbonding orbital with nonvanishing coefficients at the four centers adjacent to the ring junction[14] (starred in structure **3**), it appeared of interest to explore the effect of substituting a nitrogen for a carbon atom in the heteropentalene system, thus changing both the energy of the NBO and the reacting center. We here report on the photooxidation of pyrazolo[1,2-*a*]benzotriazole (**4**), 1,2,3-triazolo[1,2-*a*]benzotriazole (**5**), and 1,2,3-triazolo[2,1-*a*]benzotriazole (**6**).

Photooxidation of **4** in acetonitrile, sensitized by Rose Bengal (RB), gave two products (Scheme I), which were separated by chromatography and obtained as crystalline solids in yields of 40% and 18%. These compounds were identified on the basis of elemental analyses and spectroscopic properties as 3-(1-benzotriazolyl)propenal (**7**) and 3-(2-benzotriazolyl)propenal (**8**), respectively. The results are similar to those obtained in the photooxidation of the dimethyl analogue **2**.[16]

Photooxidation of **4** in methanol also gave two products, the methoxy hydroperoxides **9** and **10**, which are also derivatives of 1-benzotriazole and 2-benzotriazole. The former predominated in the reaction mixture, as indicated by its NMR spectrum. These products were rather labile, and we could isolate only one of them by chromatography. They were readily converted into propenals **7** and **8** by treating the crude reaction mixture with triphenylphosphine at room temperature[17] (data are collected in Tables I and II).

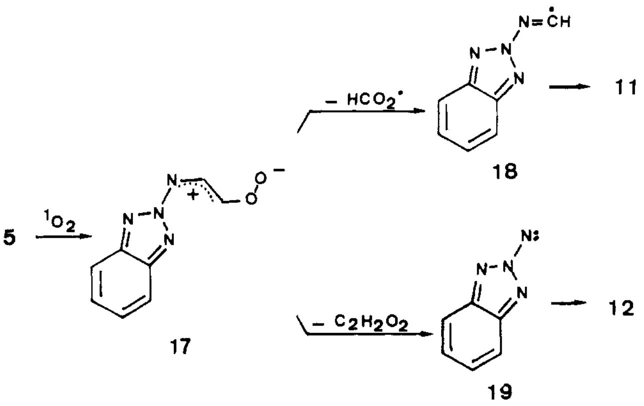
Photooxidation of **5** (Scheme II) followed a different course, not yielding any stable photooxide. Irradiation in the presence of RB or tetraphenylporphyrin (TPP) effected a very slow reaction. Two products were formed and were separated by chromatography to provide crystalline solids, one of which showed a green fluorescence. From the NMR spectrum the latter appeared to be a derivative of 2-benzotriazole, the only other absorbance being a low-field singlet signal. In the mass spectrometer the molecular ion (*m/e* 290) fragmented to give a peak at *m/e* 171 (base peak), which corresponds to loss of a neutral benzotriazole moiety, supporting the assigned structure **11**. The rigid skeleton of this structure is in accord with the observed UV spectrum and the green fluorescence. The other product, which showed a CN signal in its IR spectrum, was identified as *cis,cis*-mucononitrile (**12**) by elemental analysis and spectra. The relative yields of **11** and **12** depended on the solvent (Table I). Long irradiation

---

[16] Albini, A.; Bettinetti, G. F.; Minoli, G.; Vasconi, G. *J. Chem. Soc., Chem. Commun.* **1981**, 1089.

[17] Rigaudy, J.; Sparfel, D. *Bull. Soc. Chim. Fr.* **1972**, 3441.

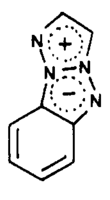
Scheme III



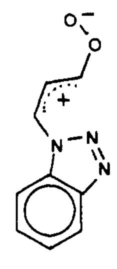
times did not increase the overall yield. Inasmuch as the formation of these products involves fragmentation of the starting material, the oxygen flowing from the irradiation vessel was examined, and carbon dioxide was detected (Scheme II).

The reaction mixture from irradiation of **6** in the presence of RB or TPP contained only starting material; TLC did not indicate formation of any new products, even after prolonged irradiation.

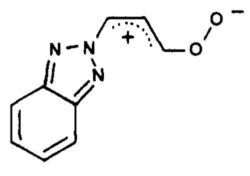
It has previously been shown that the dye-sensitized photooxidation of **1** and **2** involves singlet oxygen and that it preceeds through formation of carbonyl oxides.[15,16] Our findings can be interpreted by the same mechanism. Thus, **4** can add singlet oxygen to yield the two carbonyl oxides **13** and **14**. These intermediates can react with methanol to give methoxy hydroperoxides **9** and **10** or, in nonnucleophilic solvents, can lose an oxygen atom to form propenals **7** and **8**. As has been discussed in the photooxidation of the dimethyl derivative **2**,[16] only in the presence of hindering substituents should the carbonyl oxides become nonplanar and close intramolecularly to 1,2-dioxoles (e.g., **15**), finally rearranging to epoxy ketones (e.g., **16**). In the case of **4**, however, nothing should prevent the carbonyl oxides from assuming the more-stabilized planar trans conformations **13** and **14**, which should not rearrange but should undergo intermolecular oxygen transfer to give the propenals.



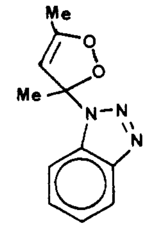
6



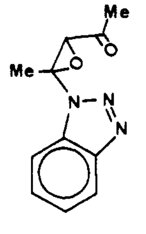
13



14



15

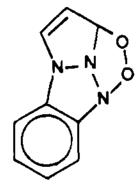


16

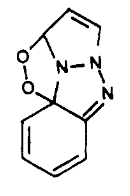
The results of the photooxidation of **5** can be similarly rationalized by assuming the formation of carbonyl oxide **17** (Scheme III), which could undergo fragmentation. Homolytic cleavage with loss of a formyloxy radical, which can fragment to give carbon dioxide, should be favored by the stability of the imino radical **18**. This radical could then dimerize to the 1,4-diazabutadiene derivative **11**.

The formation of *cis,cis*-mucononitrile can be rationalized by assuming that a $C_2H_2O_2$ fragment is lost from **17** to give 2-benzotriazolyl nitrene (**19**), which has been reported to lose nitrogen to give **12**.[18,19]

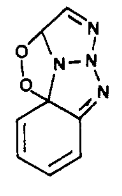
It appears that the reactions of these polyazapentalenes with singlet oxygen are regioselective. Only C–O bonds, and no N–O bonds, are formed, which is usual for reactions of singlet oxygen with nitrogen heterocycles,[20,21] and reflects the greater strength of the C–O bond. Thus, in **5**, attack occurs at C-1 and not at N-3. In the oxidation of **2**, the formation of traces of 3,5-dimethyl-1-(2-nitrophenyl)pyrazole indicates initial formation of a cycloadduct that can open in two ways.[16] In the present studies there is no evidence for intermediate cycloadducts such as **20** or **21**, which could be formally derived from addition of singlet oxygen to the azomethinimine or the azomethinylide portion of **4**, or for the analogous intermediate **22** from **5**.



20



21



22

The regioselectivity of these singlet oxygen reactions remains unexplained. In **4**, **1a**, and **1b**, but not in **2**, initial attack occurs at C-1 rather than at C-3, implying that the azomethinimine portion reacts more easily than the azomethinylide portion. However, **6** does not react at all, despite the presence of the azomethinimine structure, while **5**, which should resemble **6** in NBMO energy, reacts at the azomethinylide portion.

We have determined the rates of reaction of these polyazapentalenes with singlet oxygen, measuring the quantum yields of the RB-sensitized photoreactions of **1a**, **2**, **4**, and **5** in oxygen-saturated acetonitrile. The disappearance of starting material was determined by the lowering of the characteristic strong absorption at 340–370 nm.

The usual reaction scheme is assumed:

$$\text{sens} \xrightarrow{h\nu,\ O_2} {}^1O_2\ (\Phi_{^1O_2})$$

$$^1O_2 \rightarrow O_2\ (K_d)$$

$$^1O_2 + \text{substrate} \rightarrow \text{products}\ (K_r)$$

$$^1O_2 + \text{substrate} \rightarrow O_2\ (K_q)$$

By plotting Φ_{dis}^{-1} against $[\text{substrate}]^{-1}$ we obtained straight lines. The intercepts of these lines for **2** and **4** were very near to the reciprocal of $\Phi_{^1O_2}$, indicating that these substrates do not act as physical quenchers of $^1O_2$ (K_q negligible) but only undergo chemical reaction. By division of the slopes of the lines by the intercept, the reactivity index $\beta = K_d/K_r$ could be determined, and by use of the

---

(18) Campbell, C. D.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1965**, 192.

(19) Hall, J. H. *J. Am. Chem. Soc.* **1965**, *87*, 1147.

(20) George, M. V.; Bhat, V. *Chem. Rev.* **1979**, *79*, 447.

(21) Wasserman, H. H.; Lipshutz, B. H. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New Yrok, 1979; p 430.

Table III. Rates of Reactions of Azapentalenes 1a, 2, 4, and 5 with Singlet Oxygen in Acetonitrile

substrate	β (M)	K_r, mol^{-1} s^{-1} [a]
1a		6.3×10^7 [b]
2	0.0008	2×10^7
4	0.003	5×10^6
5	0.4	4×10^4

[a] Taking τ ($^1O_2$) = 61 μs in acetonitrile from ref 22.
[b] In chloroform-methanol (8:2), from ref 15.

literature value of the lifetime of singlet oxygen,[22] the rate of reaction K_r was calculated. The rates, shown on Table III, are of the same order of magnitude as those of electron-rich or highly conjugated aromatics[23] and of electron-rich heterocycles such as indoles.[24,25] As is usually observed, the reactivity of the azapentalenes decreases with increasing oxidation potential, from 2 to 4 to 5 and then to 6.

Triazapentalenes, and to a lesser degree tetrazapentalenes, behave as typical high-lying HOMO dipoles. Their reactivities with singlet oxygen are comparable to the reactivities of electron-deficient alkynes.[26]

Experimental Section

Apparatus. The UV-visible spectra were recorded on a Perkin-Elmer 200 spectrophotometer, the NMR spectra on a Perkin-Elmer R-12 or a Brucker WP80 instrument, using $(CH_3)_4Si$ as an internal standard, IR spectra on a Perkin-Elmer 257 spectrophotometer, and mass spectra on a Du Pont 492 spectrometer. Melting points are uncorrected.

Materials. Commercial (Merck and Carlo Erba) spectroscopic grade solvents were used after distillation and, in the case of CH_2Cl_2, treatment with Na_2CO_3; isopropylbenzene was dried by passing it through an alumina column. Column chromatography was performed with silica gel 60 HR (Merck). Rose Bengal (RB, Fluka) and *meso*-tetraphenylporphyrin (Fluka) were used as received.

Pyrazolo[1,2-*a*]benzotriazole (4). A solution of 7 g of 1-(2-nitrophenyl)pyrazole in 50 mL of isopropylbenzene was flushed with nitrogen for 20 min. Triethyl phosphite (18 mL) was added, and the mixture was heated at 150 °C for 20 h. Evaporation under reduced pressure and chromatography of the residue on silica gel, eluting with benzene–ethyl acetate (9:1), afforded 2.4 g (41%) of crystalline 4, mp 98–99 °C (from cyclohexane; lit.[27] mp 102–103 °C).

1-(2-Nitrophenyl)-1,2,3-triazole and 2-(2-Nitrophenyl)-1,2,3-triazole. A mixture of 8.45 g (0.117 mol) of 1,2,3-triazole,[28] 16.5 g (0.117 mol) of 2-fluoronitrobenzene, 12.4 g (0.117 mol) of anhydrous sodium carbonate, and 55 mL of dimethylformamide was refluxed for 20 min and then poured into 100 mL of water with vigorous stirring. An oil that slowly solidified was separated and extracted with benzene (4 × 50 mL). The extract was washed, dried, and concentrated to half the original volume. After 1 night a crystalline precipitate (9.05 g) was collected.

The mother liquor was evaporated, and the oily residue chromatographed on silica gel, eluting with benzene. After some residual 2-fluoronitrobenzene, a fraction containing pure 2-(2-nitrophenyl)-1,2,3-triazole was collected (6.6 g, 30%; oil; lit.[29] mp 27.0–27.5 °C). Further elution with benzene–ethyl acetate (8:2) gave 4.9 g of a crystalline material, which was combined with the first precipitate and recrystallized from benzene to give 1-(2-nitrophenyl)-1,2,3-triazole: 12.8 g (57%); mp 93–94 °C (lit.[30] mp 94.3–95.1 °C).

1,2,3-Triazolo[1,2-*a*]benzotriazole (5). A solution of 4 g of 1-(2-nitrophenyl)-1,2,3-triazole in 25 mL of isopropylbenzene was flushed with nitrogen, 9.4 mL of triethyl phosphite was added, and the mixture was heated at 150 °C for 7 h. Evaporation under reduced pressure yielded an oil containing some crystals. These were filtered, while the oily part was repeatedly extracted with cyclohexane. The combined extracts were evaporated and chromatographed on silica gel, eluting with benzene–ethyl acetate (9:1). The crystalline material was combined with the first precipitate and recrystallized from cyclohexane, yielding 2.3 g (70%) of 5, mp 117–119 °C (lit.[29] mp 121.6–122.2 °C).

1,2,3-Triazolo[2,1-*a*]benzotriazole (6) was prepared analogously to 5 with heating for 10 h. This product was obtained as a crystalline solid: mp 106–107 °C (lit.[30] mp 108.8–109.2); 46% yield.

General Procedure for the Dye-Sensitized Photooxidation of Compounds 4–6. Solutions containing 2 mg/mL of 4–6 saturated with oxygen in an immersion-well apparatus were irradiated with a medium-pressure mercury arc (Philips HPK 125 W) through a yellow filter ($\lambda_{tr} > 500$ nm) under the conditions given in Table I. The solution was evaporated, and the residue was chromatographed on silica gel.

Photooxidation of 4 in MeCN. Elution with benzene afforded two photooxides in 40% and 18% yields, respectively. The major product was 3-(1-benzotriazolyl)propenal (7), mp 144–145 °C (ethyl acetate). Anal. Calcd for $C_9H_7N_3O$: C, 62.42; H, 4.07; N, 24.27. Found: C, 62.54; H, 4.20; N, 24.42. The minor one was 3-(2-benzotriazolyl)propenal (8), mp 136–137 °C (cyclohexane). Anal. Found: C, 62.27; H, 4.22; N, 24.41.

Photooxidation of 4 in MeOH. The spectroscopic properties (NMR, IR) of the raw irradiation mixture were consistent with a 3:1 mixture of the two methoxy hydroperoxides 9 and 10. Since chromatographic separation afforded only a low yield of 9 and these compounds were too labile for the usual manipulation, the irradiation mixture was dissolved in a little benzene and treated with an equimolecular amount of triphenylphosphine in benzene. The slightly exothermic reaction was completed in 10 min, and chromatographic separation gave products 7 and 8 in 52% and 17% yields, respectively.

Photooxidation of 5. Elution with benzene–ethyl acetate (9:1) afforded two products, 11 and 12 (for the yields see Table I), along with unreacted starting material. Product 11 was obtained as yellow needles, mp 211–212 °C (from cyclohexane). Anal. Calcd for $C_{14}H_{10}N_8$: C, 57.92; H, 3.47; N, 38.60. Found: C, 57.85; H, 3.38; N, 38.71.

Product 12 was identical in analysis and physical properties with *cis,cis*-muconomitrile.[18,19]

Attempted Photooxidation of 6. Elution with benzene–ethyl acetate (9:1) afforded only starting material. TLC did not indicate any new product.

Rate Measurements. Solutions (4×10^{-3}–4×10^{-4} M) of 2 4–6 in MeCN containing 2×10^{-4} M RB were irradiated in spectrophotometric cells (1-cm optical path) by means of a high-pressure mercury arc (Osram HBO 200 W/2) through an interference filter (λ_{max} 543 nm, $\Delta\lambda_{1/2}$ 9 nm). The disappearance of the starting material was determined from the lowering of the absorption at ca. 360 nm in 0.1- or 1-mm cells. The light intensity was monitored by potassium Reineckate actinometry.[30]

Acknowledgment. This work was supported in part by a grant from the Italian Ministry of Education.

Registry No. 1a, 76355-39-0; 2, 60418-46-4; 4, 1738-57-4; 5, 84681-22-1; 6, 15285-01-5; 7, 50771-83-0; 8, 84681-23-2; 9, 84681-24-3; 10, 84681-25-4; 11, 84681-26-5; 12, 1557-59-1; O_2, 7782-44-7; RB, 11121-48-5; TPP, 917-23-7; 1-(2-nitrophenyl)pyrazole, 25688-17-9; triethyl phosphite, 122-52-1; 1,2,3-triazole, 288-36-8; 2-fluoronitrobenzene, 1493-27-2; 2-(2-nitrophenyl)-1,2,3-triazole, 10261-02-6; 1-(2-nitrophenyl)-1,2,3-triazole, 10560-92-6.

---

(22) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065.

(23) Saito, I.; Matsuura, T., in ref 21, p 511.

(24) Saito, I.; Matsuura, T.; Nakagawa, M.; Hino, T. *Acc. Chem. Res.* **1977**, *10*, 346.

(25) Saito, I.; Matsuura, T. In "Singlet Oxygen"; Ranby, B., Rabek, J. F., Eds.; Wiley: Chichester, 1978; p 186.

(26) Unpublished data from this laboratory.

(27) Lynch, B. M.; Hung, Y. Y. *J. Heterocycl. Chem.* **1965**, *2*, 218.

(28) Pechmann, H. V.; Bauer, W. *Chem. Ber.* **1909**, *42*, 662.

(29) Carboni, R. A.; Kauer, J. C.; Hatchard, W. R.; Harder, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 2626.

(30) Kauer, J. C.; Carboni, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2633.

(31) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.