

Photo-oxidation of Amines: a Reply

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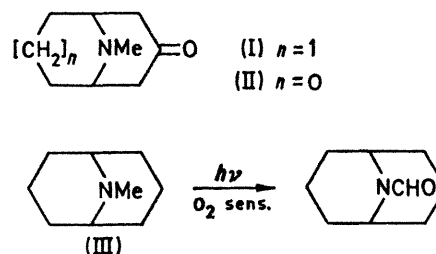
Summary New evidence for singlet oxygen involvement in the photo-oxidation of amines is presented.

RECENTLY, we reported a novel photo-oxidation of the naturally occurring bicyclic amines pseudopelletierine (I) and tropinone (II) to their *N*-formyl analogues.¹ On the basis of sensitization and quenching data we attributed this reaction to an initial attack by singlet oxygen (formed *in situ*) on the *N*-methyl group. The involvement of singlet oxygen has since been questioned by Davidson,² who suggests our reactions to be initiated by typical hydrogen abstractions involving the triplet carbonyl group of the sensitizer (when benzophenone or Rose Bengal is used) or by the excited triplet of the substrate itself when hydrocarbon sensitizers (naphthalene, triphenylene, $E_T < 67$) energetically incapable of sensitizing a simple ketone (E_T ca. 80) are used. Davidson *et al.* propose that the reaction observed in the presence of hydrocarbons is in fact *direct* resulting from light absorption by substrate. We report now conclusive evidence in favour of our original interpretation.

In our initial experiments, we relied on two criteria to handle the problem of light absorption by substrate. (i) The disappearance of starting amine normally gives curved plots for concentration *vs.* time since, as the reaction proceeds, the proportion of light absorbed by substrate decreases; however in runs where triphenylene or naphthalene were used as sensitizers, such plots were essentially linear showing that the initiating species were *not* being consumed. (ii) In direct irradiation and at concentrations of naphthalene or triphenylene such that <5% of the 3130 and 3340 Å lines were absorbed by substrate, essentially identical initial rates of reaction were measured, whereas an internal filter effect would have slowed the rate by at least 70%. The optical data for pseudopelletierine are summarized in the Table. In addition 1,4-diazabicyclo-

destroyed by radical reactions initiated by carbonyl sensitizers, *e.g.* benzophenone.

We have now carried out the oxidation of the model compound, *N*-methyl granatanine (III), *i.e.* pseudopelletierine with the carbonyl group removed. This compound is readily available from pseudopelletierine by Wolff-Kishner reduction, a considerably more effective method than the Clemmensen technique originally used.³ Since *N*-methylgranatanine is transparent in the near u.v., it is ideal for determining whether the carbonyl moiety is necessary for initiation.



Irradiation of (III) under the same conditions used for pseudopelletierine and tropinone with either naphthalene or Rose Bengal as sensitizer gave the usual reaction at a markedly higher rate. The product (60%) was characterized as its hemihydrate, m.p. 49–50.5°, and the structure was confirmed by analysis and n.m.r., mass, and i.r. spectra, which were analogous to those of the related compounds previously obtained. With both sensitizers, the plots of disappearance were linear, consistent with our mechanism.

Since the photo-oxidation of *N*-methylgranatanine sensitized by hydrocarbons is roughly four times more *rapid* than that of pseudopelletierine itself, it is clear that: (i) the reaction of *N*-methylgranatanine, and by extension those of pseudopelletierine and tropinone, involve singlet oxygen. (ii) The carbonyl function *protects* the *N*-methyl group from oxidation. The way in which this occurs is easy to imagine since the tertiary nitrogen and C(3) are well known to interact, *e.g.* in acyl migration,⁴ and in the solvolysis of tropanyl chlorides.⁵ Presumably, the carbonyl function accepts the electron-pair of the nitrogen base.⁶ If so, the first step in the oxidation is presumably an electrophilic attack by singlet oxygen on the unshared electron pair of nitrogen. Since the submission of our original Communication,¹ this mode of attack, leading to "peroxides," has been demonstrated in the reaction of singlet oxygen with double bonds.⁷

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TABLE

	Concentration M ^a	U.v. spectroscopic data			
		ϵ_{3130}	A_{3130}^b	ϵ_{3360}	A_{3360}^b
Pseudopelletierine	0.0653	11.3	0.094	0.4	0.003
Naphthalene	0.135	203	3.51	0	
Triphenylene	0.0223	630	1.79	0	

^a The concentration of pseudopelletierine was the same in both runs. ^b The path (interannular distance in the immersion well) was 1.28 mm.

[2,2,2]octane greatly reduced the rate of oxidation while being only slightly affected itself which indicates a singlet oxygen reaction since diazabicyclo-octane is rapidly

¹ M. H. Fisch, J. C. Gramain, and J. A. Olesen, *Chem. Comm.*, 1970, 13.

² R. F. Bartholomew and R. S. Davidson, *Chem. Comm.*, 1970, 1174.

³ A. Piccinini, *Gazzetta*, 1902, 32, 260.

⁴ G. Fodor and K. Nador, *J. Chem. Soc.*, 1953, 721 and references cited therein.

⁵ A. T. Bottini, C. A. Grob, E. Schumacher, and J. Zergenyi, *Helv. Chim. Acta*, 1966, 49, 2516.

⁶ *cf.* The case of amino-ketones, N. J. Leonard, *Record Chem. Progr.*, 1956, 17, 243; for an example in the tropane series, see M. R. Bell and S. Archer, *J. Amer. Chem. Soc.*, 1960, 82, 151; R. Hofmann, *Accounts Chem. Res.*, 1971, 4, 1.

⁷ W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, 91, 7771.