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THE REACTION OF ADAMANTYLIDENEADAMANTANE WITH SINGLET OXYGEN MEDIATED BY ROSE BENGAL AND CHARGE TRANSFER COMPLEXES

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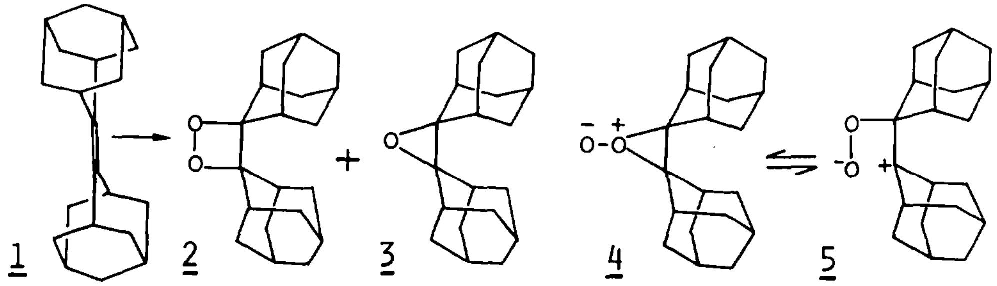
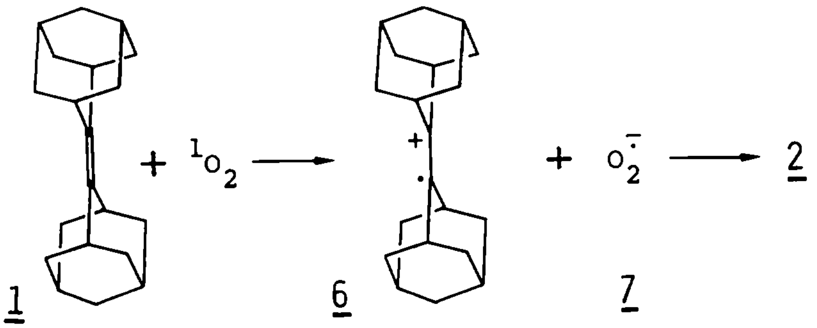
Chemically generated singlet oxygen reacts with adamantylideneadamantane (1) in acetone solution to give mainly the corresponding 1,2-dioxetane (2) together with traces of the epoxide 3. When rose bengal (RB) is added to the reaction mixture, epoxide 3 becomes the chief product at the expense of the dioxetane 2, even in the dark. Charge transfer complexes (CTCs) formed between N-ethylcarbazole and fluorene with 2,4,7-trinitrofluoren-9-one and pyromellitic dianhydride, as well as quinhydrone, behave like RB in that their addition to the reaction mixture favors epoxide formation. Their epoxidizing power is related to the energies of their CT bands. Free energies (ΔG) calculated for the interaction of the CTC with singlet oxygen ranged from -2.07 to 0.45 kcal/mol. CTCs having a ΔG greater than 0.5 kcal/mol are inefficient for the production of 3. The results are explained in terms of two different processes. The normal course is the reaction of singlet oxygen with 1 to give dioxetane. Addends such as CTCs and dimeric RB compete for singlet oxygen and convert it to superoxide radical ion, which in a secondary process is indirectly responsible for epoxidation.

INTRODUCTION

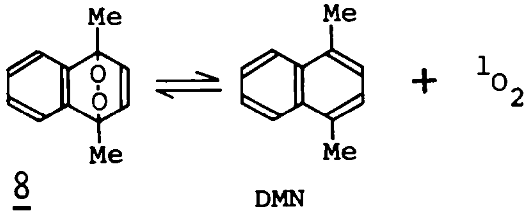
Adamantylideneadamantane (1) is an unusual olefin. Its allylic hydrogen atoms lie in the plane of the double bond which itself is sterically hindered on both faces. Moreover, ever since 1 was found to give a stable bromonium ion with bromine [1], it has been used as a model for testing mechanisms, especially those involving singlet oxygen [2]. Photochemically generated, singlet oxygen reacts with 1 to give the expected dioxetane 2, but often accompanied by variable amounts of epoxide 3 [3].



Despite the simplicity of the reaction, it has been difficult to reach definite conclusions concerning the underlying mechanisms [4]. It now seems reasonably certain that the dioxetane arises from an intermediate perepoxide 4 or its open chain form 5 [5]. It is also equally certain that the epoxide 3 does not derive from the perepoxide 4 despite their structural similarity [3a,3e]. Nevertheless, the origin of the epoxide 3 still remains obscure. Free radical mechanisms may be responsible. There are two likely alternatives. i) Adamantylideneadamantane 1, owing to its low ionization potential (7.84 eV), can easily transfer an electron to singlet oxygen [6]. The resulting long-lived radical cation 6 and superoxide radical anion 7 can either collapse to dioxetane 2 [7] or 6 and triplet oxygen can give 2 [8], thereby leaving 7 to epoxidize 1. ii) The sensitizer could reduce singlet oxygen to 7 which in turn would act on 1 giving epoxide 3 [9].



$1 + 7 \longrightarrow 3$



In fact, we found that when rose bengal (RB) is used to photo-sensitize oxygen, or if rose bengal is added to a chemical source of singlet oxygen, then epoxidation of 1 to 3 becomes a significant event [3e,10]. The present study now examines the role of RB and attempts to reveal its mode of action.

RESULTS

When 1 was exposed to 1,4-dimethyl-1,4-dihydronaphthalene-1,4-endoperoxide (8) in acetone solution at 30° in the dark, dioxetane 2 and adamantan-2-one (9) were formed. Traces of epoxide 3 were also detected (entry 1, Table 1). Oxygenation of 1 with 8 in the presence of DABCO, a singlet oxygen quencher, strongly inhibited the formation of dioxetane 2 (entry 2). Contrariwise, the admixture of 2,6-di-t-butyl-p-cresol (DTBPC), a free radical scavenger, suppressed epoxide (3) completely leaving the yield of dioxetane unchanged (entry 3).

Table 1. Formation of Dioxetane 2 and Epoxide 3 by Treatment of Adamantylideneadamantane (1) with 1,4-Dimethyl-1,4-dihydronaphthalene-1,4-peroxide (8) in Acetone Solution[a)]

			Product %		Ratio	λCT
Entry	Addend (mg)	1	2[2)]	3	3/2	(nm)
1	-	15	78	7	0.09	-
2	DABCO (10)	71	23	4	0.17	-
3	DTBPC (10)	25	75	0	0	-
4	RB (1)	18	57	25	0.44	590
5	RB (2.5)	15	34	51	1.5	
6	RB (5)	18	8	74	9.25	
7	RB (10)	35	17	58	3.41	
8	RB (50)[c)]	57	39	4	0.10	-
9	RB (5) + DABCO (10)	76	3	21	7.00	590
10	RB (5) + DTBPC (10)	70	24	6	0.25	
11	RB (2.5) + H_2O (5%)	56	39	5	0.13	
12	RB (5.0) + H_2O (5%)	48	36	16	0.44	
13	MB (5)	14	86	0[d)]	0	660
14	MB (10)	11	89	0[d)]	0	
15	QH (8.7)	15	3	82	27.3	620
16	F/TENF (6.6/14.4)	60	31	9	0.29	490
17	F/TNF (6.6/12.6)	61	35	4	0.11	465
18	F/PD (6.6/8.7)	33	30	37	1.23	460
19	EC/TENF (9.7/14.4)	63	21	16	0.76	600
20	EC/TNF (7.9/12.6)	55	28	13	0.46	550
21	EC/PD (9.7/8.7)	19	20	71	3.55	565
22	EC/AQ (9.7/8.3)	42	50	8	0.16	450
23	F/AQ (6.61/8.3)	48	46	6	0.13	390
24	EC/FO (9.7/7.2)	39	56	5	0.09	400
25	F/FO (6.6/7.2)	41	55	4	0.07	350
26	TENF	49	43	8	0.19	-
27	TNF	53	40	7	0.17	-
28	BQ (4.4)	39	11	50	4.55	-
29	PD (8.7)	35	34	31	0.91	-
30	TPPO (180)[e)]	27	73	0[d)]	0	-
31	TPPO/PD (180/8.7)[e)]	21	73	6	0.08	-
32	TPPO/BQ (180/4.4)[e)]	30	23	47	2.04	-

[a)] All experiments (except where noted) were performed in the dark at 30°C under N_2 for 48 h. 1 (10.4 mg) and 8 (110.0 mg) were dissolved in acetone (6 ml). Products assayed by weighing after separation by TLC. [b)] Sum of dioxetane (2) and adamantan-2-one (9). [c)] RB (15 mg) fixed on IRA 401 resin. [d)] Traces. [e)] No 8. 5 mg of 1.

When free RB was added to the aforementioned mixture, the proportion of epoxide (3) increased dramatically (entries 4-7). A maximum of 74 % of 3 was seen when the ratio of RB to olefin reached 1:2 by weight (entry 6). At a ratio of 1:1, the yield dropped, but epoxide still predominated (58%) (entry 7). In contrast, the addition of RB bound to an ion exchange resin (IRA 401) had little effect (cf. the ratios of 3 for entries 8 and 1). The combined presence of RB and DABCO (entry 9) accentuated epoxidation over dioxetane formation, while RB and DTBPC acted conversely (entry 10).

The combination of RB and water quenched epoxide formation (entries 11 and 12). Moreover, the addition of methylene blue to the oxygenation mixture was also ineffectual, dioxetane being the sole product of the reaction (entries 13 and 14).

At this juncture, the striking difference in behavior between RB bound to resin and free in acetone solution prompted a determination of its molecular weight under the reaction conditions. At concentrations between 0.2 and 1.1 mmol/kg, using benzil as reference, the apparent molecular weight of RB was 1194. As its actual molecular weight is 1017, the increase may be attributed to partial dimerization in solution.

Dimerization is corroborated by the appearance of characteristic peaks in the visible spectrum. Depending on pH, monomeric RB can exist as the dianion (pH > 8.5), the monoanion (pH 7-8.5) or as the colorless lactone under acidic conditions (pH<6) [11]. In aqueous solution the two anions of the monomeric form display an absorbance (λmax = 541 nm) which is flanked by a blue-shifted band (λmax = 509 nm) and a more intense red-shifted band (λmax = 563 nm). These two extra bands have been ascribed to dimers having helical and transoid sandwich (9) arrangements respectively [12]. In acetone solution, the blue-shifted band is clearly visible (λ max = 520 nm), while the red-shifted band is masked by the absorption due to the monomer. Nevertheless, a value of λmax = 590 nm was estimated for it (Table 1).

Furthermore, as bound and necessarily monomeric RB appears to be chemically inert, it might be inferred that the dimeric form is responsible for epoxide formation. As RB dimerizes by juxtaposition of the quinone and phenolate elements of the two xanthene rings (9), it was deduced that quinhydrone (QH), which possesses the same sort of structure [13], should also engender epoxide (Fig. 1). It does. Oxygenation carried out in the presence of QH gave mainly epoxide (82%) with only a trace of dioxetane (3%) (entry 15).

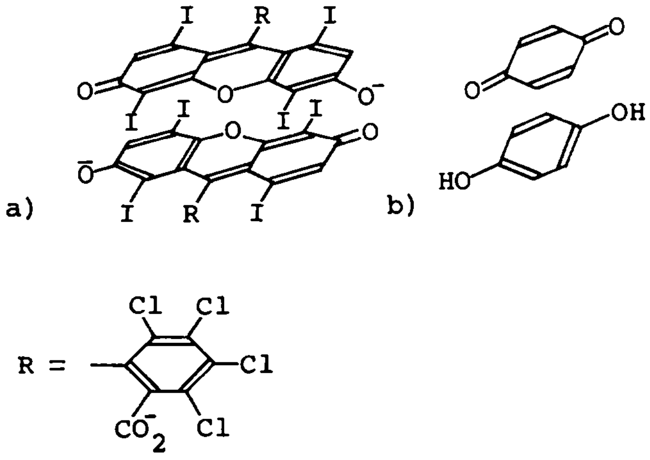


Fig. 1. Simplified depiction of the transoid sandwich arrangement of rose bengal dimer (a) compared to that of quinhydrone (b).

Other molecules related to QH were also epoxidizing. Charge-transfer complexes (CTC) were prepared from fluorene (F), a-type donor (IP = 7.94 eV) [14] and N-ethylcarbazole (EC), a n-type donor (IP = 7.43 eV) [15] and electron acceptor molecules, namely, 2,4,5,7-tetranitrofluoren-9-one (TENF) (EA = 2.23 eV), 2,4,7-trinitrofluoren-9-one (TNF) (EA = 2.10 eV), and pyromellitic dianhydride (PD) (EA = 2.04 eV) [16]. The resulting 1:1 complexes all caused epoxide production, but to differing degrees (entries 16-21). F/PD was the most effective (entry 18), while F/TNF was the least (entry 17).

On the other hand, CTCs formed between F and EC with electron acceptors, such as 9,10-anthraquinone (AQ, EA = 1.57 eV), and fluorene-9-one (FO, EA = 1.19 eV) [16], performed poorly in affording practically no epoxide (entries 22-25).

The oxygenation of 1 in the presence of equimolecular amounts of electron donors alone did not disturb the normal dioxetane reaction. The addition of equimolecular amounts of nitro group substituted electron acceptors (TENF, TNF) led to small amounts of epoxide 3 (ca. 8%), while depressing the yield of oxidized products (entries 26, 27). The greatest effect was observed with the non-nitro electron acceptors, *p*-benzoquinone (BQ) and PD, which produced much epoxide (50 and 31%) (entries 28, 29). The unexpected epoxidizing behavior of PD may be attributed to the formation of a CTC with the 1,4-dimethylnaphthalene (DMN) (IP = 7.92 eV) [17] arising from the decomposition of 8. In fact, the substitution of triphenylphosphite ozonide (TPPO) as the source of singlet oxygen, which by itself gave exclusively dioxetane 2 (entry 30), in conjunction with PD furnished very little epoxide (entry 31). On the other hand, BQ still gave epoxide (entry 32) when mixed with TPPO.

The pH profiles of all the foregoing oxygenations in the presence of RB and the CTCs were almost identical. The reaction became gradually more basic (pH 9-11) until half reaction had occurred. Thereafter, the pH declined towards the initial value, but fell short by some tenths of a pH unit.

DISCUSSION

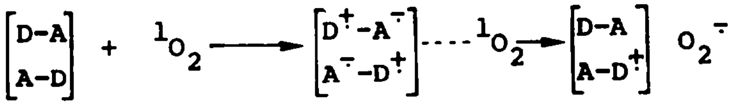
These results show that epoxide 3 is formed as a primary product either by the dye-sensitization or chemical production of singlet oxygen when xanthene dyes are present. This formerly isolated finding has been reinforced by the recent discovery that epoxides are exclusively obtained from the RB-sensitized photo-oxygenation of the syn and anti-isomers of di-t-butylbis(bicyclo[3.3.1]non-9-ylidenes) [18].

Our original suggestion was that superoxide radical anion arose initially by the interaction of monomeric rose bengal with singlet oxygen and that its protonation gave hydroperoxy radical which was the actual epoxidant [3e]. A subsequent study has confirmed that illuminated rose bengal not only produces superoxide radical anion, but singlet oxygen as well and that both species are responsible for oxygenation of suitable substrates [19]. However, another test, using p-nitro tetrazolium blue and superoxide dismutase, failed to detect superoxide supposedly produced by the interaction of RB and singlet oxygen [20].

We now believe that dimeric RB in its ground state is responsible for the epoxidation of 1. The clue to how this happens is provided by the molecular and spectral characteristics of RB and the parallelism of the behavior of RB with structurally related CTCs.

In general, the donor (D) and acceptor (A) molecules in the lowest state of a 1:1 CTC are held together by non-bonding forces [21]. Electron transfer creates the first excited state (D+...A-...). Transition between these two states accounts for the characteristic absorption or CT band [22]. In the transoid sandwich arrangement, RB is a double CTC. We believe that dimeric RB behaves like a donor-acceptor (D,A) complex and interacts with singlet oxygen to generate superoxide ion by first giving an excited complex, which on collapsing to the ground state transfers an electron from a SOMO of the acceptor to the LUMO of the oxygen molecule (Scheme 1). It can be assumed that the resulting RB cation radical is sufficiently stable to allow superoxide to react independently.

Scheme 1.



The other single CTCs seem to behave the same way. The extent of epoxidation depends on the first step, namely the efficiency of the interaction of the CTC with singlet oxygen. In terms of their epoxidizing power, the CTCs in question fall into three groups. The most effective are RB, QH, EC/PD and F/PD. They generate epoxide as the major product (3/2 = >1). The next group is less efficient. EC/TENF, EC/TNF, F/TENF and F/TNF only furnish epoxide as a minor product (3/2 = 0.1-1). The third group, comprising EC/AQ, F/AQ, EC/FO, and F/FO, is like the second group, except that epoxide is only formed in traces (**3**/**2** = 0.07-0.16).

eq. 1. $\Delta G = 23.06\ [E(D/D^{+}) - E(A^{-}/A)] - e^{2}/E\alpha - \Delta E_{0,0}$

The different powers of epoxidation may be attributed to the energies of the CT bands. The free energy change (ΔG) associated with a one electron transfer between the CTC and singlet oxygen can be estimated from the Rehm-Weller equation (eq. 1) [23]. The value of ΔG can be calculated to a first approximation by taking the energy for the CTC absorption band in acetone for the electron donor term $E(D/D^{+}.)$. The value of 0.58 V vs SCE in acetone (pH independent) is used for $E(O_2^{-}/O_2$, which corresponds to the reduction potential of the acceptor $E(A^{-}/A)$ [24]. The coulombic attraction term, $e^{2}/E\alpha$ is evaluated at 0.6 kcal/mol for an arbitrary radical ion distance of 6 Å [25]. The energy of the first excited state (Δg) of molecular oxygen (22.5 kcal/mol) is taken for $\Delta E_{0,0}$. The values ΔG so calculated for the different CTCs (Table 2) correlate well with the amount of epoxide formed and give two distinct curves (Fig. 2). The upper curve represents the epoxidizing power of QH, RB and the non-nitrated CTCs, as well as the supposed DMN/PD. The greatest quantity of epoxide is produced by the CTC having the absorption band of lowest energy, which also means that an electron is transferred to singlet oxygen exothermically (1-2 kcal/mol). The ideal lower limit for epoxidation (ΔG=0) should be reached when the CTC absorption band has a λmax of 487 nm, which corresponds to an energy of 9.73 kcal/mol (2.45 eV). However, as the CTC bands are usually broad, substantial amounts of epoxide are observed for values of λmax as low as 460 nm (10.3 kcal/mol or 2.7 eV), thereby extending the real limit for epoxidation to ΔG = 0.5 kcal/mol.

Table 2. Absorption maxima of the CT bands of RB and some CTCs in acetone together with the corresponding calculated free energies of interaction with singlet oxygen (ΔG)

	QH	RB	EC/PD	F/PD	DMN/PD	EC/TENF	EC/TNF	F/TENF
ΔG (kcal/mol)	-2.07	-1.69	-1.26	0.45	0.58	-1.82	-1.10	-0.16
λCT (nm)	620	590	565	465	460	600	550	490

	F/TNF	EC/AQ	F/AQ	EC/FO	F/FO
ΔG (kcal/mol)	0.45	0.58	2.48	2.10	3.94
λCT (nm)	465	460	~390	400	~350

The lower curve shows that the CTCs composed of nitrated acceptors perform more poorly than expected. The lower production of epoxide may be due to the quenching of superoxide radical anion, which should be particularly effective for nitro derivatives, since tetranitromethane is an efficient scavenger [26]. CTCs having ΔG>0.5 kcal/mol, e.g. F/AQ, EC/AQ, F/FO and EC/FO are not epoxidizing agents.

In all the foregoing cases, singlet oxygen is undoubtedly the source of superoxide radical anion. Triplet oxygen can be excluded for energy reasons; the values of ΔG would have to be more exothermic by at least 22.5 kcal/mol. Moreover, the possibility that **1**, owing to its low IP [6], might form a CTC with any one of the acceptors was excluded by experiment.

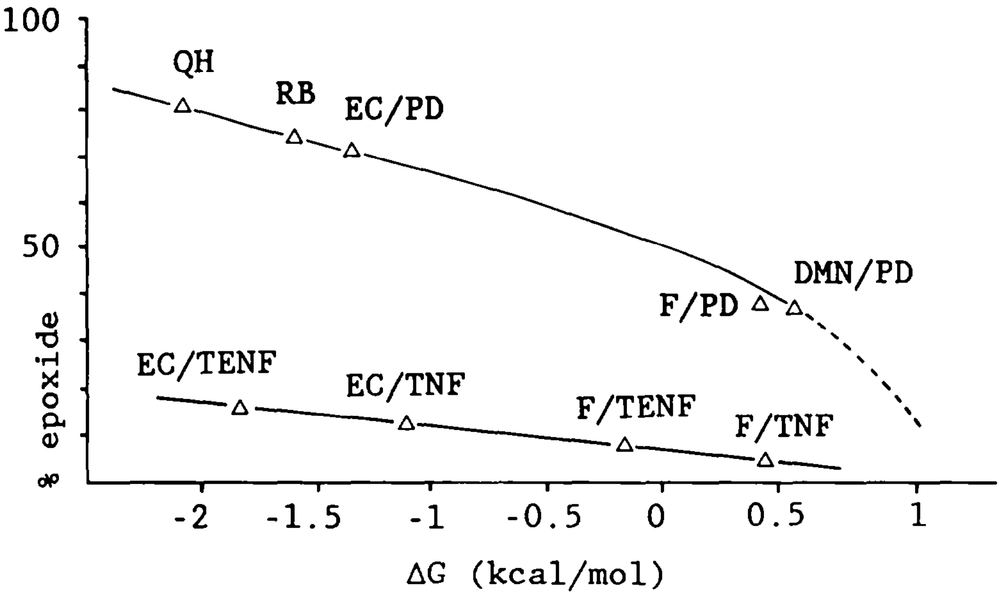
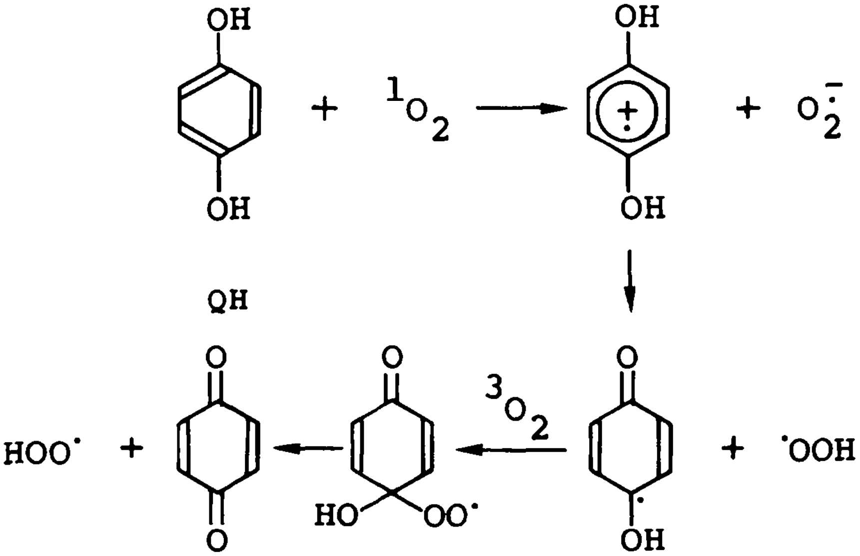


Fig. 2. Amount of epoxide (3) formed by the action of chemically generated singlet oxygen on adamantylideneadamantane (1) in the presence of some CTCs related to their calculated free energies of interaction with singlet oxygen (ΔG).

Although all the CTCs produce superoxide radical anion initially, other species such as hydroperoxy radical could well be formed, especially from QH. The radical cation remaining, after QH has formed superoxide radical anion, could react further with triplet oxygen to give more hydroperoxy radical (Scheme 2). Hydrogen abstraction would furnish hydrogen peroxide [27].

Scheme 2



The present results are relevant to the oxidative photo-bleaching of xanthene dyes (D) such as eosin and erythrosin [9]. Evidence was adduced for the formation of molecular complexes of the ion pair type $D^+ \ldots O_2^-$, arising from the interaction of oxygen with $D^+ \ldots D^-$, when the dye concentration was high (D-D mechanism). Moreover, hydrogen peroxide was formed in illuminated concentrated aqueous solutions of eosin under oxygen. In our experiments there is no photo-excitation of the xanthene dye (RB), and thus no D-D mechanism as such. It is now seen that the dimeric association alone is sufficient to cause reaction with chemically generated singlet oxygen to furnish superoxide and eventually hydrogen peroxide.

$$eq.\ 2.\quad 2O_2^- + H_2O \rightarrow O_2 + {}^-OOH + {}^-OH$$

$$eq.3.\quad 2{\cdot}OOH \rightarrow O_2 + HOOH$$

How 1 is actually oxidized by superoxide radical anion or its derivatives is problematical. Traces of water, especially at alkaline pH, which is characteristic of the reaction conditions, could cause disproportionation of superoxide and hydroperoxy radicals to hydrogen peroxide (eqs.2,3) [24b,28]. Evidence for the discrete existence of superoxide radical anion and the possibility that hydrogen peroxide is the reagent responsible for epoxidation will be discussed elsewhere.

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EXPERIMENTAL PART

General. - Thin layer chromatography (TLC) silica gel 60 F_{254} *Merck*. Preparative layer chromatography: silica gel 60 F_{254} (thickness 2 mm). All solvents were analytical grade *Merck*. Physical constant and spectra were determined using the following instruments. Melting point (m.p.): *Reichert* hot-stage microscope (uncorrected). IR spectra: *Perkin-Elmer* 681 spectrometer. UV-VIS spectra: *Kontron* Uvikon spectrometer. ^{1}H-NMR spectra: *Bruker* WH 360 spectrometer. The degree of association of RB was measured with a *Knauer* vapor pressure osmometer. pH measurements were performed with a *Metrohm* 632 pH meter coupled with a *Metrohm* Laborgraph E 478 recorder (combination glass electrode).

Materials. - Adamantylideneadamantane [29], 1,4-dimethyl-1,4-dihydronaphthalene 1,4-endoperoxide [30] and triphenylphosphite ozonide (TPPO) [31] were prepared and purified. Rose bengal (RB) (*Fluka*, purum) was purified by column chromatography on Florisil (*Fluka*) (acetone:ether 2:1). Quinhydrone (QH) (*Fluka*, purum) was twice sublimed at 1 mm/HG. m.p. 168°C. 1,4-Benzoquinone (BQ) (*Fluka*, purum) was sublimed. m.p. 113.5°C. N-ethylcarbazole (EC) (*EGA-Chemie*) and fluorene (F) (*Fluka*, purum) were twice recrystallized from EtOH, giving melting points of 68°C and 115-6°C respectively. 2,4,7-Trinitrofluoren-9-one (TNF) (*Fluka*, purum) and 2,4,5,7-tetranitrofluoren-9-one (TENF) (*Aldrich*) were twice recrystallized from CH_2Cl_2, giving melting points 175°C and 253°C respectively. 1,2,4,5-Benzenetetracarboxylic acid dianhydride (pyromellitic dianhydride) (PD) (*Fluka*, pract.) was recrystallized from CH_2Cl_2, m.p. 285-6°C. 9,10-Anthraquinone (AQ) (*Fluka*, purum) was crystallized from EtOH, m.p. 284-5°C. 9-Fluorenone (FO) (*Fluka*, puriss.) was used without further purification, m.p. 82-3°C.

In a typical reaction, adamantylideneadamantane (1) (10.7 mg, 0.04 mmol) was dissolved in acetone (3 ml). A solution of RB or the CTC (1:1) in acetone (3 ml) or acetone containing 5% H_2O was then added. The amounts of RB and CTC actually used are shown in Table 1.

1,4-Dimethyl-1,4-dihydronaphthalene 1,4-endoperoxide (8) (110 mg, 0.6 mmol) was next added to the reaction mixture and the resulting solutions were incubated at 30°C in the dark for 48 h under nitrogen. At the end of the reaction, the products were separated by preparative TLC (pentane:ether, 9:1).

Triphenylphosphite ozonide (TPPO) was also used as a source of singlet oxygen. Triphenylphosphite (155 mg, 0.25 mmol) was ozonized at -78°C in CH_2Cl_2. The solvent was evaporated almost to dryness at -40°C. A pre-cooled solution (-10°C) of 1 (5 mg, 0.02 mmol) and acceptors [BQ (4.4 mg, 0.04 mmol) or PD (8.7 mg, 0.04 mmol)] in acetone (10 ml) was added to the TPPO. The mixture was kept at -15°C for 1 h and then allowed to warm to room temperature for 2 h. The products were separated by preparative TLC. The variation of the pH of the reactions was followed by using a glass microelectrode which was inserted through the plastic cap of the reaction vessel. All the results so obtained are recorded in Table 1.

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