Photo-oxidation of 1,3-Dimethylpyrazolo[1,2-*a*]benzotriazole

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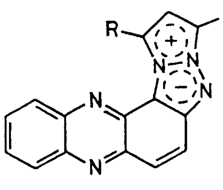
Summary The dye-sensitized photo-oxidation of the title mesomeric betaine yields two pairs of epoxy-ketones and α,β-unsaturated ketones, formally arising from addition of singlet oxygen to its two 1,3-dipolar mesomeric forms (**2a**) and (**2b**); in methanol, stable methoxy-hydroperoxides are obtained.

THE dye-sensitized photo-oxidation of heterocyclic molecules forms an important part of the literature on singlet oxygen reactions.[1] However, little information about the reaction of singlet oxygen with heterocyclic betaines has been available up to now, being confined to some recent data about the photo-oxidation of sydnones and related systems,[2] *i.e.* mesoionic compounds according to the definition by Ramsden.[3a] In these cases the reaction, although rationalized as occurring through initial oxygen addition, results, in the end, in extensive fragmentation.

We recently reported that 5*H*-pyrazolo[1′ : 2′—1 : 2]-1,2,3-triazolo[5,4-*a*]phenazin-4-ium inner salt (**1**) gives a photo-oxide in high yield without fragmentation.[4] We report here the photo-oxidation of the model system pyrazolo[1,2-*a*]-benzotriazole (**2**), a betainic triazapentalene of type B according to Ramsden's classification of heteropentalene mesoionic betaines.[3b] This compound can be represented, *inter alia*, by the dipolar structures (**2a**) and (**2b**).



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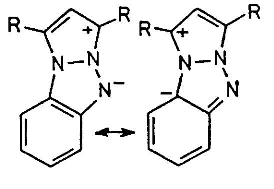


(2a) (2b)

We have found that singlet oxygen also adds to (**2**; R = Me) although in a more complex manner. Two groups of products are formed in aprotic solvents, *viz*. the 1-substituted benzotriazole derivatives (**5**) and (**6**) and the 2-substituted benzotriazole derivatives (**10**) and (**11**). The two groups of products are formed in roughly equivalent yields and are readily distinguishable on the basis of their n.m.r. and u.v. spectra.[5] The epoxy-ketones (**5**) and (**10**) predominate, but substantial amounts of the α,β-unsaturated ketones (**6**) and (**11**) are formed.

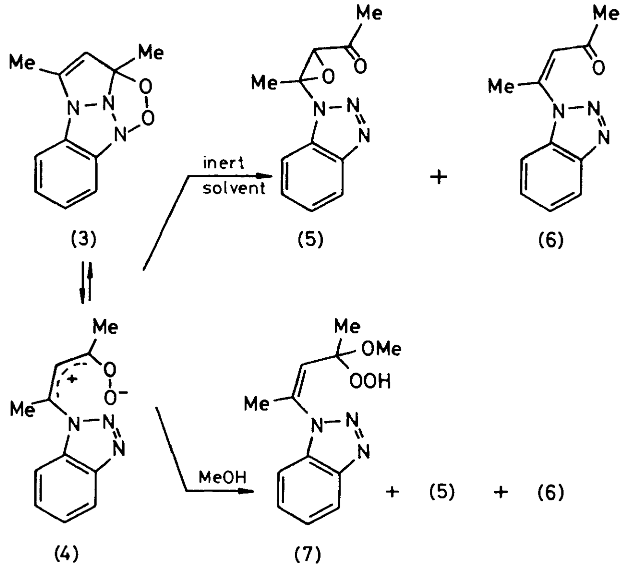
The formation of these photo-oxides may be interpreted as occurring through the intermediates (**4**) and (**9**) arising from attack of singlet oxygen at positions 3 and 5 [see (**2a**)] or at positions 1 and 9a (**2b**) of the molecule respectively, and possibly involving the cycloadducts (**3**) and (**8**). This contrasts with the behaviour of compound (**1**), which only undergoes singlet oxygen attack at the (**2a**)-type portion.

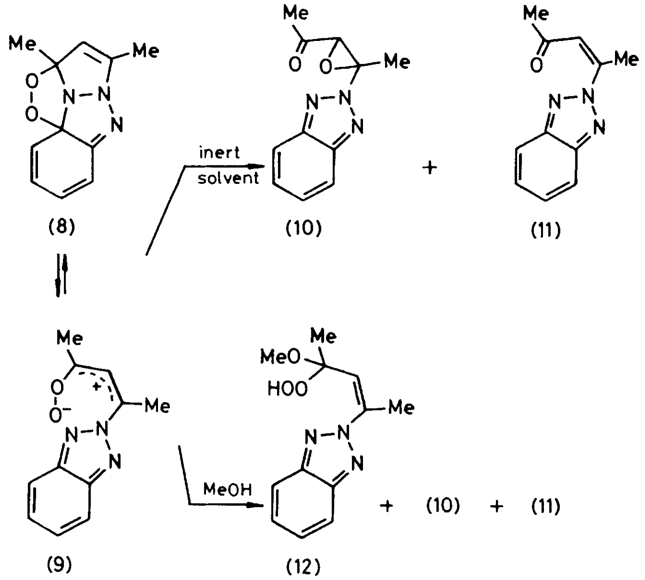
TABLE. % Yield of the photoproducts from the dye-sensitized photo-oxidation of (**2**).[a]

Solvent	(**5**)	(**6**)	(**10**)	(**11**)	(**7**)	(**12**)
Acetonitrile[b]	20	17	38	12		
CCl_4[c]	13		12			
Methanol[b,d]	7	11	4	6	29	17

[a] By irradiation (λ > 500 nm) of 8 × 10^{-3} M solutions of (**2**) while flushing with oxygen. Isolated yields after silica gel chromatography are reported. All products gave satisfactory elemental analysis. Attribution of the photoproducts to the series of 1-substituted benzotriazole derivatives or to the series of 2-substituted benzotriazole derivatives was based on u.v. spectra (*cf*., ref. 5) and on the symmetry of the aromatic n.m.r. signal. Within both series the epoxy-ketones (**5**) and (**10**) were characterized, *inter alia*, by the signal of the oxiran proton, δ *ca*. 3·9, as opposed to the olefinic proton, δ *ca*. 6·0—6·5 characteristic of the α, β-unsaturated ketones (**6**) and (**11**) *cf*. ref. 4. The methoxy-hydroperoxides were recognized from their easy conversion into the corresponding α,β-unsaturated ketones, as well as from their spectroscopic properties, *e.g*. –OOH in their i.r. and n.m.r. spectra. [b] Rose Bengal (300 mg/l) as sensitizer. [c] Tetraphenylporphine (40 mg/l) as sensitizer. [d] Benzotriazole (16% yield) arising from the decomposition of the hydroperoxides (**7**) and (**12**) was also isolated.

The time required for the photo-oxidation and the product distribution between 1- and 2-substituted benzotriazole derivatives do not vary much with solvent polarity in going from carbon tetrachloride to acetonitrile or methanol. This points to an addition process[6] not involving intermediates significantly more polar than the starting material.





Hoping to gain more mechanistic insight, the photo-oxidation was carried out in the presence of trimethylsilylketone, which has been demonstrated by Ando to function as a trap for carbonyl oxides.[7] However no modification of the product distribution, nor formation of

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† On sensitized photo-oxidation (λ_{irr} 500 nm), while flushing with oxygen. The reaction is strongly quenched by Dabco (1,4-diazabicyclo[2.2.2]octane).

‡ Evidence for singlet oxygen addition to 1,3-dipoles is as yet limited and often indirect, despite theoretical expectations: D. Bethell and R. McKeivor, *J. Chem. Soc., Perkin Trans.* 2, 1977, 327; D. P. Highley and R. W. Murray, *J. Am. Chem. Soc.*, 1974, **96**, 3330; K. Okada and T. Mukai, *Tetrahedron Lett.*, 1980, 359; T. Y. Ching and C. S. Foote, *ibid.*, 1975, 3771; W. Ando, S. Kohmoto, and K. Nishirawa, *J. Chem. Soc., Chem. Commun.*, 1978, 894; H. Takeshita, A. Mori, and S. Ohta, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2437.

the expected trapping product, trimethylsilylbenzoate, was detected. On the contrary, more information came from the photo-oxidation in alcohols. Indeed, (**5**), (**6**), (**10**), and (**11**) are minor products in methanol and are replaced by the two remarkably stable methoxy-hydroperoxides (**7**) and (**12**), the expected products from the trapping by methanol of (**4**) and (**9**).

The present results show that mesomeric betaines of this type are capable of undergoing singlet oxygen addition formally to different 1,3-dipolar limiting structures.‡ The addition yields epoxy-ketones in aprotic solvents and methoxy-hydroperoxides in methanol, in a way reminiscent of the singlet oxygen addition to activated dienes and electron-rich heterocycles.[8]

This work was supported in part by the Italian Ministry of Education.

(*Received*, 8*th July* 1981; *Com.* 791.)

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[1] For a recent review of the photo-oxidation of nitrogen heterocycles see M. V. George and V. Bhat, *Chem. Rev.*, 1979, **79**, 447.

[2] V. Bhat, V. M. Dixit, B. G. Ugarker, A. M. Trozzolo, and M. V. George, *J. Org. Chem.*, 1979, **44**, 2957; V. M. Dixit, V. Bhat, A. M. Trozzolo, and M. V. George, *ibid.*, p. 4169; N. H. Toubro, B. Hansen, N. Harrit, A. Holm, and K. T. Potts, *Tetrahedron*, 1979, **35**, 229; H. Kato, K. Tani, H. Kurumisawa, and Y. Tamura, *Chem. Lett.*, 1980, 721; H. Gotthardt, O. M. Huss, and S. Sohay-Tribbensee, *Chem. Ber.*, 1981, **114**, 285.

[3] (a) W. D. Ollis and C. A. Ramsden, *Adv. Heterocycl. Chem.*, 1976, **19**, 1; (b) C. A. Ramsden, *Tetrahedron*, 1977, **33**, 3203.

[4] A. Albini, G. F. Bettinetti, G. Minoli, and S. Pietra, *J. Chem. Soc., Perkin Trans.* 1, 1980, 2904.

[5] *Cf.* J. Der Kosh, O. E. Polansky, E. Rieger, and G. Derflinger, *Monatsh. Chem.*, 1961, **92**, 1131.

[6] R. Gompper, *Angew. Chem.*, 1969, **81**, 348; *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 312.

[7] A. Sekiguchi, Y. Kabe, and W. Ando, *J. Chem. Soc., Chem. Commun.*, 1979, 233.

[8] R. W. Denny and A. Nickon, *Org. React.*, 1973, **20**, 133; T. Matsuura and I. Saito, in 'Photochemistry of Heterocyclic Compounds,' ed. O. Buchardt, Wiley, New York, 1976, p. 456.