

Singlet Oxygen Reactions with 9,10-Diphenylanthracene Peroxide¹

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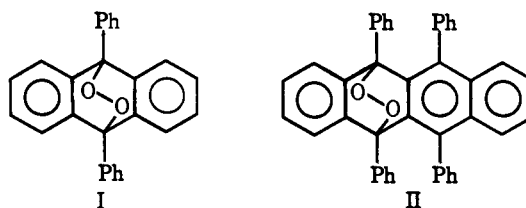
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Abstract: The thermal decomposition of 9,10-diphenylanthracene peroxide in the presence of a series of ten representative substrates has been studied. The oxidation products are formed in good to excellent yield along with 9,10-diphenylanthracene. The structures of the oxygenated products are the same as those observed in parallel dye-sensitized photooxygenation reactions. The method thus provides a synthetically useful chemical method for carrying out singlet oxygen reactions. A mechanism consisting of (a) dissociation of 9,10-diphenylanthracene peroxide to 9,10-diphenylanthracene and singlet oxygen followed by (b) reaction of singlet oxygen with the substrate is in accord with the kinetic studies which have been carried out.

Since the discovery by Dufraisse³ in 1926 that solutions of the red hydrocarbon rubrene (5,6,11,12-tetraphenylanthracene) become colorless upon exposure to light and air as a result of transannular peroxide formation, over 150 such polycyclic aromatic "endoperoxides" have been described in the literature.⁴ In contrast to dialkyl peroxides which commonly suffer oxygen-oxygen bond homolysis upon heating, many of these aromatic peroxides undergo loss of molecular oxygen upon thermolysis with regeneration of the polyacene.⁴ *A priori* considerations of spin conservation suggest that the molecular oxygen produced in this way is of singlet multiplicity. The present work was initiated in order to test this idea and, in addition, to provide a convenient new reagent for bringing about the singlet oxygen oxygenation of organic acceptor molecules in solution.

Choice and Preparation of Transannular Peroxides. It has been previously shown that the ease of release of molecular oxygen by polyacene peroxides upon thermolysis depends primarily on the nature of the aromatic system and on the type of substituents in the meso positions.^{4,5} In general, it appears that peroxides in the anthracene series give greater yields of oxygen than those in the naphthalene series and that aryl substituents in the meso positions lead to increased oxygen release relative to alkyl or hydrogen. Accordingly, the peroxide chosen for study was 9,10-diphenylanthracene peroxide (I) (DPAP) which is reported⁶ to release 96% of its oxygen as molecular oxygen when heated to 180° *in vacuo*. By comparison, rubrene peroxide (II) (reported³ to give up to an 80% yield of oxygen at 140–150°) was briefly investigated and found to be much less satisfactory as a singlet oxygen source.

Both peroxides used in this study could be conveniently prepared by photolysis of aerated carbon disulfide solutions of 9,10-diphenylanthracene and ru-



brene, respectively.⁷ These reactions presumably involve the addition of singlet ¹Δ_g oxygen across the meso positions of the aromatic rings.⁸ Samples of I and II prepared in this manner were colorless, crystalline compounds which appeared to be indefinitely stable when stored in the solid state at 0–5°. No difficulties were encountered in the handling of these peroxides, but safety shields were nonetheless routinely employed.

Decomposition of Peroxides I and II in the Presence of Singlet Oxygen Acceptors. Preliminary qualitative experiments indicated that 9,10-diphenylanthracene peroxide (I) dissociated at an appreciable rate at 80° in refluxing benzene. The rate constant for this dissociation in the presence of an excess of a reactive singlet oxygen acceptor was subsequently determined (see Experimental Section) to be $1.2 \pm 0.1 \times 10^{-5} \text{ sec}^{-1}$ (half-life = 16 hr).

Accordingly, 9,10-diphenylanthracene peroxide was allowed to decompose in refluxing benzene solution in the presence of a variety of known singlet oxygen acceptors. In most cases the mole ratio of peroxide to acceptor was 2:1, although in some runs, ratios ranging from 10:1 to slightly less than 1:1 were used (see Table I^{9–17}). The solutions were refluxed for at least one

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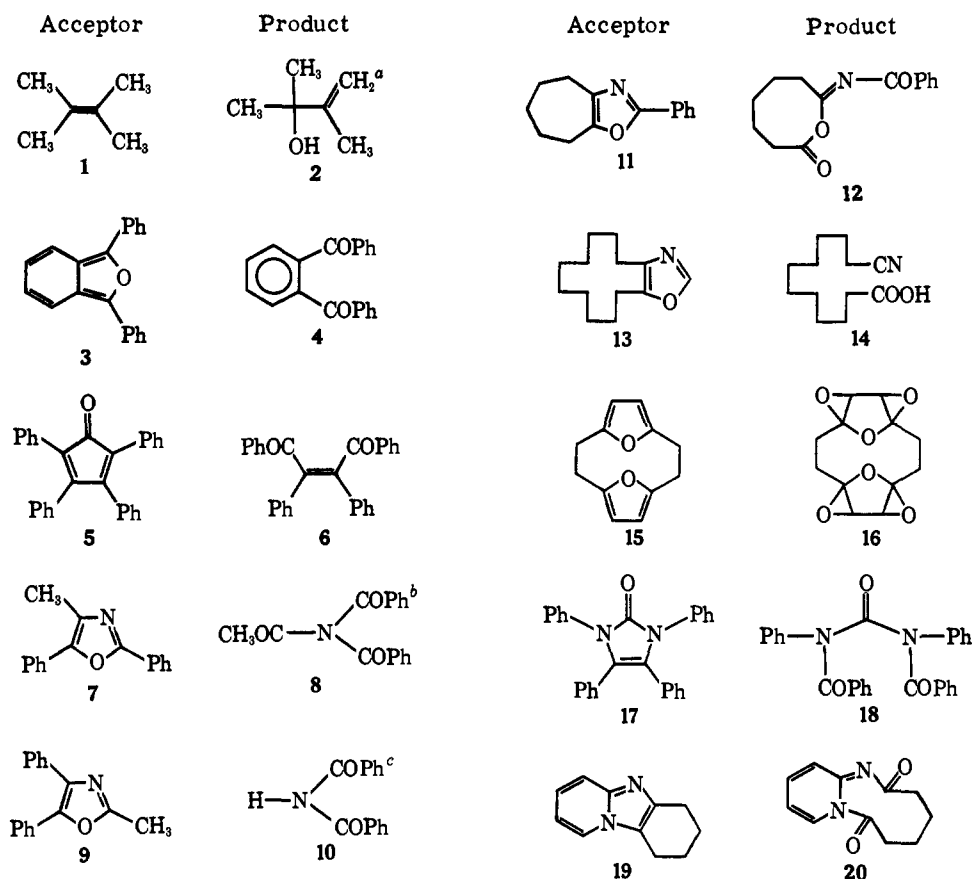
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Table I. Decomposition of 9,10-Diphenylanthracene Peroxide with Acceptors

Acceptor	Mole ratio of peroxide to acceptor	Solvent	Time, hr	Product	Yield, %	Reference to previous oxygenation results
1	1:1	Benzene	93	2	25	9
3	2:1	Benzene	37	4	99	10, 17
5	2:1	Benzene	72	6	40	9b, 9d, 11, 17
7	2:1	Benzene	94	8	92 ^a	12
9	2:1	DMSO	17.5	10	25 ^b	12
11	1:1	Benzene	54	12	75	13
13	10:1	Toluene	6.75	14	62	14
15	0.6:1	Benzene	30.5	16	80	15
17	2.3:1	Benzene	135	18	80	16
19	0.8:1	Benzene	121	20	67	16

^a Includes 10% dibenzamide from hydrolyses of **8** during chromatography. ^b Starting material **9** (75%) was recovered. Product **10** is formed from the hydrolysis of **8** during the aqueous work-up.

Chart I. Acceptors Studied and Products Obtained



^a After reduction of initially formed hydroperoxide. ^b Plus dibenzamide (10%) formed during work-up. ^c Resulting from hydrolysis of **8** during aqueous work-up.

peroxide half-life and in one case for as long as 135 hr. The structures of the compounds oxygenated and the resulting products are shown in Chart I. The ratio of peroxide to acceptor, solvent used, reaction time, yield of oxygenated product(s), and literature references to the same oxygenations using other sources of singlet oxygen are compiled in Table I.

Aprotic solvents other than benzene (e.g., toluene, chloroform, or dimethyl sulfoxide) may also be used. Alcoholic solvents are not suitable since they react with 9,10-diphenylanthracene peroxide. For example, refluxing 9,10-diphenylanthracene peroxide in ethanol gives mixtures containing phenol and methoxylated

anthracene derivatives.¹⁸ Only small amounts (35%) of 9,10-diphenylanthracene are formed.

Rubrene peroxide (II) proved to be considerably less efficient than 9,10-diphenylanthracene peroxide in bringing about typical singlet oxygen reactions. For example, 1,3-diphenylisobenzofuran (**3**) was converted to *o*-dibenzoylbenzene (**4**) in only 36% yield (plus 60% recovered starting material) upon treatment with a 2:1 mole excess of rubrene peroxide in refluxing benzene for 48 hr. Under the same conditions the yield of *o*-dibenzoylbenzene was 99% with 9,10-diphenylanthracene peroxide (cf. Table I).

(16) M. L. Wolff, Ph.D. Thesis, Yale University, 1970.

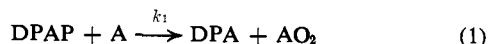
(17) J. R. Scheffer and M. D. Ouchi, *Tetrahedron Lett.*, 223 (1969).

(18) P. F. Southern and W. A. Waters, *J. Chem. Soc.*, 4340 (1960), have observed similar reactions during the decomposition of 9-methyl-10-phenylanthracene peroxide in the presence of various protic solvents.

The results listed in Table I demonstrate the synthetic utility of using 9,10-diphenylanthracene peroxide in singlet oxygen-like oxygenations. All three major types of singlet oxygen reactions, *i.e.*, the ene reaction,¹⁹ the 4 + 2 cycloaddition reaction,⁴ and the "ozonolytic" cleavage of electron-rich double bonds,²⁰ are represented.²¹ In every case the reactions using 9,10-diphenylanthracene peroxide exactly parallel, with comparable yields, the results obtained using other proven sources of singlet oxygen. Thus, ¹Δ_g oxygen is strongly implicated as the species responsible for oxygenation in the decomposition of 9,10-diphenylanthracene peroxide (see also section on Kinetic Studies).

Advantages of the Peroxide Decomposition Method in Singlet Oxygen Reactions. For many applications the use of 9,10-diphenylanthracene peroxide may prove superior to existing methods of oxygenation. For example, problems of sensitizer decomposition and substrate or product photolysis which may be associated with photooxidations are avoided. In addition, the present method offers a potentially wider range of solvents compared with photooxygenation reactions where the solubility of sensitizer dyes is a limiting factor. Similarly, the strongly basic solutions and stringent solvent requirements of the sodium hypochlorite-hydrogen peroxide²² and bromine-alkaline hydrogen peroxide²³ methods of generating singlet oxygen are eliminated. The need for working at reduced pressures as in the microwave discharge methods of Corey⁸ and Scheffer¹⁷ is obviated, and the special low temperature techniques and accompanying solubility problems of the triphenyl phosphite-ozone complex method^{9d} are avoided. The work-up required in oxygenations using 9,10-diphenylanthracene peroxide consists simply of solvent evaporation followed by column chromatography (nonvolatile products) or distillation (volatile products) to remove the 9,10-diphenylanthracene by-product and is similar to the work-up involved in photooxygenations (sensitizer removal) and triphenyl phosphite-ozone complex oxidations (removal of triphenyl phosphate). Aqueous work-ups as in the hydrogen peroxide methods may be avoided.

Kinetics and Mechanism. *A priori*, two kinetically distinct mechanisms may be considered for the oxygenation of acceptor molecules using 9,10-diphenylanthracene peroxide. The first of these (eq 1) involves direct



bimolecular oxygen transfer from 9,10-diphenylanthracene peroxide (DPAP) to the acceptor (A) to give 9,10-diphenylanthracene (DPA) and oxygenated acceptor (AO₂). The rate of this process will of course be proportional to the product of the concentrations of 9,10-diphenylanthracene peroxide and acceptor as shown in eq 2.

$$-d[\text{A}]/dt = k_1[\text{DPAP}][\text{A}] \quad (2)$$

The second mechanism (eq 3-5) involves dissociation of 9,10-diphenylanthracene peroxide to 9,10-diphenyl-

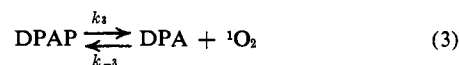
(19) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(20) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970), and references cited therein.

(21) For oxygenation of an enolate anion using 9,10-diphenylanthracene peroxide see R. H. Young and H. Hart, *Chem. Commun.*, 827 (1967).

(22) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(23) E. McKeown and W. A. Waters, *J. Chem. Soc. B*, 1040 (1966).



anthracene and singlet oxygen followed by reaction of the latter with the acceptor to give product.²⁴ Included in this mechanism are the nonproduct forming and hence competing steps of peroxide regeneration (k_{-3}) and singlet oxygen radiationless decay (k_4). Application of the steady-state assumption for [¹O₂] in eq 3-5 leads, at low conversions when $k_{-3}[\text{DPA}][{}^1\text{O}_2] \simeq 0$, to rate expression 6. If the second mechanism

$$-d[\text{A}]/dt = k_3k_5[\text{DPAP}][\text{A}]/(k_4 + k_5[\text{A}]) \quad (6)$$

(singlet oxygen) is operative, it seems clear, in view of the high yields of oxygenated products generally obtained, that the decay of singlet oxygen to its ground state (eq 4) cannot normally compete with the bimolecular reaction of ¹O₂ with the substrate (eq 5) under the conditions used in this study. Thus, with reactive acceptors, the condition that $k_5[\text{A}] \gg k_4$ is met, and eq 6 can be simplified to

$$-d[\text{A}]/dt = k_3[\text{DPAP}] \quad (7)$$

Experimentally, eq 2 and 7 were tested by determining the relative rates of oxygenation of 2-methyl-4,5-diphenyloxazole (9) and of tetracyclone (5) and noting the rate effects which resulted from changing the concentrations of 9,10-diphenylanthracene peroxide or of the acceptors 5 and 9. These results are shown in Table II;

Table II. Approximate Relative Rates of Oxygenation of Acceptors 5 and 9^a

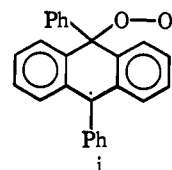
Acceptor	[A], M	[DPAP], M	Relative rate
5	2 × 10 ⁻²	4 × 10 ⁻²	2.57
5	2 × 10 ⁻²	8 × 10 ⁻²	5.50
5	4 × 10 ⁻²	8 × 10 ⁻²	6.67
9	2 × 10 ⁻²	4 × 10 ⁻²	0.137
9	4 × 10 ⁻²	4 × 10 ⁻²	0.136
9	4 × 10 ⁻²	8 × 10 ⁻²	0.279
9	2 × 10 ⁻²	8 × 10 ⁻²	0.233

^a Determined in refluxing benzene at low (<25%) conversion.

the procedures used in determining these relative rates are detailed in the Experimental Section.

The general trend of the results in Table II is quite clear: the relative rates of oxygenation are essentially independent of acceptor concentration and approxi-

(24) A third mechanism, kinetically indistinguishable from path one (eq 1 and 2), involving reversible 9,10-diphenylanthracene peroxide carbon-oxygen bond cleavage to give moloxide *i* followed by a bimolecu-



lar moloxide-acceptor reaction to give 9,10-diphenylanthracene and product is less likely in view of the general failure to observe or to provide evidence for such intermediates in photooxygenation reactions (*e.g.*, T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966)). Attempts in the present work to trap such a species using good hydrogen atom donors (*e.g.*, diisopropyl ether) were unsuccessful.

mately directly proportional to the 9,10-diphenylanthracene peroxide concentration within the range of concentrations studied. The latter concentrations are the same as those used in standard photooxygenation reactions. These results thus rule out a mechanism involving direct bimolecular oxygen transfer from peroxide to acceptors **5** and **9** and support the intermediacy of singlet oxygen in these and related oxygenations.²⁵ A further conclusion, as mentioned previously, is that k_{-1} , the solution rate constant for decay of singlet oxygen to its ground state, is at least 1 order of magnitude smaller than the term $k_3[A]$ of eq 6. This need not be the case for sluggish singlet oxygen acceptors which must compete less successfully for singlet oxygen not only with the decay pathway but also with 9,10-diphenylanthracene. In these cases, product yields are likely to be low, although increasing the reactant concentrations and the initial peroxide/acceptor ratios may be of some benefit.

Finally, the activation energy for the decomposition of 9,10-diphenylanthracene peroxide to 9,10-diphenylanthracene and singlet oxygen was determined from the rate constants for the oxygenation of tetracyclone at three different temperatures (81, 100, and 111°). The activation energy thus obtained was 27.8 ± 0.2 kcal/mol. It is interesting to compare this value with the activation energy of 29.8 kcal/mol estimated²⁶ for the thermal decomposition of anthracene endoperoxide. This latter value, however, is the activation energy necessary for oxygen-oxygen bond homolysis in anthracene endoperoxide, not for release of molecular oxygen. In fact, no oxygen at all can be detected in the thermolysis of anthracene peroxide.²⁷ The peroxide bond homolysis pathway is demonstrated by the observation that styrene is rapidly polymerized when anthracene peroxide is thermolyzed in its presence.^{26,28} Significantly, the polymerization of styrene and methyl methacrylate *could not* be initiated by the thermal decomposition of 9,10-diphenylanthracene peroxide.¹⁸

Kearns, *et al.*,²⁹ have made predictions based on theoretical correlation diagrams to the effect that polyacene endoperoxides will decompose thermally to the parent aromatic system and $^1\Delta_g$ oxygen only if the resulting gain in resonance energy by the hydrocarbon is sufficiently great (*ca.* 30 kcal/mol) to make this the preferred decomposition pathway; otherwise oxygen-oxygen bond homolysis will predominate. This theory may be something of an oversimplification for substituted anthracenes in view of the fact that anthracene and 9,10-diphenylanthracene should have very similar polynuclear resonance energies due to the inability (for steric reasons) of the phenyl groups of the latter to achieve coplanarity with the anthracene ring.³⁰

(25) While the results presented herein provide strong support for the intermediacy of $^1\Delta_g$ oxygen in the thermal decomposition of 9,10-diphenylanthracene peroxide, it would be desirable to have direct spectral evidence for its presence in these reactions. However, attempts to detect the characteristic emission spectrum of $^1\Delta_g$ oxygen from the thermolysis of 9,10-diphenylanthracene peroxide, both in solution and in the gas phase, have to date been unsuccessful (J. R. Scheffer, E. A. Ogryzlo, and R. D. Ashford, unpublished results).

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(27) C. Dufraisse and M. Gerard, *C. R. Acad. Sci.*, **201**, 428 (1935).

(28) J. W. Breitenbach and A. Kastell, *Monatsh. Chem.*, **84**, 645 (1953).

(29) A. U. Khan and D. R. Kearns, *Advan. Chem. Ser.*, No. 77, 143 (1968); D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, **10**, 193 (1969); D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

Experimental Section³¹

Preparation of 9,10-Diphenylanthracene Peroxide. The following procedure is a modification of the method of Dufraisse and Etienne.³² A solution of 5.0 g of purified (mp 254°) 9,10-diphenylanthracene in 3.5 l. of carbon disulfide (Matheson Spectroquality) was cooled by an immersed cold water condenser and saturated with oxygen. The magnetically stirred solution was irradiated with a 275-W Sylvania RS sun lamp from a distance of 12 in. until tlc on silica gel (50% hexane-benzene) showed little remaining 9,10-diphenylanthracene (48 hr). *Caution must be exercised during this procedure due to the low flash point of carbon disulfide and to the hazardous nature of carbon disulfide-oxygen mixtures.* Removal of the solvent under reduced pressure at <30° to a volume of approximately 250 ml followed by addition of 750 ml of 40-60° petroleum ether afforded, after filtration, 5.58 g (102%) of 9,10-diphenylanthracene peroxide, dec 178-180°, mp 252°. The peroxide could be further purified by dissolving it in cold benzene (100 ml), treatment with Norit, filtration, and removal of solvent *in vacuo* to a volume of *ca.* 40 ml. Dropwise addition of petroleum ether (200 ml) and filtration yielded 4.93 g (90%) of the peroxide as white crystals, dec 180-181°, mp 254°, whose uv spectrum showed no 9,10-diphenylanthracene present. The peroxide showed no sign of decomposition during storage at 0-5° over a period of 9 months.

Preparation of Rubrene Peroxide. A solution of 4.0 g (7.5 mmol) of rubrene in 3.0 l. of carbon disulfide was irradiated (Caution!) for 5.0 hr from a distance of 18 in. with a 275-W Sylvania RS sun lamp. Dry air was continuously passed through the stirred solution by means of a fritted gas dispersion tube. During this time, the solution turned from brilliant orange to light yellow. Carbon disulfide was removed *in vacuo* until approximately 250 ml of solution remained. Low boiling petroleum ether (500 ml) was added and the solution again concentrated to 250 ml *in vacuo*. This solution was further diluted with 350 ml of petroleum ether and allowed to stand overnight at 5°. Filtration followed by washing with cold petroleum ether afforded 3.95 g (93%) of light yellow rubrene peroxide, mp 170° (decomposes with gas evolution and turns bright red). Rubrene peroxide could be recrystallized from carbon disulfide to yield large colorless crystals, mp 155° dec.

Oxygenation of 2,3-Dimethyl-2-butene (1) with 9,10-Diphenylanthracene Peroxide. A solution of 1.45 g (4 mmol) of 9,10-diphenylanthracene peroxide and 0.337 g (4 mmol) of 2,3-dimethyl-2-butene in 50 ml of benzene was refluxed in the dark under nitrogen for 93 hr. The solution was then cooled to 0° by means of an ice bath and 1.50 g (5.7 mmol) of triphenylphosphine in 10 ml of benzene added dropwise during 10 min. The resulting solution was stirred for 0.5 hr at 0° and 2.0 hr at room temperature under nitrogen. The majority of the benzene was then removed by careful distillation (bath temperature <90°) and the residue subjected to bulb-to-bulb distillation. Vapor phase chromatography (20 ft preparative column packed with 15% Carbowax on Chromosorb W, column temperature 90°) of the bulb-to-bulb distillate indicated an approximately 25% yield of 2,3-dimethyl-1-buten-3-ol (2). A collected sample of this material was identical in every respect (nmr, ir, and vpc retention time) with an authentic sample of 2,3-dimethyl-1-buten-3-ol prepared by the method of Schenck and Schulte-Elte.³³

Oxygenation of 1,3-Diphenylisobenzofuran (3) with 9,10-Diphenylanthracene Peroxide. A solution of 0.27 g (1 mmol) of 1,3-diphenylisobenzofuran and 0.724 g (2 mmol) of 9,10-diphenylanthracene peroxide in 50 ml of benzene was refluxed in the dark for 37 hr. At the end of this time none of the highly fluorescent 1,3-diphenylisobenzofuran could be detected by tlc. The residue after removal of benzene *in vacuo* was chromatographed on a 35 × 2 cm silica gel (Davison Chemical, Grade 923, 100-200 mesh) column slurry

(30) The two phenyl groups of 9,10-diphenylanthracene have been shown to be twisted by *ca.* 66° relative to the anthracene nucleus: T. D. S. Hamilton, *Photochem. Photobiol.*, **3**, 153 (1964).

(31) Melting points were determined with either a Mel-Temp capillary apparatus or a Kofler micro hot stage apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237 spectrophotometer, and nuclear magnetic resonance spectra were recorded on Varian A-60A and HA-100 spectrometers using tetramethylsilane as an internal standard. Ultraviolet spectra were taken on Cary Model 11, Bausch and Lomb Model 550, and Beckman DB-G recording spectrophotometers, and mass spectra were obtained using Hitachi (RMU-6) and AEI (MS-9) spectrometers. All solvents were purified and dried by standard procedures prior to use.

(32) C. Dufraisse and A. Etienne, *C. R. Acad. Sci.*, **201**, 280 (1935).

packed with 5% ether-hexane; 100-ml fractions were collected. Fractions 1-14 (hexane) contained 0.31 g of 9,10-diphenylanthracene. Fractions 15-24 (2% ether-hexane) contained 0.35 g of unreacted 9,10-diphenylanthracene peroxide. Fractions 25-28 (4% ether-hexane), 29-34 (6% ether-hexane), and 35-36 (10% ether-hexane) were essentially empty and were discarded. Fractions 37-43 (10% ether-hexane) and 44-46 (12% ether-hexane) contained 0.28 g of a white solid, mp 136-147°. Recrystallization of this material from chloroform-hexane yielded needles, mp 145-147°, identical in every respect (mp, mmp, ir) with authentic *o*-dibenzoylbenzene obtained from the photooxygenation of 1,3-diphenylisobenzofuran.¹⁰ The overall yield of *o*-dibenzoylbenzene (4) was 99%.

Refluxing a benzene solution of 9,10-diphenylanthracene and 1,3-diphenylisobenzofuran (1:1 mole ratio) in the dark for 37 hr followed by column chromatography on silica gel resulted in essentially quantitative recovery of starting materials.

Oxygenation of 1,3-Diphenylisobenzofuran (3) with Rubrene Peroxide. A solution consisting of 1.13 g (2 mmol) of rubrene peroxide and 0.27 g (1 mmol) of 1,3-diphenylisobenzofuran in 50 ml of anhydrous benzene was refluxed in the dark under nitrogen for 48 hr. Benzene was removed *in vacuo* and the residue was chromatographed on a 60 × 2 cm silica gel chromatography column slurry packed in 5% ether-hexane; 150-ml fractions were collected. Fractions 1-5 (hexane) were empty. Fractions 6-9 (hexane) and 10-12 (2% ether-hexane) contained 0.162 g of unreacted 1,3-diphenylisobenzofuran. Fractions 13-22 (2% ether-hexane) contained 1.05 g of a mixture of rubrene and an unknown compound which was subsequently shown to arise from rearrangement of rubrene peroxide during chromatography. This compound was not characterized. Fractions 23-28 (4% ether-hexane), 29-34 (6% ether-hexane), 35-37 (8% ether-hexane), and 38-45 (10% ether-hexane) were essentially empty. Fractions 46-48 (10% ether-hexane) and 49-53 (15% ether-hexane) contained 0.102 g of crude *o*-dibenzoylbenzene, mp 135-145°. Recrystallization from ether gave colorless crystals, mp 146-147°, whose infrared spectrum was superimposable with that of authentic *o*-dibenzoylbenzene. The mixture melting point was undepressed. The crude yield of *o*-dibenzoylbenzene was 36%. In a control experiment, 1,3-diphenylisobenzofuran was recovered unchanged after 48 hr reflux in benzene in the presence of an equimolar amount of rubrene.

Oxygenation of Tetracyclopentadienone (Tetracyclone) (5) with 9,10-Diphenylanthracene Peroxide. A solution of 0.384 g (1 mmol) of tetracyclone and 0.724 g (2 mmol) of 9,10-diphenylanthracene peroxide in 50 ml of benzene was refluxed in the dark for 72 hr. Benzene was removed *in vacuo* and the residue chromatographed on a 40 × 2 cm silica gel column slurry packed with 5% ether-hexane; 100 ml-fractions were collected. Fractions 1 and 2 (hexane) were empty. Fractions 3-10 (1% ether-hexane) contained 0.600 g of 9,10-diphenylanthracene. Fractions 11-15 (2% ether-hexane) contained a mixture consisting of approximately 0.07 g of 9,10-diphenylanthracene peroxide and 0.225 g of unreacted tetracyclone. Fractions 16-19 (4% ether-hexane) and 20-24 (8% ether-hexane) were empty. Fractions 25-29 (10% ether-hexane) contained 0.160 g of white solid, mp 210-213°. Recrystallization of this material from ethanol afforded 0.120 g of colorless needles, mp 214-216°, whose ir spectrum (KBr) was identical with that reported³³ for *cis*-dibenzoylstilbene (6). The reported melting point of *cis*-dibenzoylstilbene is 215.9-216.3°. The yield of crystalline *cis*-dibenzoylstilbene was 40%. A control experiment was carried out by refluxing a benzene solution of 0.384 g (1 mmol) of tetracyclone and 0.482 g (1.5 mmol) of 9,10-diphenylanthracene in the dark for 72 hr and gave a >96% recovery of starting material after column chromatography on silica gel.

Oxygenation of 2,5-Diphenyl-4-methyloxazole (7) with 9,10-Diphenylanthracene Peroxide. The 2,5-diphenyl-4-methyloxazole (7) was prepared by the method of Cleland and Niemann.³⁶ A solution of 0.724 g (2 mmol) of 9,10-diphenylanthracene peroxide and 0.235 g (1 mmol) of 2,5-diphenyl-4-methyloxazole in 50 ml of anhydrous benzene was refluxed under nitrogen in the dark for 94 hr. Removal of benzene *in vacuo* afforded 0.960 g of yellow solid which was placed on a 50 × 2 cm deactivated silica gel chromatography column slurry packed with 5% ether-hexane. Deactivated

silica gel was prepared by swirling 300 g of Davison 100-200 mesh silica gel with 500 ml of water, cooling, filtering, and drying for 8 hr at 90°; 100-ml fractions were collected. Fractions 1-5 (hexane) contained 0.538 g of 9,10-diphenylanthracene. Fractions 6-8 (2% ether-hexane) and 9-10 (5% ether-hexane) contained 0.080 g of 9,10-diphenylanthracene peroxide which was identical (ir, mp) with the starting peroxide. Fractions 11-13 (9% ether-hexane) and 14-15 (14% ether-hexane) were essentially empty and were discarded. Fractions 16 (14% ether-hexane) and 17-20 (20% ether-hexane) contained 0.170 g of crystalline *N*-acetyldibenzamide (8). Recrystallization from ether-hexane afforded material melting at 64-65° which was identical in every respect (mp, mmp, ir, and nmr) with authentic *N*-acetyldibenzamide obtained from the dye-sensitized photooxidation of 2,5-diphenyl-4-methyloxazole.¹² Finally, fractions 21-25 (50% ether-hexane) and 26-30 (ether) contained 0.062 g of material, mp 147-149° after recrystallization from ether, which was identical (mp, mmp, and ir) with authentic dibenzamide (10) prepared independently by the method of Thompson.³⁶ Dibenzamide apparently results from hydrolysis of *N*-acetyldibenzamide during chromatography since this diamide could not be detected (ir) in the crude reaction mixture prior to chromatography. Indeed, chromatography on activated silica gel resulted in complete hydrolysis of *N*-acetyldibenzamide. The overall yield of di- and triamide was 92%. Refluxing a benzene solution of the oxazole and 9,10-diphenylanthracene (1:1 mole ratio) for 94 hr followed by chromatography resulted in quantitative recovery of the starting materials.

Oxygenation of 2-Methyl-4,5-diphenyloxazole (9) with 9,10-Diphenylanthracene Peroxide. A solution of 0.095 g (0.4 mmol) of 2-methyl-4,5-diphenyloxazole³⁷ and 9,10-diphenylanthracene peroxide (0.291 g, 0.8 mmol) in 20 ml of dimethyl sulfoxide was heated for 17.5 hr at 80-82°. The mixture was poured into water and extracted with chloroform; the evaporated extracts were freed from dimethyl sulfoxide by bulb-to-bulb distillation. Chromatography on deactivated silica gel yielded the following products: 9,10-diphenylanthracene (0.129 g), 9,10-diphenylanthracene peroxide (0.144 g), 2-methyl-4,5-diphenyloxazole (0.071 g), and dibenzamide (10) (0.022 g, 25%) resulting from the hydrolysis of *N*-acetyldibenzamide (8) during the aqueous work-up.

Oxygenation of 2-Phenyl-4,5-pentamethyleneoxazole (11) with 9,10-Diphenylanthracene Peroxide. The 2-phenyl-4,5-pentamethyleneoxazole (11), mp 38-39°, was prepared³⁸ from 2-bromocycloheptanone and benzamide in 55% yield by the method of Friedman, Sparks, and Adams³⁹ and showed the following spectral characteristics: ir (CHCl₃) 1630 (C=C) and 1550 (C=N) cm⁻¹; nmr (CDCl₃) τ 1.8-2.2 (m, 2), 2.3-2.7 (m, 3), 7.27 (m, 4), and 8.30 (m, 6).

Anal. Calcd for C₁₄H₁₃NO: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.73; H, 6.95; N, 6.80.

A 50-ml benzene solution containing the oxazole 11 (0.098 g, 0.45 mmol) and 9,10-diphenylanthracene peroxide (0.187 g, 0.52 mmol) was refluxed for 54 hr. The crude reaction mixture after removal of benzene *in vacuo* was subjected to preparative thin layer chromatography (Merck 1 mm silica gel plate, 50% benzene-hexane) to give 0.083 g (75%) of *N*-benzoyliminopimelic anhydride (12) which was identical with a sample prepared by dye-sensitized photooxygenation of 2-phenyl-4,5-pentamethyleneoxazole (11) in methanol.³⁸ *N*-Benzoyliminopimelic anhydride, mp 94-94.5°, was characterized on the basis of the following data: ir (CHCl₃) 1745, 1680, and 1660 cm⁻¹; nmr (CDCl₃) τ 2.0-2.5 (m, 5), 6.8-7.2 (m, 4), and 7.9-8.3 (m, 6).

Anal. Calcd for C₁₄H₁₃NO₃: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.45; H, 6.10; N, 5.66.

Oxygenation of 4,5-Decamethyleneoxazole (13) with 9,10-Diphenylanthracene Peroxide. The 4,5-decamethyleneoxazole (bp 84-85° (0.15 mm)) was prepared in 46% yield by treatment of 2-hydroxycyclododecanone with formamide in sulfuric acid by a modification of the method of Bredereck and Gompper.⁴⁰ A solution of the oxazole (0.032 g, 0.16 mmol) and 9,10-diphenylanthracene peroxide (0.58 g, 1.6 mmol) in 20 ml of toluene was refluxed for 6.75 hr. Chromatography of the crude reaction mixture on deactivated silica gel afforded 9,10-diphenylanthracene (0.50 g, 95%)

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and ω -cyanoundecanoic acid (**14**) (0.021 g, 62%), mp 53–54°. The latter material was identical (mp, mmp, ir) with an authentic sample prepared by dye-sensitized photooxygenation of 4,5-decamethyleneoxazole in methylene chloride and hydrolysis of the mixed anhydride primary product.¹⁴

Oxygenation of [2.2](2,5)Furanophane (15) with 9,10-Diphenylanthracene Peroxide. A benzene solution (5 ml) of [2.2](2,5)-furanophane (**15**)⁴¹ (0.350 g, 1.85 mmol) and 9,10-diphenylanthracene peroxide (0.424 g, 1.15 mmol) was refluxed for 30.5 hr. The reaction mixture was cooled and the precipitated white solid (0.28 g, 80%) was filtered, repeatedly washed with organic solvents, and extracted (Soxhlet) with methylene chloride to give [2.2](2,5)-furanophane tetraepoxide (**16**), mp 182° (lit.¹⁵ mp 181–182°), which gave the corresponding tetramethoxy compound, mp 160° (lit.¹⁵ mp 161–162°), upon refluxing in methanol. These results exactly paralleled the dye-sensitized photooxygenation results.¹⁵

Oxygenation of Tetraphenylimidazolinone (17) with 9,10-Diphenylanthracene Peroxide. Tetraphenylimidazolinone (**17**) was prepared by the method of Biltz.⁴² A solution of this material (1.24 g, 3.2 mmol) and 2.7 g (7.5 mmol) of 9,10-diphenylanthracene peroxide in 50 ml of benzene was refluxed for 135 hr. A portion of the crude reaction mixture was subjected to preparative tlc (67% benzene–chloroform eluent) and gave *sym*-dibenzoyldiphenylurea (**18**) in 80% yield which was identical in all respects with an authentic sample.⁴² *sym*-Dibenzoyldiphenylurea was also produced when tetraphenylimidazolinone was subjected to dye-sensitized photooxygenation conditions (81% yield) or to oxygenation using hydrogen peroxide–sodium hypochlorite mixtures (78% yield).¹⁶

Oxygenation of 2,3-Butanoimidazo[1,2-*a*]pyridine (19) with 9,10-Diphenylanthracene Peroxide. The 2,3-butanoimidazo[1,2-*a*]pyridine (**19**) was prepared according to the procedure of Campbell and McCall.⁴³ A solution of 1.69 g (9.8 mmol) of **19** and 2.7 g (7.5 mmol) of 9,10-diphenylanthracene peroxide in 20 ml of benzene was refluxed for 121 hr. A portion of the crude reaction mixture was subjected to thin layer chromatography (20% acetone–benzene eluent) and yielded 1,8-diazabicyclo[7.4.0]trideca-8,10,12-triene-2,7-dione (**20**) in 67% yield. This material was identical (mass spectrum, ir) with the product formed upon photooxidation of pyrimidazole **19** in methanol or methylene chloride.¹⁶

The 1,8-diazabicyclo[7.4.0]trideca-8,10,12-triene-2,7-dione (**20**), mp 162–163.5°, was characterized¹⁶ on the basis of the following: ir 1690 and 1650 cm^{-1} ; nmr τ 1.28 (broad d, 1), 2.10 (t of d, 1), 2.65 (q of d, 2), 7.0 (m, 4), and 8.0 (m, 4); uv_{max} (MeOH) 215 (log ϵ 4.0), 260 (3.6), sh 263 (3.0), and sh 283 (3.0) nm; mass spectrum (70 eV) m/e 204 (M^+), 176, and 94.

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.31; H, 5.91; N, 13.36.

Determination of k_1 , the Rate Constant for Dissociation of 9,10-Diphenylanthracene Peroxide to 9,10-Diphenylanthracene and Singlet Oxygen. In the presence of a large excess of a reactive acceptor A, eq 3–5 (Scheme I) yield the following rate equation for the disappearance of 9,10-diphenylanthracene peroxide (DPAP): $d[\text{DPAP}]/dt = -k_1[\text{DPAP}]$. Thus a plot of $\ln [\text{DPAP}]$ vs. time determined under these conditions should give a straight line whose slope determines k_1 . Accordingly, 9,10-diphenylanthracene peroxide ($8.25 \times 10^{-2} M$) was decomposed in refluxing benzene in the presence of an excess (0.8 or 0.4 M) of the acceptor 2-methyl-4,5-diphenyloxazole (**9**). The appearance of 9,10-diphenylanthracene ($\lambda_{\text{max}}^{\text{EIOH}}$ 392 nm, ϵ 12,750) was monitored at suitable intervals by quantitative ultraviolet spectroscopy and the term $\ln [\text{DPAP}]$ calculated from the relationship $\ln [\text{DPAP}] = \ln ([\text{DPAP}]_0 -$

[DPAP]). The data from a typical run at 81.6° were as follows (time in minutes, $\ln [\text{DPAP}] \times 10^2$): 0, 2.110; 10, 2.107; 20, 2.099; 30, 2.093; 40, 2.086; 50, 2.079; 60, 2.073; 70, 2.067; 85, 2.055; 100, 2.043; 120, 2.029; 140, 2.020; 160, 2.001; 190, 1.981; 220, 1.959; 250, 1.940; 280, 1.917; 310, 1.895; 340, 1.878; 370, 1.852; 400, 1.829; 430, 1.793; 460, 1.785. Since *ca.* 10 min was required for the solution to reach reflux temperature, the intercept was not included in the process of finding the straight line which best fit the data. The average result of four such runs gave a value for k_1 of $1.2 \pm 0.1 \times 10^{-8} \text{ sec}^{-1}$ (half-life = 16 hr). This is in good agreement with the value for k_1 ($2.5 \times 10^{-8} \text{ sec}^{-1}$) determined² at 90° in methylene chloride.

Effect of Reactant Concentrations on Rate. The average relative rates of oxygenation of tetracyclone (**5**) and 2-methyl-4,5-diphenyloxazole (**9**) over a period of 6 hr and the changes in average rate resulting from varying the concentrations of 9,10-diphenylanthracene peroxide or of **5** and **9** were estimated assuming that the rate is proportional to the amount of acceptor, A, converted to product AO_2 per unit time, *i.e.*, $\text{rate} \propto ([A]_0 - [A])/t$. The amount of acceptor, A, remaining at time t (6 hr) was determined in the case of tetracyclone (**5**) from quantitative ultraviolet spectroscopy of the crude reaction mixture. The uv_{max} of tetracyclone (505 nm) could be monitored without interference from other reactants or products all of which absorb below 400 nm. The ratio of the amount of 2-methyl-4,5-diphenyloxazole (**9**) remaining to the amount of product, *N*-acetyldibenzamide (**8**), produced after 6 hr in the oxygenation of **9** was determined by nmr integration of their respective methyl resonances in benzene solution. In benzene the two singlets are distinct and adjacent, a situation which allows for rapid and reliable integration of the peak areas. From this ratio the value of $[A]$ could easily be calculated. In the oxygenation of both **5** and **9** the conversions were kept low (<25%) in order to minimize the back reaction of singlet oxygen with 9,10-diphenylanthracene. The overall results are shown in Table II.

Determination of the Activation Energy for the Dissociation of 9,10-Diphenylanthracene Peroxide. The value of k_1 was estimated at three different temperatures (80.9, 100.2, and 111.2°) by plotting $\log [A]$ vs. time using tetracyclone (**5**) as the acceptor A and assuming that the disappearance of tetracyclone paralleled the disappearance of 9,10-diphenylanthracene peroxide. This method was chosen for the ease with which the concentration of tetracyclone can be determined using quantitative ultraviolet spectroscopy. An isosbestic point in the uv spectra confirmed that $-d[A]/dt = d[\text{DPAP}]/dt$. At 80.9° the results were (time in minutes, $\log [A]$) 3, 0.9590; 48, 0.9445; 123, 0.9243; 258, 0.9085; 360, 0.8808; 823, 0.7924; 1003, 0.7559; 1440, 0.6721. The value of k_1 so determined was $7.5 \times 10^{-8} \text{ sec}^{-1}$. At 100.2° the results were (time in minutes, $\log [A]$) 5, 0.9912; 35, 0.9243; 85, 0.8513; 105, 0.8096; 135, 0.7634. From this k_1 was estimated as $5.9 \times 10^{-8} \text{ sec}^{-1}$. At 111.2° the values were (time in minutes, $\log [A]$) 9, 0.9494; 24, 0.8865; 41, 0.7924; 59, 0.7324; 70, 0.6812; 84, 0.6128; and k_1 was determined to be $1.7 \times 10^{-4} \text{ sec}^{-1}$. The internal consistency of these three rate constants was shown by the fact that any one of them could be accurately calculated from the other two. The average value of E_a which can be calculated using these three rate constants is $27.8 \pm 0.2 \text{ kcal/mol}$.

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