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The Dye-Sensitized Photo-oxygenation of Biadmantylidene

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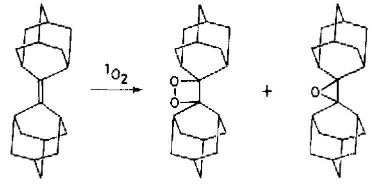
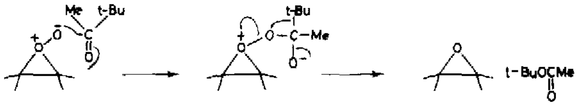
The mechanistically interesting claim was recently made that the dye-sensitized photo-oxygenation of biadmantylidene (1) in pinacolone as solvent gave the corresponding dioxetane (2) and epoxide (3) while solvent was converted to t-butyl acetate.[1]



1 2 3

This result was interpreted as proof that a perepoxide was initially formed and that, before it expanded to dioxetane, it lost its supernumerary oxygen atom to pinacolone in a Baeyer-Villiger type oxidation.



Subsequently, it was discovered that similar olefins, such as binorbornylidene and norbornene, gave dioxetanes and epoxides not only in pinacolone, but also in inert solvents.[2,3] Clearly a re-examination of 1 is necessary. We now present the corrected results together with the discovery that *the dioxetane-epoxide ratio depends on the sensitizer used.*

Photo-oxygenations were carried out with different sensitizers in a variety of solvents.[4] *meso*-Tetraphenylporphin uniformly gives dioxetane in most solvents. Contrary to the earlier report,[1] hardly any epoxide is formed in pinacolone. *Moreover a careful search uncovered no trace of t-butyl acetate.*

In benzene and carbon tetrachloride, epoxide is formed as the minor product (Table 1). However, by appropriately changing the sensitizer, epoxide can be made the major product (Table 2). Rose Bengal consistently gives epoxide in nearly all solvents, somewhat less in pinacolone; but even here, it is significant that no t-butyl was found (Table 3).

Certainly, epoxide does not arise by any chemical process involving solvent. Nevertheless, solvent does play a small role in influencing the product composition, but the greatest effect by far is caused by the sensitizer.

Table 1. Photo-oxygenation of 1 using *meso*-Tetraphenylporphin as Sensitizer

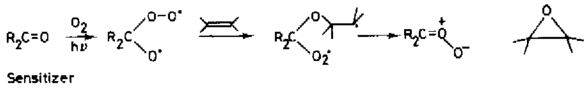
Solvent	% Dioxetane 2	% Epoxide 3
2-Propanol	100	---
Ethyl acetate	100	---
Acetone	>95	trace
Pinacolone	>95	trace
Methylene chloride	>95	trace
Chloroform	>95	trace
Carbon tetrachloride	75	25
Benzene	90	10

Table 2. Photo-oxygenation of 1 in Acetone

Sensitizer	% Dioxetane 2	% Epoxide 3
meso-Tetraphenylporphin	>95	trace
Methylene Blue	>95	trace
Rhodamine B	95	5
Eosin	95	5
Fluorescein	90	10
Erythrosin	30	70
Rose Bengal	trace	>95

Why is Rose Bengal (RB) (and to a lesser extent, Erythrosin) so completely different from the other sensitizers and how does the epoxide arise? These are difficult questions, however clues are provided by two further tests. Inclusion of DABCO, a singlet oxygen quencher,[6] drastically slows down oxidation using RB. When 2,6-di-t-butyl-p-cresol (DBPC), a free radical inhibitor,[7] is added, the rate is scarcely affected except that now the product composition dramatically changes to favour dioxetane (Table 3).

These results can be accommodated by assuming that the formation of dioxetane from singlet oxygen is the normal reaction which is in competition with a side reaction affording epoxide. The latter could arise in two ways. RB could be behaving like benzil on irradiation[8] to produce an excited sensitizer oxygen radical which adds to olefin and then cleaves to epoxide and sensitizer oxide.



An alternative is that oxygen and RB produce a charge transfer complex which subsequently, either *via* the sensitizer radical cation or the superoxide radical anion, brings about epoxidation. This seems likely since RB (and Erythrosin), unlike the other sensitizers, bear iodine substituents and thus are better suited to transferring an electron to oxygen. These and other possibilities are under investigation.

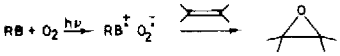


Table 3. Photo-oxygenation of 1 using Rose Bengal

Solvent	% Dioxetane 2		% Epoxide 3
2-Propanol	trace		>95
Ethyl acetate	trace		>95
Acetone	trace		>95
Pinacolone	10		90
Methylene chloride	trace		>95
Acetone + quencher[a]	---	retardation[b]	---
Acetone + inhibitor[c]	90		10

a) DABCO was present as 0.005 M. b) Only about 5% conversion of 1 after 2 hrs.

c) DBPC was present as 0.12 M.

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4) For our general procedure see ref 5. The usual tests were made to ensure that singlet oxygen was the primary oxidizing species. Solutions of 1 (0.018 M) and sensitizer (10^{-3} to 10^{-4} M) were irradiated for 1½ to 2 hrs., until complete oxidation. Product compositions were estimated by thin layer chromatography using calibrated standard solutions of 2 and 3; errors were ±5%.

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