260. The Reaction of Biadamantylidene with Singlet Oxygen in the Presence of Dyes [1]

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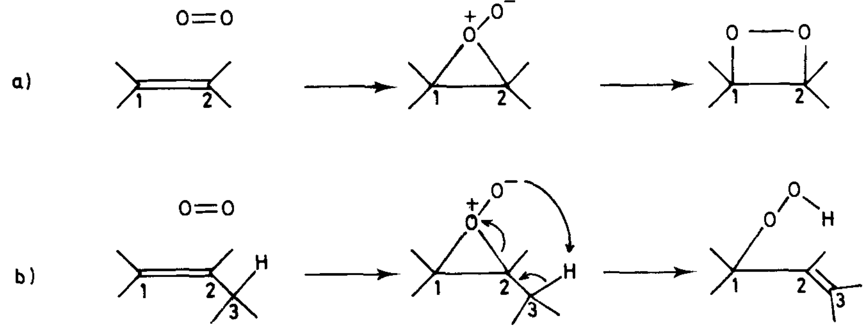
Summary

Singlet oxygen, generated chemically or photogenetically, reacts with biadamantylidene to give the corresponding dioxetane and epoxide only. When methylene blue (MB) or *meso*-tetraphenylporphin (*m*-TPP) is used as sensitizer the normal reaction course occurs giving dioxetane as the preponderant product in 2-propanol, ethyl acetate, acetone, pinacolone, methylene chloride, chloroform, carbon tetrachloride and benzene, although in the last two solvents some 10-25% of epoxide is formed. When erythrosin and rose bengal (RB) are used, epoxide becomes the main product (70-95%). Epoxide does not derive from chemical reaction with the solvent. Pinacolone, for example, is *not* oxidized to *t*-butyl acetate.

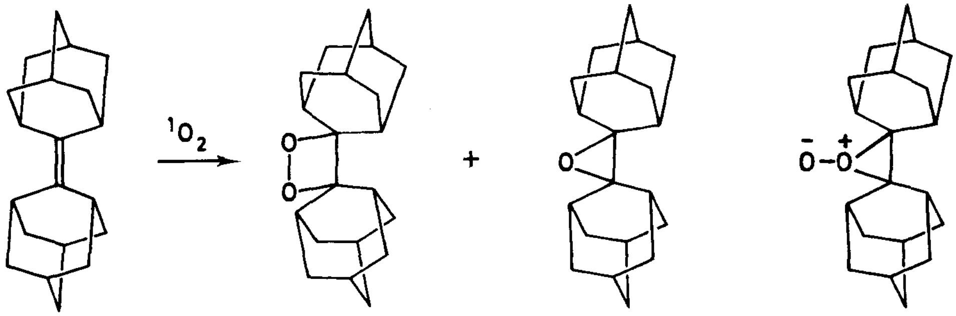
The rose bengal reaction involves both singlet oxygen and radicals, since diazabicyclooctane (DABCO) and di-*t*-butyl-*p*-cresol interfere with the oxidation. A mechanistic scheme is proposed in which sensitizer and oxygen combine to produce sensitizer radical cation and superoxide radical anion. Subsequently, hydroperoxy radical, deriving from superoxide, reacts with substrate to give epoxide and hydroxy radical. The latter adds to substrate to give a new radical which captures triplet oxygen. Epoxide is formed by loss of hydroperoxy radical and the chain starts anew. The dioxetane is formed separately either by [2+2]-cycloaddition or stepwise addition.

Introduction. - Unlike *N*-oxides, *O*-oxides or perepoxides have never been directly observed, yet their intermediacy has been invoked to explain the formation of allylic hydroperoxides and dioxetanes from appropriate olefins on reaction with singlet oxygen [2]. In both cases the formation of the perepoxide has been presumed to be the primary event. Subsequently, expansion or rupture of the three-membered ring leads to the products, namely the dioxetane and the allylically rearranged hydroperoxide *(Scheme 1)*. In the case of hindered olefins where there are no allylic hydrogen atoms available, the only possible course leads to dioxetane. On account of the steric congestion around the double bond, as the ring expansion step will be hampered, the lifetime of the putative perepoxide should be prolonged so that it could at least be trapped, if not positively identified as such. A typical and perplexing case is that of biadamantylidene (**1**). It was originally reported that

Scheme 1. *Reaction of singlet oxygen with an olefin to give* a) *dioxetane and* b) *hydroperoxide by ring enlargement and rearrangement respectively of the intermediate perepoxide*

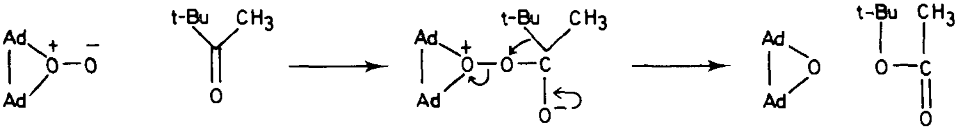


Scheme 2



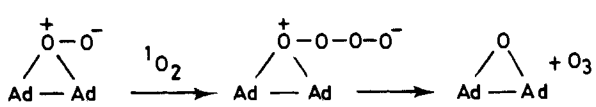
1 **2** **3** **4**

Scheme 3. *Reduction of perepoxide by pinacolone* via *a* Baeyer-Villiger *intermediate to give epoxide and* t-*butyl acetate*



singlet oxygen, produced photochemically using tetraphenylporphin as sensitizer in pinacolone, gave the dioxetane **2** and the epoxide **3** *(Scheme 2)*. Particularly intriguing was the conclusion that the epoxide derived from the hypothetical perepoxide **4** through the intervention of pinacolone which was allegedly oxidized to *t*-butyl acetate *(Scheme 3)* [3]. It was later discovered that expoxide **3** was formed in substantial amounts even in inert solvents [4]. Nonetheless, the perepoxide hypothesis has been upheld by arguing that singlet oxygen attaches itself to the perepoxide to form the tetra-oxygen zwitterion which loses ozone giving the epoxide *(Scheme 4)* [4].

Scheme 4



In contrast to this clear-cut mechanistic picture, we now show that the reaction of singlet oxygen, produced either chemically or photogenetically, with biadamantylidene is in fact a far more complex process and depends on the nature of the dye, no matter whether it is used as a sensitizer or simply as a reagent.

Results and Discussion. - *Dye-sensitized photo-oxygenation of biadamantylidene* (**1**). The photo-oxidation of **1** was carried out by following our procedure [5] and the reaction mixture was analysed by thin-layer chromatography.

When *meso*-tetraphenylporphin (*m*-TPP) was used as sensitizer, the major product was dioxetane regardless of which solvent was used *(Table 1)*. Contrary to the earlier report [3], scarcely any epoxide is formed in pinacolone. Moreover, no trace of *t*-butyl acetate was detected¹). Nevertheless, in benzene and carbon tetrachloride, epoxide is formed as the minor product. Surprisingly, epoxide can become the major product when the sensitizer is suitably varied *(Table 2)*. This effect is seen best with rose bengal (RB) and to a lesser extent with erythrosin. Rose bengal consistently gives epoxide in all solvents, but less in pinacolone and it is significant that even here no *t*-butyl acetate was found *(Table 3)*. Clearly, the dioxetane/epoxide ratio depends primarily on the sensitizer and to a slight degree on the solvent. This finding is borne out by the effect of concentration of sensitizer

Table 1. *Photo-oxygenation of* **1** *using* meso-*tetraphenylporphin as sensitizer*

Solvent	% Dioxetane **2**	% Epoxide **3**	**Solvent**	% Dioxetane **2**	% Epoxide **3**
2-Propanol	100	-	Methylene chloride	>95	trace
Ethyl acetate	100	-	Chloroform	>95	trace
Acetone	>95	trace	Carbon tetrachloride	80	20
Pinacolone	>95	trace	Benzene	90	10

Table 2. *Photo-oxygenation of* **1** *in acetone*

Sensitizer	% Dioxetane **2**	% Epoxide **3**	**Sensitizer**	% Dioxetane **2**	% Epoxide **3**
meso-Tetraphenylporphin	>95	trace	Fluorescein	90	10
Methylene blue	>95	trace	Erythrosin	30	70
Rhodamine B	95	5	Rose bengal	trace	>95
Eosin	95	5	Ⓟ-rose bengal [6]	20	80

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¹) Although yields of 81 and 19% were reported [3] for the dioxetane and epoxide, no mention is made of the amount of *t*-butyl acetate obtained.

on the product distribution. The normal sensitizers *meso*-tetraphenylporphin and methylene blue (MB) cause no significant change in the dioxetane/epoxide ratio when their concentrations are varied *(Table 4)*. On the other hand, decreasing the concentration of the abnormal sensitizer, rose bengal, switches the product ratio towards dioxetane *(Table 5)*.

Table 3. *Photo-oxygenation of* **1** *using Rose Bengal*

Solvent	% Dioxetane **2**	% Epoxide **3**	**Solvent**	% Dioxetane **2**	% Epoxide **3**
2-Propanol	trace	> 95	Pinacolone	10	90
Ethyl acetate	trace	> 95	Methylene chloride	trace	> 95
Acetone	trace	> 95			

Table 4. *Effect of the sensitizer concentration on the product distribution*

Sensitizer: methylene blue (MB) Solvent: acetone, [Ad = Ad]: 0.019M; irradiation time, 1 h

Sensitizer conc./M	% Dioxetane **2**	% Epoxide **3**	Remarks
10^{-5}	> 95	trace	(a) bleaching of dye, (b) oxidation not completed
10^{-4}	> 95	trace	(a) + (b)
10^{-3}	> 95	trace	(b)
10^{-2}	> 95	trace	

Sensitizer: ***meso*****-tetraphenylporphin** (*m*TPP) Solvent: CCl_4, [Ad = Ad]: 0.019M; irradiation time, 1 h

Sensitizer conc./M	% Dioxetane **2**	% Epoxide **3**	Remarks
10^{-5}	75	25	(a) bleaching of dye, (b) oxidation not completed
10^{-4}	85	15	(a) + (b)
10^{-3}	90	10	
10^{-2}	> 95	trace	

Table 5. *Effect of sensitizer concentration on the product distribution*

Sensitizer: rose bengal (RB) Solvent: acetone, [Ad = Ad]: 0.019M; irradiation time, 1 h

Sensitizer conc./M	% Dioxetane **2**	% Epoxide **3**	Remarks
10^{-5}	95	5	(a) bleaching of dye, (b) reaction not completed
10^{-4}	70	30	(a) + (b)
10^{-3}	20	80	(a) + (b)
10^{-2}	5	95	(a) + (b)

Solvent: ethyl acetate, [Ad = Ad]: 0.019M; irradiation time, 30 min

Sensitizer conc./M	% Dioxetane **2**	% Epoxide **3**	Remarks
10^{-5}	95	trace	(a) bleaching of dye, (b) reaction not completed
10^{-4}	60	40	(a) + (b)
10^{-3}	25	75	(b)
10^{-2}	trace	> 95	

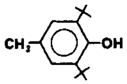
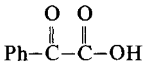
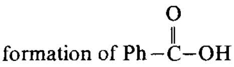
To find out more about the strange behaviour of rose bengal several additional experiments were carried out. The results are summarized in *Table 6*. The use of polymer-bound rose bengal [6] as sensitizer only slightly affected the product ratio. Using a 1:1 mixture of methylene blue and rose bengal a product ratio of essentially 1:1 was observed. Addition of DABCO, an efficient singlet oxygen quencher [7], retarded the oxidation rate appreciably. The addition of a radical inhibitor scarcely affected the rate [8], but the product ratio changed to strongly favour dioxetane.

When singlet oxygen was generated by the chemical decomposition of triphenylphosphite ozonide in acetone [9], dioxetane was formed to some 90%. Repetition of the experiment, but in the presence of rose bengal, once again, altered the product ratio to favour epoxide.

When 2-methylnorbornene was added, using the same concentration of sensitizer and olefins, the oxidation of 2-methylnorbornene [10] was slowed down by a factor of 6 due to the presence of **1**. The product ratio obtained from **1** was normal, however, namely 90% dioxetane and 10% epoxide. At higher sensitizer concentration more epoxide was formed. In both instances the sensitizer was bleached completely.

Discussion. - The photo-oxygenation of **1** in eight different solvents yields a mixture of dioxetane **2** and epoxide **3**. The product ratio depends slightly on the solvent and to a much greater extent on the sensitizer. Clearly, at least two unconnected mechanisms are operating. The principal or normal reaction course is dioxetane formation which is most probably the result of an allowed [2+2]-cycloaddition [11]. The best explanation so far to account for epoxide **3** is the assumption

Table 6. *Oxidation of* **1** *in acetone*

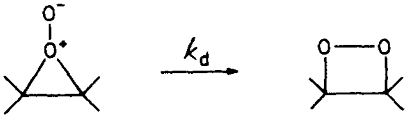
$^1O_2$-Source	'Quencher'	% Dioxetane **2**	% Epoxide **3**	Remarks
hν, RB	DABCO	oxidation	slowed-down	considerably
hν, RB		90	10	
hν	-	-	-	no oxidation observed
$(PhO)_3PO_3$	-	90	10	
$(PhO)_3PO_3$	RB[b])	60	40	RB bleached
$(PhO)_3PO_3$[a])	RB[b])	-	-	RB bleached
hν, RB[b])	2-methylnorbornene	90	10	RB bleached
hν, RB	 $Ph-\overset{O}{\overset{\Vert}{C}}-\overset{O}{\overset{\Vert}{C}}-OH$	60	40	 formation of $Ph-\overset{O}{\overset{\Vert}{C}}-OH$
hν, RB, MB[c])	-	55	45	
hν, Ⓟ-RB[d])	-	20	80	

[a]) No biadamantylidene present.
[b]) $[RB] = 10^{-3}$ M.
[c]) $[RB] = 10^{-3}$, $[MB] = 10^{-3}$ M.
[d]) See [6].

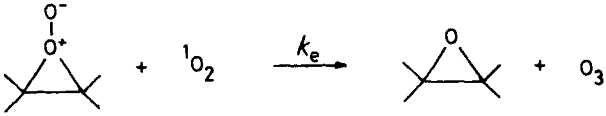
that the perepoxide **4** initially formed reacts with a second molecule of singlet oxygen giving ozone and the epoxide [4] [12]. Some kinetic evidence has been presented in favour of this mechanism [4]. A steady state treatment affords the following expression:

$$\frac{\mathrm{d\,(epoxide)}}{\mathrm{d\,(dioxetane)}} = 2\,\frac{k_e}{k_d}\cdot\left[{}^1O_2\right]$$

where k_d :



k_e :

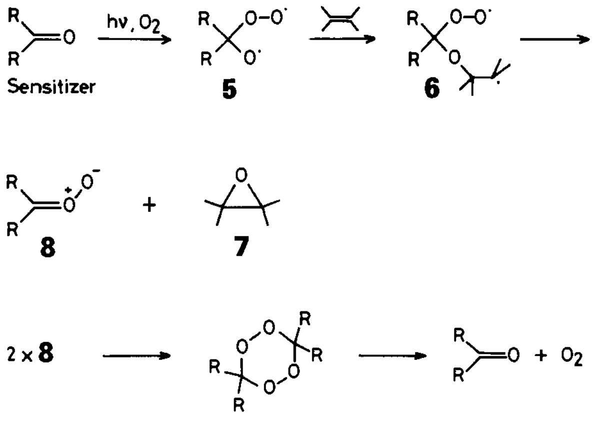


Variations of the light intensity, and the olefin or sensitizer concentration do indeed shift the ratio in the predicted direction. Solvents in which the lifetime of singlet oxygen is longer ought to favour more epoxide. This expectation is confirmed by our experiments. In benzene and carbon tetrachloride, long lifetimes (24 and 700 µs respectively) [13] engender relatively high yields of epoxide *(Table 1)*. The product ratio in these solvents was not altered on adding a radical quencher, thereby indicating that dioxetane and epoxide arise *via* a non-radical mechanism.

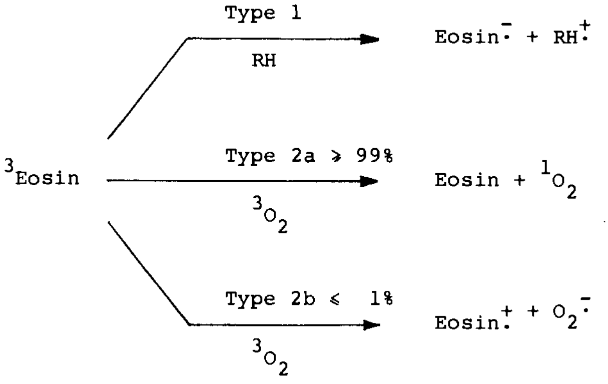
The change observed with rose bengal and erythrosin cannot be explained by the foregoing mechanism. Radicals must be implicated as is seen from the effect of di-*t*-butyl-*p*-cresol *(Table 6)*. Singlet oxygen also has to intervene somewhere as DABCO almost stops the oxidation. At first sight, the different behaviour of rose bengal and erythrosin might be due to their carbonyl functions, since *meso*-tetraphenylporphin and methylene blue possess none. Epoxide could then possibly arise by a mechanism similar to that suggested for the benzophenone-sensitized epoxidation of olefins [14]. The excited sensitizer might capture a molecule of triplet oxygen to give the diradical **5** *(Scheme 5)*. Next, olefin would add to give **6**, which on fragmentation affords the epoxide **7** and the carbonyl oxide **8**. The latter, by dimerization and fragmentation, would regenerate ground-state sensitizer and oxygen. Unfortunately, this scheme fails in two important respects. The first is that sensitization with rose bengal alone or when bound to polymer leads to essentially the same result. Secondly, when the oxygenation is carried out with chemically produced singlet oxygen in the presence of rose bengal, an equally high percentage of epoxide is obtained. Obviously, the correct mechanism must be sought elsewhere.

A triplet sensitizer can exhibit two distinct types of reaction *(Scheme 6)*. In the first *(Type 1)* the sensitizer interacts directly with the substrate molecule (RH)

Scheme 5



Scheme 6

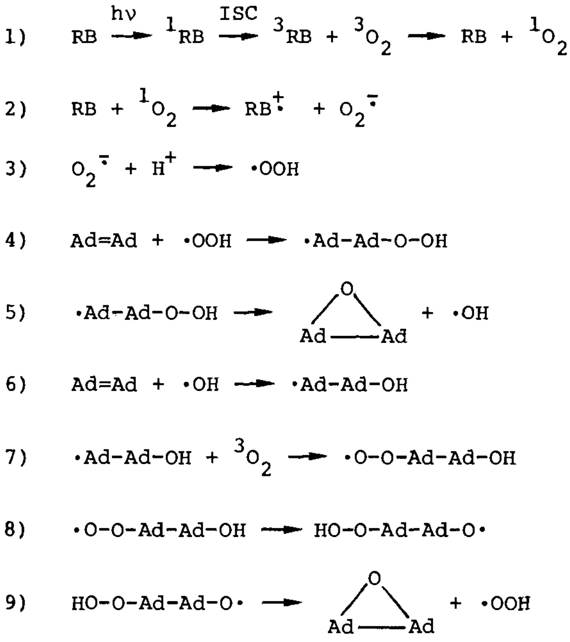


transferring either a hydrogen atom or an electron. The resulting radicals can then react with oxygen. In the second, the sensitizer triplet interacts with ground-state oxygen to produce either singlet oxygen *(Type 2a)* or, by electron transfer, superoxide radical anion *(Type 2b)* [15]. This last process, when it occurs, usually does so only to a small extent [16]. Bleaching of the dye is often associated with this electron transfer and thus constitutes an index of *Type 2b* behaviour.

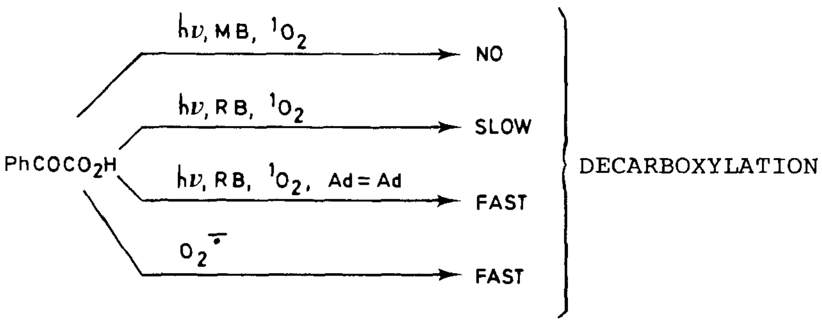
The pronounced abnormal oxidation observed with rose bengal and erythrosin may very well involve such electron transfer *(Type 2b)*. A possible reaction sequence which would explain all the experimental facts is depicted in *Scheme 7*. Many of the steps correspond to known or accepted processes. *Step 1* is the normal *(Type 2a)* and *Step 2* is the abnormal process *(Type 2b)*. In *Step 3*, a proton is provided by the medium to generate the hydroperoxy radical. Addition of the latter to biadamantylidene *(Step 4)* followed by cyclization to epoxide generates hydroxyl radical *(Step 5)* which now sets up another molecule of olefin *(Step 6)* for addition of triplet oxygen *(Step 7)*. The adduct so obtained transfers hydrogen *(Step 8)* and the chain is completed by scission to hydroperoxy radical and epoxide *(Step 9)*. Substitution of triphenylphosphite ozonide as the source of singlet oxygen brings about immediate bleaching of rose bengal, whereas superoxide radical anion itself leaves it unchanged.

Evidence for the formation of superoxide in *Step 2* is provided by adding phenylglyoxylic acid to the mixture of rose bengal and biadamantylidene **1** *(Scheme 8)*. Phenylglyoxylic acid is inert towards singlet oxygen [17], but undergoes

Scheme 7



Scheme 8



efficient decarboxylation with superoxide anion [18]. In the presence of rose bengal in acetone the decarboxylation of phenylglyoxylic acid takes place sluggishly (50% in 2 h of irradiation). Addition of biadamantylidene speeds up decarboxylation and after 15 min no ketoacid is left. We therefore deduce that superoxide anion is formed in *Step 2.*

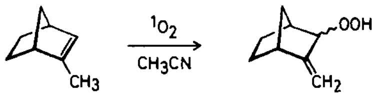
Although there is only one reported example of epoxidation by superoxide radical anion [19], its conjugate acid, · O–OH, is well recognized as an agent of chain autoepoxidation [20], consequently the remaining steps in *Scheme 7* are perfectly reasonable.

This scheme nicely accommodates the experimental results *(Table 6)*. For example, DABCO stops the oxidation because singlet oxygen is quenched. Di-*t*-butyl-*p*-cresol does not affect the overall reaction but merely inhibits the radical pathway allowing dioxetane to appear as the main product. Added 2-methylnorbornene has a normalizing effect, as it reacts very efficiently with singlet oxygen [10], making *Step 2* less likely and therefore decreasing radical oxidation. A similar effect is observed on adding phenylglyoxylic acid. Here superoxide radical ion is chemically quenched, *Steps 3* and *4* are aborted and once again dioxetane shows up as the preponderant oxidation product.

As an additional check on the validity of our scheme a filter experiment was undertaken *(Table 7)*. The photooxygenation of **1** was performed using rose bengal and methylene blue. The latter alone gives mainly dioxetane, whereas the former alone favours epoxide. If a red filter is inserted, the methylene blue still functions as sensitizer, but with diminished efficiency, while rose bengal becomes totally inoperative. When both sensitizers are mixed and used together, with the red filter, the epoxide becomes the main product. Clearly, singlet oxygen produced photochemically from methylene blue is reacting with rose bengal generating the pair of

Table 7. *Photo-oxygenation of* **1** *using filtered light*

Test



Sensitizer	Red Filter[a])	Oxidation
RB	out	50% after 17 min
RB	in	0% after 40 min
MB	in	50% after 34 min

Experiment: [Ad = Ad] = 10^{-2}M in acetone. Irradiation time: 2 h

Sensitizer conc./M	Red filter	Oxidation	% Dioxetane **2**	% Epoxide **3**
RB 2×10^{-3}	out	100%	5	95
RB 2×10^{-3}	in	0	-	-
MB 2×10^{-3}	in	50	95	5
RB 10^{-2} MB 2×10^{-3}	in	30	5	95

[a]) Filter: *Schott* RG 645; transmission 645 nm 50%, 620 nm 10^{-4}%.

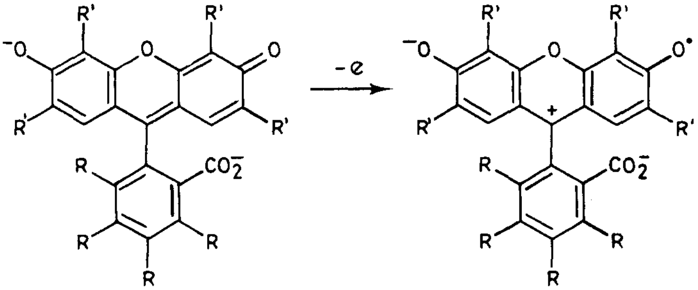
Table 8. *Effect of added superoxide radical anion on product distribution obtained from photo-oxygenation of* **1**

Conditions: [Ad=Ad]= 10^{-2}M; solvent acetone (2 ml); [eosin]= 10^{-3}M; irradiation time, 2 h

18-Crown-6 ether	KO_2	Oxidation	% Dioxetane **2**	% Epoxide **3**
1) -	-	100%	95	5
2) 100 mg	-	100	95	5
3) 100 mg	20 mg	100	5	95
4) 100 mg[a])	20 mg	0	-	-

[a]) Nitrogen used instead of oxygen.

Scheme 9



	R'	R
Fluorescein	H	H
Eosin	Br	H
Erythrosin	I	H
Rose Bengal	I	Cl

radical ions *(Step 2)*. Energy transfer from the singlet or triplet states of methylene blue to rose bengal is improbable as they lie much higher than those of methylene blue[2]).

Having invoked the intermediacy of superoxide radical anion, its effect on the product distribution was monitored by incorporating it as such in the photo-oxygenation experiment. The radical anion was generated by dissolving potassium superoxide in 18-crown-6 ether. Straight photo-oxygenation using eosin gave chiefly dioxetane. Admixing crown ether alone had no effect. However, addition of superoxide caused epoxide to predominante. As the dioxetane and the olefin **1** are inert towards superoxide, it can be safely concluded that singlet oxygen is efficiently quenched [23] by superoxide, leaving the latter still available for the subsequent reduction step to epoxide.

One last question is why is rose bengal so markedly different from the other sensitizers in the same class? The reason must lie in the nature of the substituent.

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[2]) For methylene blue $E_s \approx 43$ and $E_T = 34$ kcal/mol and for rose bengal $E_s \sim 50$ and $E_T = 39.5$ kcal/mol. The E_s of rose bengal is estimated from its UV. spectrum [21] [22].

Rose bengal, having chlorine and iodine atoms as substituents, is much better able to stabilize its radical cation than eosin or fluorescein which only have bromine substituents or none *(Scheme 9)*.

Conclusion. - We have established that the dye-sensitized photooxygenation of hindered olefins proceeds by at least two independent processes. The first is dioxetane formation, probably the consequence of a [2+2]-cycloaddition. The second is a subsidiary, radical process giving epoxide; this can become competitive when the sensitizer is capable of forming a stable radical cation. Nevertheless, it is not ruled out that the peroxide precedes dioxetane formation.

This is the first example of electron transfer from sensitizer to di-oxygen to give radical cation and anion resulting in oxidation of an olefin to epoxide [24]. Nevertheless, this process might be more general. The photo-oxygenation of 2-methyl-2-pentene in the presence of sodium azide is a case in point [25]. In essence, when methylene blue, eosin B and rhodamine B were used as sensitizers large amounts of azidohydroperoxide (AO_2HN_3) were formed (~85%). The use of rose bengal and erythrosin, on the other hand, resulted in little incorporation of azide, the chief product being hydroperoxides (AO_2) (~90%). These results were explained by assuming direct involvement of sensitizer in the generation of hydroperoxide (AO_2). A radical mechanism was suggested for the formation of the azidohydroperoxides. From our findings we would infer the reverse. Rose bengal and erythrosin give almost no azidohydroperoxide because azide radicals, probably formed by quenching of singlet oxygen, are immediately trapped by the sensitizer, thereby slowing down the production of the radical product (AO_2HN_3).

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Experimental Part

Synthesis of biadamantylidene (**1**). 8 g (0.053 mol) 2-adamantanone were condensed using $TiCl_3$/$LiAlH_4$ in tetrahydrofuran [26] and gave 6.4 g of a mixture containing adamantane, adamantanol and biadamantylidene (**1**). The alcohol was separated by silica gel column chromatography using pentane as solvent. Separation of the alkene was effected on a 20% $AgNO_3$/silica-gel column with pentane: 2.0 g (34%) colourless crystals, m.p. 184-186° ([27] 184-187°).

Biadamantylidene dioxetane (**2**). 80.0 mg (0.3 mmol) **1** in 10 ml ethyl acetate/MB reagent were photo-oxygenated in the usual way for 2 h. After evaporation of the solvent, **2** was purified on a silica-gel column with pentane: 83.1 mg (94%) pure dioxetane. NMR. and IR. spectra were in accordance with the literature values [28].

Biadamantylidene epoxide (**3**). Epoxidation of **1** with *m*-chloroperbenzoic acid yielded **3** [29].

Oxidation of **1** *in different solvents and with different sensitizers.* 10 mg (0.037 mmol) of **1** in 2 ml of solvent/sensitizers reagent (concentration of sensitizer $10^{-2}-10^{-3}$ mol/l) were photo-oxygenated for 1½-2 h according to [5]. The reaction mixture was analysed by TLC. (ether/pentane 1:9) Rf **1** = 0.75, Rf **2** = 0.44, Rf **3** = 0.25. The results are summarized in *Tables 1, 2* and *3*. The ratios obtained are semi-quantitative in nature and no attempt has been made to attain accuracy which is not necessary for this study. We distinguish essentially between three extreme situations, (1) all epoxide and traces of dioxetane, (2) all dioxetane and traces of epoxide, and (3) intermediate mixtures. No comparison is made between or significance attached to similar product ratios.

Oxidation of **1** *in acetone in the presence of DABCO.* 3 ml of a solution of RB in acetone containing 10 mg (0.037 mmol) of **1** and 2.2 mg (0.010 mmol) of DABCO were oxidized in the usual way for 2 h. Analysis indicated little conversion to dioxetane and epoxide (~5%).

Oxidation of **1** *in acetone in the presence of di-*t*-butyl-*p*-cresol.* A mixture of 10 mg (0.037 mmol) of **1** and 50 mg (0.23 mmol) of di-*t*-butyl-*p*-cresol were photo-oxygenated. Reaction was complete after 30 min. TLC. revealed the formation of 90% dioxetane and 10% epoxide.

Oxidation of **1** *in acetone in the presence of 2-methylnorbornene.* A mixture of 10 mg (0.037 mmol) of **1** and 10 mg (0.09 mmol) of 2-methylnorbornene in 2 ml of a 10^{-3}M solution of RB in acetone was oxidized for 30 min. The sensitizer was completely bleached and TLC. revealed, besides unreacted **1**, 90% dioxetane and 10% epoxide.

Oxidation of **1** *in acetone with triphenyl phosphite ozonide.* 360 mg (1 mmol) of $(PhO)_3PO_3$ were prepared in CH_2Cl_2. Solvent was then evaporated at −40°. A pre-cooled solution of 10 mg (0.037 mmol) of **1** in 10 ml acetone was then added to $(PhO)_3PO_3$. The mixture was kept at −15° for 1 h and then at 20° for ½ h. TLC. revealed the presence of 90% of dioxetane and 10% of epoxide. The oxidation was more than 80% complete.

Oxidation of **1** *in pinacolone.* 10 mg (0.037 mmol) of **1** in 2 ml of purified pinacolone and RB or *m*-TPP as sensitizer were photo-oxygenated for 2 h. GLC. (20% FFAP/chromosorb WAW, 5 m) revealed no trace of *t*-butyl acetate. The lower limit of detectability of the *t*-butyl acetate was $2 \cdot 10^{-2}$ mmol/l (corresponding to 1% conversion).

Oxidation of **1** *in acetone in the presence of phenylglyoxylic acid.* A mixture of 10 mg (0.037 mmol) of **1** and 2.1 mg (0.014 mmol) of phenylglyoxylic acid in 2 ml acetone/RB reagent were photo-oxygenated for 15 min. GLC. (SP-1200, chromosorb W) showed solely benzoic acid as product. TLC. revealed the presence of 60% dioxetane and 40% epoxide in addition to unreacted **1**.

A test reaction showed that phenylglyoxylic acid is also decarboxylated in the absence of **1**, albeit at a much slower rate. After 2 h only 50% of the ketoacid reacted.

Oxidation of **1** *in the presence of superoxide anion.* A mixture of 38 mg (0.14 mmol) of **1**, 30 mg (2.4 mmol) of KO_2, 350 mg (1.3 mmol) of 18-crown-6 ether in 10 ml of a 10^{-3}M solution of eosin in acetone was photo-oxygenated for 2 h. TLC. revealed the formation of 5% dioxetane and 95% epoxide. Separation on a silica-gel column yielded 32 mg (80%) of pure epoxide. Control experiments showed that dioxetane and epoxide are stable under the reaction conditions.

Oxidation of **1** *with a mixture of rose bengal and methylene blue as sensitizer.* 10 mg (0.037 mmol) of **1** in 2 ml of a solution of RB and MB in acetone (concentration of sensitizers: 10^{-3}M) were photo-oxygenated for 2 h. TLC. indicated complete conversion and the formation of 55% dioxetane and 45% epoxide.

Oxidation of **1** *with a polymer-bound sensitizer.* a) *Synthesis of the polymer-bound sensitizer.* The polymer-bound sensitizer was obtained accordingly to [6] using a chloromethylated styrenedivinylbenzene copolymer (*Fluka,* 3.5 mmol of Cl/g of polymer). b) *Oxidation.* A suspension of 10 mg Ⓟ-RB and 10 mg (0.037 mmol) of **1** in 2 ml acetone was oxidized for 2 h. TLC. revealed 80% oxidation and the formation of 80% epoxide and 20% dioxetane.

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