Determination of Kinetics. Kinetic experiments were conducted by heating sealed NMR tubes containing 20% (w/v) solutions of the triene substrate in toluene-d_8 (0.1 g in 0.5 mL) under Ar at 110 ± 2 °C in a constant temperature bath.

The tubes were withdrawn at intervals and cooled rapidly to room temperature in a stream of air, and the disappearance of the triene was monitored by NMR. Repetitive integration (seven to nine measurements) of an appropriate resonance (usually the β olefinic proton of the dienophile which resonated at lowest field) was utilized to establish the change in concentration of triene with time. Data points were collected through ~3 half-lives (~80% conversion) and were plotted log [triene] vs. time. All reactions showed good first-order kinetic behavior (linear plots) through ~3 half-lives. The $T_{1/2}$ and first-order rate constants were obtained from the raw data after least-squares treatment.

Acknowledgment. We wish to thank the National Science Foundation for support of these studies in the form of Research Grants CHE-78-07525 and CHE-80-05176.

Registry No. 2, 79919-74-7; **3**, 75887-42-2; **4**, 79898-46-7; **5**, 79898-47-8; **6**, 79898-48-9; **7**, 79898-49-0; **8**, 79898-50-3; **9**, 79898-51-4; **10**, 79898-52-5; **11**, 79898-53-6; **12**, 79898-54-7; **13**, 79898-55-8; (±)-**14**, 79898-56-9; (±)-**15**, 79898-57-0; (±)-**16**, 79898-58-1; (±)-**17**, 79898-59-2; (±)-**18**, 79952-31-1; (±)-**19**, 79898-60-5; (±)-**20**, 79952-32-2; (±)-**22**, 79898-61-6; 3-methyl-2-butenyl vinyl ether, 928-41-6; 3-methyl-2-buten-1-ol, 556-82-1; 3,3-dimethyl-4-pentenal, 919-93-7; 1,1-dimethoxy-3,3-dimethyl-4-pentene, 79898-62-7; 3,3-dimethyl-5,5-dimethoxypentan-1-ol, 75887-37-5; 3,3-dimethyl-5,5-dimethoxypentanal, 64600-45-9; 3,3-dibromomethylacrylic acid, 75887-43-3; 3-bromomethyl-4-hydroxy-2-butenoic lactone, 58588-90-2; 3-[(*E*)-4,4-dimethyl-6,6-dimethoxy-1-hexen-1-yl]-4-hydroxy-2-butenoic lactone, 79898-63-8; 3-[(1*E*,6*Z*)-7-cyano-4,4-dimethyl-1,6-heptadien-1-yl]-4-hydroxy-2-butenoic lactone, 79898-64-9; 5,5-dimethoxy-1-pentanol, 79898-65-0; 5,5-dimethoxypentanal, 50789-30-5; 3-[(*E*)-6,6-dimethoxy-1-hexen-1-yl]-4-hydroxy-2-butenoic lactone, 79898-66-1; 3,3-dimethylacrylic acid, 541-47-9; ethyl vinyl ether, 109-92-2; dimethyl malonate, 108-59-8; methyl cyanoacetate, 105-34-0; *tert*-butyl cyanoacetate, 1116-98-9; malonitrile, 109-77-3; carbomethoxymethylene triphenylphosphorane, 2605-67-6; diethyl cyanomethylphosphonate, 2537-48-6; 5,5-dimethoxy-1-pentene, 14152-71-7.

Supplementary Material Available: Tables of fractional coordinates, bond angles, and distances for diester lactone **14**, and an ORTEP drawing of **14** (4 pages). Order information is given on any current masthead page.

Chemiluminescence of Organic Peroxides. Thermal Generation of an *o*-Xylylene Peroxide[1]

Jimmie P. Smith, Alan K. Schrock, and Gary B. Schuster*[†]

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received April 4, 1981*

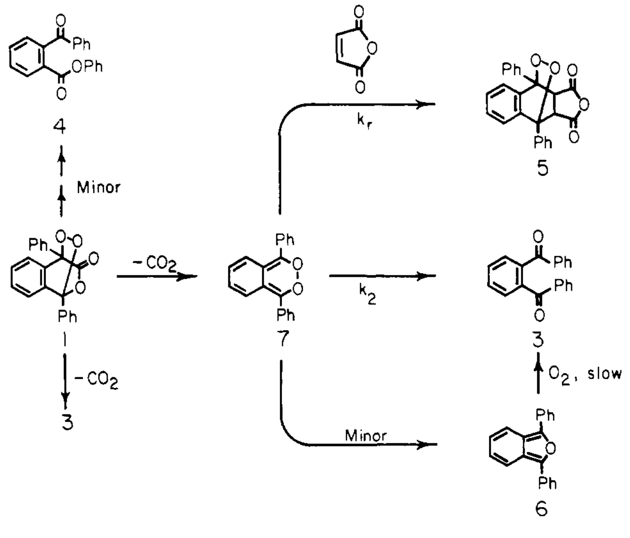
Abstract: Thermolysis of 1,4-diphenyl-1,4-dioxa-2,3-benzopyrone (endoperoxide **1**) in *p*-xylene solution generates chemiluminescence. Three products are formed from thermolysis of **1**. The major product, trapped in 70% yield by added maleic anhydride, is 1,4-diphenyl-2,3-benzodioxin (*o*-xylylene peroxide **7**). This peroxide eventually becomes *o*-dibenzoylbenzene **3** which is isolated from the reaction in 85% yield. The two other products, 1,3-diphenylisobenzofuran (**6**) and phenyl *o*-benzoylbenzoate (**4**), are isolated in yields of ca. 2% and 5%, respectively. The observed chemiluminescence results from interaction of **7** with an added fluorescent activator or with the product 1,3-diphenylisobenzofuran according to the chemically initiated electron-exchange luminescence (CIEEL) mechanism.

The molecules and mechanisms responsible for chemiluminescence and bioluminescence have been of considerable interest to chemists since the dawn of the science.[2] Much recent interest in this topic has centered on the thermal chemistry of organic peroxides.[3] Our efforts to discover new chemiluminescent systems and to probe the mechanism of electronically excited state generation led to the synthesis and investigation of new heterocyclic examples of this functional group. In this report we describe the preparation, characterization, and thermal reactions of endoperoxide **1**. The properties of this molecule provide further insight into the chemistry of organic peroxides and into the mechanistic details of chemiluminescence.

Results and Discussion

Synthesis. The preparation of endoperoxide **1** proceeds straightforwardly by photooxygenation of the previously described lactone **2**.[4] Irradiation of an acetone solution of **2** and methylene blue with visible light, filtered so that only the sensitizer is excited, at 0 °C under O$_2$ leads to the rapid consumption of the lactone. Removal of the sensitizer by filtration through silica gel, evaporation of the solvent, and recrystallization of the resulting residue gives a peroxidic white solid. The structure of this material was deduced from spectroscopic, osmometric, and microanalytic investigation to be endoperoxide **1** (eq 1). The details of the

Scheme I



[†] Fellow of the Alfred P. Sloan Foundation (1977–1979) and the Dreyfus Foundation (1979–1984).

(1) Smith, J. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 2564.

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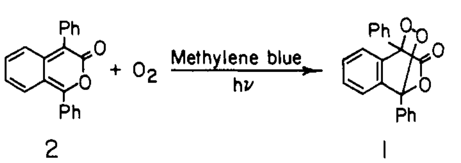
structural assignment are presented in the Experimental Section.



(1)

Thermolysis of Endoperoxide 1. The thermal reactions of peroxide **1** are on the surface quite simple, but, as we will describe below, there is a hidden complexity that becomes apparent only on detailed investigation. When a solution of **1** in benzene, or *p*-xylene, is heated to ca. 100 °C under nitrogen, the first change observed is that what was a clear, colorless solution has become deep yellow. Prolonged heating causes the yellow to fade, and the resulting solution is again colorless. If oxygen is not rigorously excluded from the thermolysis solution, the yellow color never develops. The stable products of the thermolysis reaction are isolated by evaporation of the solvent, separated by gas or high pressure liquid chromatography, and identified by comparison with authentic samples as *o*-dibenzoylbenzene (**3**), phenyl *o*-benzoylbenzoate (**4**), and 1,3-diphenylisobenzofuran with yields of 85%, 5%, and 2%, respectively (Scheme I). Presumably CO_2 is formed simultaneously with the identified solid products, but we did not attempt to isolate or to detect it.

On the presumption that an intermediate product is a precursor to diketone **3**, we carried out the thermolysis of **1** in the presence of maleic anhydride. A 1.0×10^{-3} M *p*-xylene solution of **1** containing 5.1×10^{-5} M maleic anhydride on thermolysis in the absence of oxygen does not turn yellow but gives a yield of diketone **3** that is essentially the same as in the absence of anhydride. Increasing the maleic anhydride concentration to 1.5×10^{-2} M results in a reduction of the yield of ester **4** and diketone **3** to 25% of the values in the absence of maleic anhydride. However, further increases in the maleic anhydride concentration beyond 1.5×10^{-2} M do not result in any further reduction of the yields. The major product of the reaction in the presence of a high concentration of maleic anhydride is the Diels–Alder trapping product **5**. This compound is isolated by evaporation of the solvent, sublimation of the excess maleic anhydride, and then recrystallization, in 70% yield. The details of the structural assignment are given in the Experimental Section.[5]

The maleic anhydride trapping experiments show that there are at least two intermediate products formed from thermolysis of **1**. The first is the yellow compound that is completely trapped at low anhydride concentration that we have identified as furan **6**. The second is a precursor to diketone **3** that is trapped efficiently at high anhydride concentrations to give **5**. Also, there is a direct, or at least untrappable, path leading from endoperoxide **1** to diketone **3** that accounts for about one-third of this product. To confirm these assertions and to define further the reaction path and structures of the intermediates, we undertook a detailed kinetic and spectroscopic investigation of this reaction.

The least ambiguous method to determine the rate of reaction of endoperoxide **1** is by infrared spectroscopy. Peroxide **1** has a strong absorption due to the lactone carbonyl group at 1785 cm^{-1}. As the thermal reaction proceeds, the intensity of this absorption decreases while the intensity of the carbonyl absorption at 1680 cm^{-1} due to diketone **3** increases. Monitoring the extent of reaction of a 1.0×10^{-2} M solution of **1** in *p*-xylene at 112 °C as a function of time by infrared spectroscopy shows that the reaction obeys a first-order kinetic law with a rate constant (k_1) of $(4.72 \pm 0.06) \times 10^{-4}\ s^{-1}$ (Figure 1). This corresponds to a half-life for endoperoxide **1** of about 24 min under these conditions. Similarly, the rate of appearance of diketone **3** can be analyzed by infrared spectroscopy. The half-time for appearance of this product is approximately the same as for the consumption of **1**. This observation indicates that whatever intermediate is involved in the conversion of **1** to **3**, it is short-lived when compared to endoperoxide **1**.

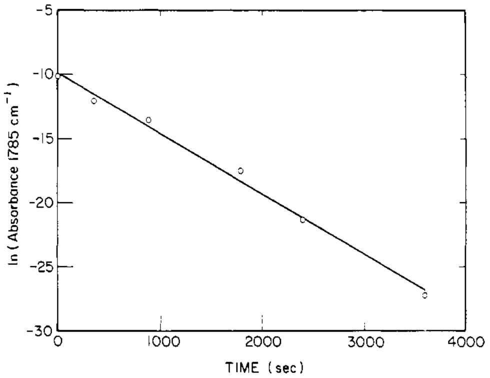


Figure 1. Rate of reaction of endoperoxide **1** in *p*-xylene at 112 °C determined by infrared spectroscopy.

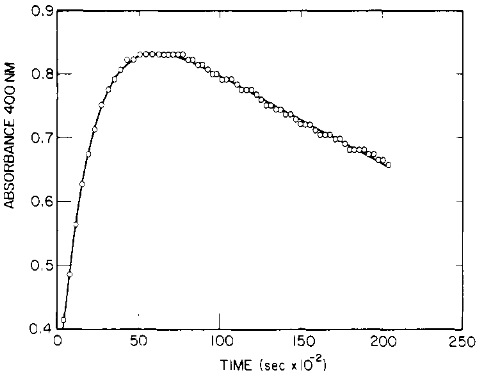


Figure 2. The time dependency of the buildup and decay of the absorption at 400 nm due to furan **6** formed from thermolysis of endoperoxide **1** at 112 °C in *p*-xylene.

The course of the thermal reactions of **1** can be followed also by ultraviolet–visible spectroscopy. As noted above, the reaction mixture turns yellow as the thermolysis proceeds. This is due to the formation of furan **6**. Measuring the absorbance at 400 nm as a function of time during the thermolysis of the endoperoxide provides kinetic data on the formation and reaction of **6**. Heating a 5.0×10^{-4} M *p*-xylene solution of **1** at 112 °C causes an increase in absorbance at 400 nm which grows to a maximum in ca. 65 min and then slowly decreases. The data, shown in Figure 2, can be interpreted within a simple consecutive reaction model. The rate constant for formation of the furan derived from these data is $(4.84 \pm 0.1) \times 10^{-4}\ s^{-1}$. This value is the same, within experimental error, as that obtained for disappearance of endoperoxide **1** by infrared spectroscopy (k_1). The rate constant for decay of the absorbance at 400 nm is $(1.97 \pm 0.05) \times 10^{-5}\ s^{-1}$ which corresponds to a half-life of 587 min. Thus, the slowly reacting furan cannot be a major source of the rapidly appearing diketone product. These kinetic findings support the maleic anhydride trapping results that indicate at least two intermediate products are formed on thermolysis of **1**.

The yield of furan **6** can be estimated by titration with maleic anhydride as well as by the spectroscopic procedure. The kinetics of its formation and reaction reveal that its concentration reaches a maximum 65 min after the thermolysis of **1** has begun. Also, at this time 78% of the total amount that will be formed is present in solution. Addition of a maleic anhydride solution to the reaction at this point bleaches the yellow color. We estimate that the total yield of furan **6** is ca. 3% on the basis of the initial endoperoxide concentration by this procedure. This is the same value obtained by the spectroscopic procedure. Thus, the entire yellow color developed in the reaction is due to furan **6** and not to *o*-xylylene peroxide **7** as we originally claimed.[1] The furan is a minor reaction product from endoperoxide **1**, but, as described below, it plays a critical role in the direct chemiluminescence[6] of this system.

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[2] Harvey, E. N. "Bioluminescence"; Academic Press: New York, 1952.

[3] Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* in press.

[4] Jones, D. W.; Wife, R. L. *J. Chem. Soc., Perkin Trans. 1 1976* 1654.

[5] The stereochemistry of this adduct is not known.

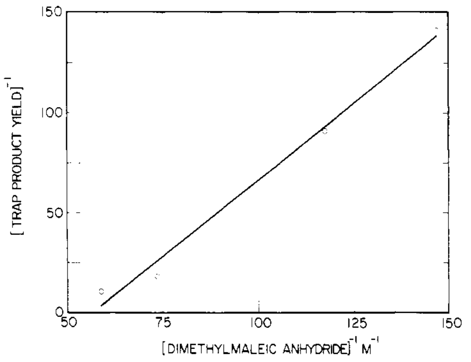

Figure 3. Double-reciprocal plot of the trapped product yield from thermolysis of endoperoxide **1** in the presence of dimethylmaleic anhydride against the concentration of anhydride.

The minor products, furan **6** and ester **4**, appear to be the result of oxidation–reduction reactions. Conceivably peroxide **7** could oxidize diketone **3** directly to give furan **6** and phenyl ester **4**. This possibility is eliminated because the yields of furan and ester are both linearly dependent on the initial endoperoxide concentration. However, adding cyclopentanone, which can be readily oxidized to δ-valerolactone, increases the yield of furan **6** and concomitantly decreases the amount of ester **4** formed in the reaction. Furthermore, when a large excess of diketone **3** is added to the endoperoxide solution, the yields of both the furan **6** and phenyl ester **4** are increased. These results, in conjunction with the observation that maleic anhydride inhibits the formation of ester, indicate that peroxide **7** is reduced to form furan **6** (vide infra) and that the diketone can be oxidized to form ester **4**. However, it is clear that this is not a simple one step oxidation–reduction reaction.

The major intermediate formed from thermolysis of endoperoxide **1** is a precursor to diketone **3** and can be trapped with maleic anhydride to give **5** in 70% yield. It is important to note that maleic anhydride does not react with endoperoxide **1** directly. Thus the measured rate of reaction of **1** is independent of the maleic anhydride concentration. The structure of the major intermediate is revealed by the structure of its trapping product to be *o*-xylylene peroxide **7**. This compound is the first example of this class of conjugated cyclic unsaturated peroxides, and, therefore, we investigated its properties in some detail.

Cleavage of the oxygen–oxygen bond of *o*-xylylene peroxide **7**, in principle, can lead directly to diketone **3**. This reaction is exothermic by ca. 90 kcal/mol. From this point of view it is surprising that **7** lives long enough under the reaction conditions to be trapped by dieneophiles such as maleic anhydride. We decided to use this trapping reaction to obtain an estimate of the lifetime of peroxide **7**. The thermal reaction of **7** with maleic anhydride is too fast to use under these conditions so we substituted dimethylmaleic anhydide. The thermal conversion of **7** to **3** is in competition with the reaction of **7** with dimethylmaleic anhydride. Thus, as the anhydride concentration increases the yield of diketone decreases. After correction for the uninhibitable production of **3**, the double reciprocal plot of the yield of **3** against dimethylmaleic anhydide concentration (Figure 3) gives a straight line. The slope of this line is the ratio of the rate constant for the unimolecular thermal reaction of **7** (k_2) to that of the bimolecular trapping reaction with dimethylmaleic anhydide (k_r). Unfortunately, there is no way to measure directly the latter value. However, if we assume that dimethylmaleic anhydride reacts with **7** with a rate constant similar to that for its reaction with 1,3-diphenyisobenzofuran (which **7** resembles closely), we can approximate the lifetime of the *o*-xylylene peroxide. We determined the bimolecular rate constant for the furan and the anhydride at 112 °C in *p*-xylene solution to be $(2.02 \pm 0.01) \times 10^{-1}$ M^{-1} s^{-1}. From this value and from the slope of the line shown in Figure 3, we estimate the half-life of **7** to be ca. 20 s under these conditions. Thus, though by no means easily isolable, the *o*-xylylene peroxide, at least by this estimate, has modest thermal stability.

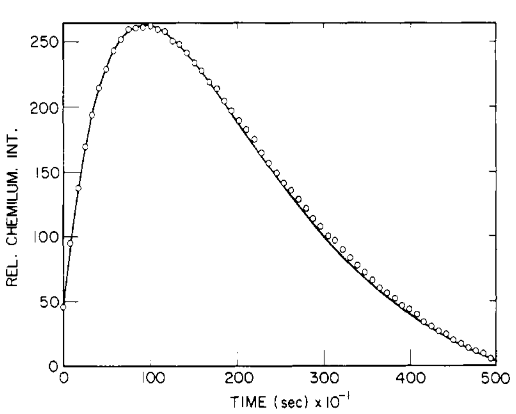

Figure 4. The time dependency of the buildup and decay of the direct chemiluminescence from thermolysis of a 1×10^{-3} M solution of **1** in *p*-xylene at 112 °C. The circles are the data, and the line is the least-squares fit to a two exponential system; see text.

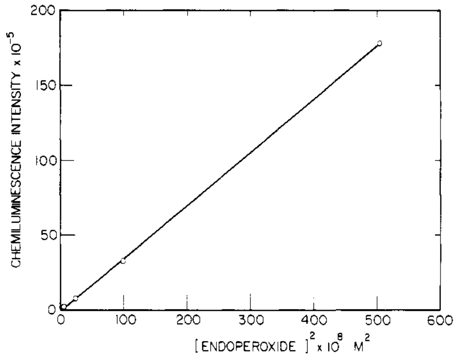

Figure 5. Dependence of the integrated direct chemiluminescence intensity from **1** on the square of the peroxide concentration in *p*-xylene at 112 °C.

Chemiluminescence of Endoperoxide 1. The chemiluminescence observed during the thermolysis of endoperoxide **1** can be separated operationally into two types. The first type, direct chemiluminescence, is the generation of light from solutions of **1** alone. The second type, activated chemiluminescence,[6] is light formation by reaction of solutions of **1** and some added molecule (the activator). Although experimentally different, as will be shown below, for endoperoxide **1** these two types are in fact conceptually identical.

Heating a 1×10^{-3} M solution of **1** in *p*-xylene at 112 °C results in a buildup of chemiluminescence intensity to a peak ca. 20 min after the reaction begins followed by a decay of the light intensity to background levels (Figure 4). The total chemiluminescence intensity observed in this experiment is directly proportional to the square of the initial endoperoxide concentration (Figure 5). And the chemiluminescence spectrum is identical with the fluorescence spectrum of the 1,3-diphenylisobenzofuran formed as a side product. Nonlinear least-squares analysis of the kinetics of buildup and decay of the chemiluminescent emission provides two rate parameters. The first is $(4.12 \pm 0.1) \times 10^{-4}$ s^{-1}, which is identical with the rate constant (k_1) for reaction of **1** derived from the infrared and ultraviolet kinetic analyses. This finding indicates that reaction of the endoperoxide is somehow responsible for light generation. The second rate parameter is $(1.06 \pm 0.2) \times 10^{-3}$ s^{-1}. It is important to note that this rate parameter is, within experimental error, twice the magnitude of the first.

When an additional fluorescent molecule is included with endoperoxide **1** in the reacting solution quite different results are obtained. For example, when 5×10^{-4} M perylene is included in the reaction mixture, the chemiluminescent emission spectrum shifts to the fluorescence spectrum of perylene. The intensity of the perylene activated chemiluminescence does not rise to a maximum and then decay as it does in the absence of perylene but starts at its maximum value and then decays exponentially

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(6) Dixon, B. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 3116.

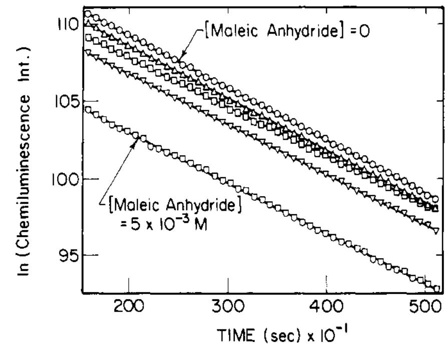


Figure 6. Log of the perylene activated chemiluminescence from **1** in *p*-xylene at 112 °C against time at various concentrations of maleic anhydride.

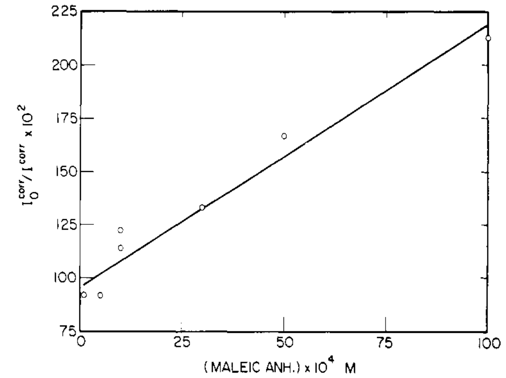
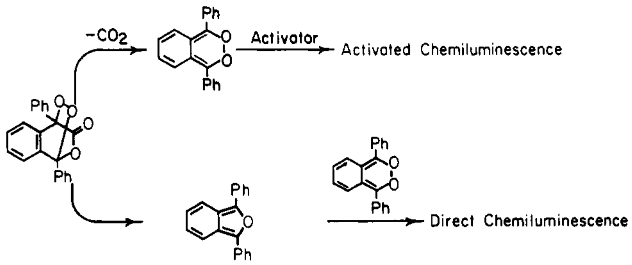


Figure 7. Quenching of perylene activated chemiluminescence of **1** by maleic anhydride.

Scheme II



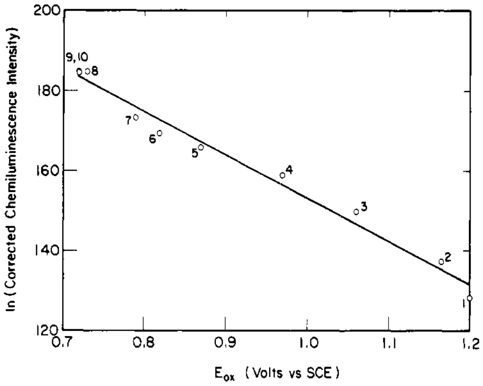


Figure 8. Response of the chemiluminescent intensity to the oxidation potential of the activator (1×10^{-4} M) in *p*-xylene at 112 °C. The points correspond to following compounds: (1) 9,10-diphenylanthracene (DPA); (2) 9,10-diphenylethynylanthracene (DPEA); (3) perylene; (4) 5,12-diphenylethynyltetracene (DPET); (5) tetracene; (7) 1,3-diphenylisobenzofuran; (8) 7-(dimethylamino)-2-methylphenazine; (9) 9-(dimethylamino)benzo[b]phenazine; (10) acridine orange free base.

with a rate constant at 112 °C in *p*-xylene of $(4.63 \pm 0.12) \times 10^{-4}$ s^{-1}, a value identical with that which we have assigned to the reaction of endoperoxide **1** (k_1, Figure 6). Finally, the total perylene activated chemiluminescence is much more intense than that observed without added activator, and its intensity is proportional to the first power of the endoperoxide concentration, not its square as it is in the absence of activator.

These findings seem to suggest that there may be two different mechanisms operating to produce chemiluminescence from endoperoxide **1**. In fact that is not the case. The chemiluminescence observed in the presence and absence of activator is the result of the same fundamental processes.

The activated chemiluminescence could presumably result from the interaction of activator with endoperoxide **1** or with the intermediate *o*-xylylene peroxide **7**. Since *o*-xylylene peroxide **7** is much shorter lived than endoperoxide **1**, it is not possible to decide based on kinetics which peroxide reacts with the activator to generate excited states. However, it is possible to use the specific trapping of **7** by maleic anhydride to distinguish these possibilities.

Additions of increasing amounts of maleic anhydride to solutions of endoperoxide **1** and perylene result in a decrease in the activated chemiluminescence intensity without changing the rate of decay of the chemiluminescent emission (Figure 6). Part of the decrease in chemiluminescence intensity is a result of the quenching of excited perylene by maleic anhydride.[7] The Stern–Volmer quenching constant for this process was determined by adding maleic anhydride to photoexcited perylene at 95 °C to be 115 ± 7 M^{-1}. The activated chemiluminescence intensity when corrected for quenching of perylene fluorescence still decreases with increasing maleic anhydride concentration. Figure 7 is a plot of these data according the eq 2, where I^{corr} and I_0^{corr} are the corrected

$$\frac{I_0^{corr}}{I^{corr}} = 1 + \frac{k_r}{k_2}[\text{maleic anhydride}] \qquad (2)$$

intensities in the presence and absence of maleic anhydride, respectively, k_r is the rate constant for the bimolecular reaction of *o*-xylylene peroxide **7** with the anhydride, and k_2 is the rate constant for unimolecular thermolysis of **7**. These findings indicate that the generation of excited states in this system is the result of an interaction between the activator and a species capable of reaction with maleic anhydride. The observation that the rate of reaction is independent of maleic anhydride concentration (Figure 6) confirms our conclusion that trapping product **5** comes from an intermediate, not directly from endoperoxide **1**. These results show that it is the interaction between activator and *o*-xylylene peroxide **7** that is responsible for generation of the chemiluminescence (Scheme II).

We examined the nature of the interaction of the *o*-xylylene peroxide with the fluorescent activators that leads to electronically excited states. The structure of the activator greatly affects the intensity of the observed chemiluminescence. For example, comparison of 9,10-diphenylanthracene with acridine orange free base reveals that at equal concentrations the latter generates 300 times more light than the former. However, neither the anthracene nor the acridine orange affect the overall rate of reaction. Similarly, we examined the light generating efficiency of eight other activators choosen from amines, conjugated furans, and aromatic hydrocarbons. The chemiluminescence intensity, corrected for activator fluorescence efficiency at 112 °C (a quantity directly proportional to the yield of excited singlet states), for 5×10^{-4} M activator varies linearly with the one-electron oxidation potential ($E_{ox.}$) of the activator (Figure 8). This observation is prime evidence for the operation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism.[8] This conclusion has recently been challenged,[9] but the objection has been shown to be unwarranted for this case.[10] Further support for the op-

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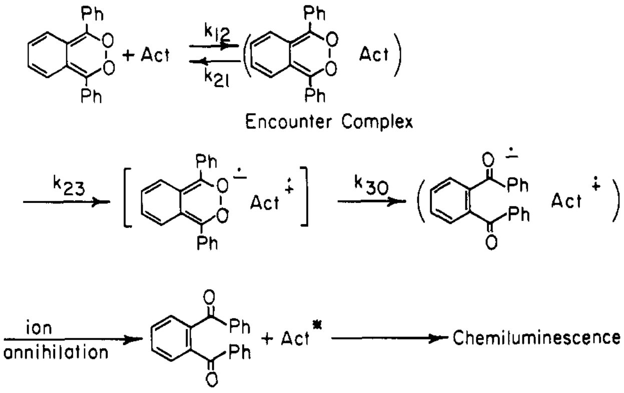
[7] The singlet energy of maleic anhydride is well above that of perylene. Thus, the quenching is probably the result of exciplex formation. For another example see: Quina, F. H.; Hamlet, Z.; Carroll, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 2240.

[8] Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366. Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 6107.

[9] Walling, C. *J. Am. Chem. Soc.* **1980**, *102*, 6855.

[10] Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519.

Scheme III



eration of the CIEEL mechanism comes from the observation that dimethyldihydrodibenzo[*b,i*]phenazine (DMBI) as activator fails to generate the expected amount of light (vide infra).

The CIEEL mechanism applied to *o*-xylylene peroxide **7** is shown in Scheme III. The first step is formation of an encounter complex. For most of the peroxides we have studied no evidence of this complex has been obtained[11] except for those cases where the activators are certain metalloporphyrins.[12] Thus we conclude that there is little if any stabilization of this complex of activator with *o*-xylylene peroxide **7**. Electron transfer from the activator to the peroxide generates, as an intermediate or, more likely, a transition state, the peroxide radical anion. Cleavage of the oxygen–oxygen bond forms *o*-dibenzoylbenzene radical anion in the same solvent cage as activator radical cation. Annihilation of these oppositely charged ions, if sufficiently energetic, forms the excited singlet state of the activator which we detect by its emission. This mechanism explains the observed intensity dependence on activator oxidation potential and the failure of DMBI to generate the expected amount of light. That is, the annihilation of $DMBI^{+}\cdot$ and $3^{-}\cdot$ is not sufficiently energetic to form the excited singlet state of DMBI and must therefore produce either the product ground states or their nonemissive triplets.[13]

The direct chemiluminescence in the absence of added activator can also be understood within the CIEEL mechanism. In this case, however, the activator is furan **6** which is formed as a side product by the reaction (Scheme II). Thus at the initiation of the reaction there is no activator and therefore no light. As the reaction proceeds, furan is formed and the chemiluminescence intensity grows. Finally, as endoperoxide **1** is consumed, the steady-state concentration of *o*-xylylene peroxide declines and the light intensity decreases. Quantitatively, this mechanism leads to the prediction that the light intensity–time profile for the direct chemiluminescence should be of the form

$$I(t) = e^{-k_1 t} - e^{-2k_1 t} \qquad (3)$$

which is precisely what is observed (Figure 4), where k_1 is the previously defined rate constant for consumption of endoperoxide. Also, this scheme accounts for the unusual dependency of the direct chemiluminescence on the square of the initial concentration of endoperoxide **1**. In essence, it takes two molecules of **1** to produce a photon, one to generate the furan (internal activator), the second to form *o*-xylylene peroxide **7**.

Conclusions

This investigation has revealed several interesting facets of the thermal chemistry of endoperoxide **1** and intermediates derived therefrom. Among these is the finding that thermolysis of **1** leads to three reactions: decarboxylation to *o*-xylylene peroxide **7** (70%), decarboxylation and ring cleavage directly to diketone **3** (25%), and an oxidation–reduction sequence to form eventually ketoester **4** (5%) and furan **6** (2%).

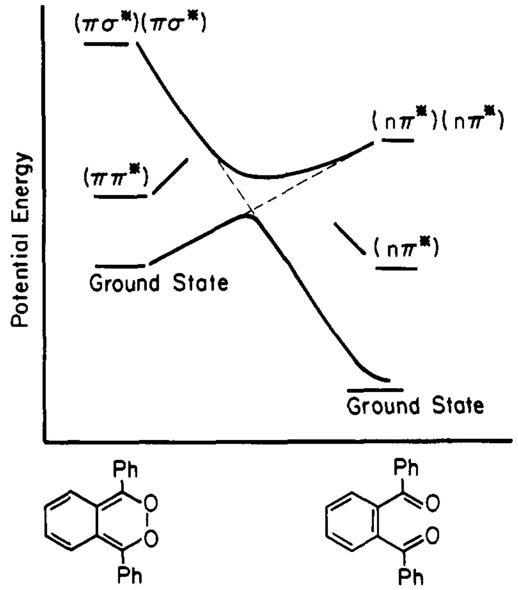
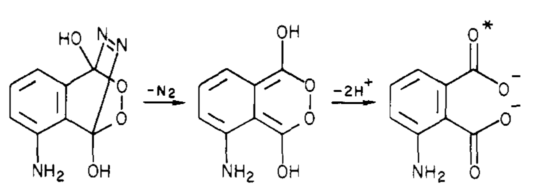


Figure 9. State correlation diagram for the thermal conversion of *o*-xylylene peroxide to *o*-dibenzoylbenzene.

The chemiluminescence that accompanies thermolysis of **1** is a result of the interaction of *o*-xylylene peroxide **7** with either the internal activator (direct chemiluminescence) or an added activator (activated chemiluminescence) according to the CIEEL mechanism. The yield of electronically excited states from thermolysis of **1** is estimated to be ca. 1% by comparison with tetramethyldioxetane.[3] This low yield is due in part to the relatively rapid, non-light-producing thermal conversion of **7** to **3** that is in competition with excited-state formation.

The chemiluminescence of **1** may serve as a model for the excitation step of luminol chemiluminescence.[14] Unfortunately, there is very little direct evidence for the structure of the ground-state intermediate immediately preceding excited-state formation in the luminol system. Early speculation, and recent experimental evidence,[15] has placed azoendoperoxide **8** on the reaction path. By analogy with endoperoxide **1**, loss of nitrogen from **8** would generate *o*-xylylene peroxide **9**. Conversion of **9** to excited aminophthalic acid, the observed emitting species in luminol chemiluminescence, may occur by intramolecular electron transfer in analogy to some amino-substituted dioxetanes.[16] Our findings described above provide some support for this reaction path which is outlined in eq 4.



8 **9** (4)

Finally, we were surprised by the stability of *o*-xylylene peroxide **7**. Our estimate of a 20-s half-life at 112 °C should be considered as no more than a rough guide to the actual thermal properties of this molecule. However, that measurement in conjunction with the efficient trapping with relatively low maleic anhydride concentrations indicates that **7** has more than a fleeting existence. This unusual "stability" may be traced to the electronic properties

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(13) The oxidation potential of DMBI is 0.46 V and the reduction—potential of *o*-dibenzoylbenzene is—1.5 V (vs. SCE) which corresponds approximately to the release of 45 kcal/mol on annihilation. The singlet energy of DMBI is 70 kcal/mol. Schuster, G. B.; Schmidt, S. P.; Dixon, B. G. *J. Phys. Chem.* **1980**, *84*, 1841.

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of this structure. Figure 9 shows a schematic state correlation diagram for the thermal reaction of **7** according to the formalism proposed by Michl[17] which he applied to the reaction of luminol.[18] The key point is that *if a rigid separation between π and σ symmetry is maintained throughout the conversion of* **7** *to* **3**, the ground-state of the *o*-xylylene peroxide correlates with a very high energy doubly $n\pi^*$ excited state of diketone **3**. Similarly, a high energy doubly excited $\pi\sigma^*$ state of **7** correlates with the ground state of **3**. The avoided crossing of these two states provides a path for the thermal conversion of **7** to **3**. This analysis suggests that the thermal stability of **7** results from the fact that its conversion to **3** is "forbidden". A second prediction resulting from analysis of Figure 9 is that excitation of **7** to its lowest $\pi\pi^*$ state should not result in its spontaneous conversion to either ground- or excited-state **3**. Conversion of $\pi\pi^*$ excited **7** to **3** is also a forbidden reaction and, as such, is an exception to the commonly observed alternation between ground- and excited-state reactivity. Our investigation of this prediction, and the other properties of *o*-xylylene peroxides, is continuing.

Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian A-60A, A-56-60, EM-390, and HR-220 spectrometers. ^{13}C magnetic resonance spectra were recorded on a JEOL FX-60 spectrometer. Chemical shifts are relative to tetramethylsilane used as an internal standard. IR spectra were obtained with a Perkin-Elmer 137 sodium chloride instrument, a Perkin-Elmer 237B grating infrared spectrophotometer, or a Beckman IR 12 spectrophotometer. UV–vis, absorption spectra were recorded on a Beckman Acta MVI, a Carey 14, or a Perkin-Elmer 552 spectrophotometer. Mass spectra were obtained with a Varian MAT CH-5 and 731 mass spectrometers. Gas chromatographic analyses were carried out by using a Varian Aerograph Model Series 2700 chromatograph equipped with flame ionization detectors. A 6-ft glass column packed with SE-30 (3%) on Chromosorb Q was used unless otherwise noted. Photoexcitation and emission spectra were recorded on a Farrand Mark I spectrofluorometer or by photon counting to permit direct comparison with chemiluminescence emission spectra. Elemental analysis, active oxygen and molecular weight determinations were performed by J. Nemeth and Associates, Department of Chemistry, University of Illinois, Urbana, IL. All melting points are uncorrected.

Chemiluminescence Measurements. The photon-counting technique was used, employing an EMI 9813B or 9816B photomultiplier tube. Spectral resolution was achieved with a Jarrel-Ash 0.25 M monochromator, equipped with a grating with 1180 grooves/mm. The band-pass under high-resolution conditions is calculated to be 5 nm. Under low-resolution conditions the band-pass is calculated to be 26 nm. The data were collected in a 128 channel digital input buffer with a variable time per channel of 1–800 s. The buffer was interfaced with a Wang series 2000 computer which was used for all data analysis. Sample temperature was regulated to within ±0.1 °C by means of an electrically heated cell holder. A National Bureau of Standards thermometer was used to calibrate sample temperatures. Pyrex cuvettes equipped with Teflon stopcocks were used for all chemiluminescence experiments. In all cases the solvent was *p*-xylene. It was purified by washing with sulfuric acid, drying over calcium chloride, filtration through basic alumina, and finally distillation.

Activators. Rubrene, tetracene, 1,3-diphenylisobenzofuran, and 9,10-diphenylanthracene (Aldrich) were chromatographed on alumina with benzene as eluent and were recrystallized from benzene. 9,10-(Phenylethynyl)anthracene (DPEA), 5,12-bis(phenylethynyl)tetracene (DPET) were prepared by published procedures[19] and were purified by chromatography.

1,4-Diphenyl-1,4-dioxa-2,3-benzopyrone (Endoperoxide 1). A solution of 100 mg (0.3 mmol) of 1,4-diphenyl-2,3-benzopyrone (lactone **2**)[4] and 10 mg of methylene blue in 20 mL of acetone was prepared and cooled in an ice-water bath. The solution was saturated with oxygen and then maintained under an oxygen atmosphere while being irradiated with the output of a 250-W tungsten–halogen lamp filtered through a Corning CS2-59 glass plate (only the methylene blue absorbs) for 4 h. The reaction solution was filtered through ca. 2 cm of silica gel to remove the methylene blue, the solvent was removed under reduced pressure, and the residue was recrystallized from pentane–CH_2Cl_2 to give **1** (36 mg, 32%) as a white solid: mp 109 °C (with decomposition); ^1H NMR ($CDCl_3$) δ 7.0–6.8 (d, 2 H), 7.9–7.2 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 166, 136, 133.5 130.3, 130.2, 129.6, 129.3, 128.8, 128.2, 126.9, 126.5, 124.7, 123.2, 123.0, 105.9 82.4; IR ($CHCl_3$) 2950, 1735, 1525, 1460, 1330 cm^{-1}; MS (field desorption, low resolution), *m/e* (relative abundance) 298 (2.38), 287 (13), 286 (61), 271 (2), 270 (10), 210 (9), 209 (61), 105 (15); 44 (base peak); mol wt (osmometry) required 330, found 328 ± 4; active oxygen content, 87 ± 10% of theoretical.

Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.24. Found: C, 76.34; H, 4.27.

Thermolysis of Endoperoxide 1. A solution of 21 mg (0.07 mmol) of **1** in 5 mL of benzene was refluxed under nitrogen for 6 h. As the reaction progresses, the initially colorless solution first turns yellow then colorless. The products of the reaction were identified and quantitated by using gas chromatography by comparison with authentic *o*-dibenzoylbenzene (Aldrich) 85% and phenyl *o*-benzoylbenzoate 5%.

Thermolysis of 1 with Maleic Anhydride. A solution of 102 mg (0.31 mmol) of endoperoxide **1** and 30.2 mg (0.31 mmol) of maleic anhydride was prepared in 10.0 mL of benzene. The solution was refluxed under nitrogen for 6 h, and then the solvent was evaporated under reduced pressure, leaving a solid white residue. The residue was transferred to a vacuum sublimator and evacuated (0.01 mm) at room temperature for 24 h to remove the excess unreacted maleic anhydride. The remaining product, a white solid (120 mg), was recrystallized from pentane–CH_2Cl_2 to give adduct **5**: mp 145 °C (with decomposition); ^1H NMR ($CDCl_3$) δ 7.85–7.0 (m, 14 H), 4.1 (s, 2 H); mol wt (osmometry required 384; found 381 ± 5; active oxygen content 94.4 ± 6% of theoretical; IR ($CHCl_3$) 2980, 1870, 1690, 1600, 1490 cm^{-1}.

Anal. Calcd for $C_{24}H_{16}O_5$: C, 74.99; H, 4.20. Found: C, 74.65; H, 4.28.

The stereochemistry of the adduct is not revealed by these results.

Rate of Reaction of 1 Determined by Infrared Spectroscopy. A 0.1 M solution of **1** in *p*-xylene was prepared and deoxygenated by purging with dry Ar. The solution was heated to 112 °C, and six 400-μL aliquots were removed over a 1-h period and stored at 0 °C for later analysis. The infrared spectra of the aliquots was determined on a Beckman IR-12 spectrophotometer. The optical densities at 1785 cm^{-1}, which earlier had been shown to be directly proportional to the concentration of **1**, were employed (Figure 1) to give the rate constant for reaction of **1**.

Rate of Appearance and Consumption of the Yellow Intermediate by UV–Visible Spectroscopy. A 1×10^{-3} M solution of **1** in *p*-xylene was prepared and deoxygenated by purging with dry Ar. The sample was placed in a cell holder heated to 112 °C in the sample compartment of a Perkin-Elmer 552 spectrometer. The optical density at 400 nm was recorded at 256 equally spaced points over a period of 10 h, and the results were plotted as shown in Figure 2. Nonlinear least-squares analysis of these data gives two rate parameters (see text).

Chemiluminescence from 1 with and without Added Activators. The intensity of chemiluminescence from **1** in the presence and absence of added activator was monitored at 112 °C by photon counting. Figure 4 shows the results for a 1×10^{-3} M solution of **1** in deoxygenated *p*-xylene with no activator. The total chemiluminescent intensity at 450 nm was computed by determining the area under this curve. Similarly, the total chemiluminescent intensity for starting endoperoxide **1** concentrations from 2.2×10^{-3} M to 2.5×10^{-4} M was determined. This intensity was shown (Figure 5) to be proportional to the square of the concentration of **1**. The chemiluminescence of solutions containing added activators corresponds to the fluorescence of the activator. For example, solutions of **1** (1×10^{-3} M) and rubrene [(1×10^{-5}) – (8×10^{-4} M)] in deoxygenated *p*-xylene exhibit chemiluminescence that decays, independent of the initial concentration of **1** or rubrene, with a first-order rate constant at 112 °C of 3.9×10^{-4} s^{-1}. Moreover, the rubrene concentration does not change, as indicated by its optical absorption, during the course of the experiment. The total chemiluminescent intensities in the presence of various activators (1×10^{-4} M) and 1×10^{-3} M **1** in *p*-xylene were obtained by integrating the intensity at the fluorescence maximum under low-resolution conditions and then correcting for the spectral response of the photomultiplier tube and monochromator according to data supplied by the manufacturer. These data, as well as the oxidation potentials and fluorescence efficiencies of the activators, are shown in Table I.

Quenching of Perylene Activated Chemiluminescence of 1 with Maleic Anhydride. The integrated chemiluminescence intensity at 475 nm (low resolution) from a deoxygenated *p*-xylene solution of **1** (5×10^{-4} M) and perylene (5×10^{-4} M) at 112 °C was measured as described above. Similarly, the integrated intensity was determined for eight solutions containing between 1×10^{-4} and 1×10^{-2} M maleic anhydride. The total *intensity in the presence of maleic anhydride* was corrected for quenching of perylene fluorescence measured at 98 °C using the Stern–Volmer equation. The ratio of intensity in the absence of anhydride to the corrected intensity in its presence is plotted in Figure 7. The decay of

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Table I. Total Intensities for Activators Used in Chemiluminescence Study

activator	ϕ_{fl}[a]	λ,[b] nm	ox. pot.,[c] V	corr tot intens[d]
acridine orange	1.0	515	0.72	1.05×10^8
9-dimethylamino[*b*]-benzophenazine	0.14	515	0.73	1.06×10^8
7-dimethylamino-2-methylphenazine	0.22	528	0.74	1.01×10^8
1,3-diphenyliso-benzofuran	0.96	475	0.79	3.40×10^7
rubrene	0.56	585	0.82	2.28×10^7
tetracene	0.21	486	0.87	1.59×10^7
DPET	0.66	583	0.97	8.08×10^6
perylene	0.84	475	1.06	3.20×10^6
DPEA	0.96	490	1.16	9.25×10^5
DPA	0.85	420	1.20	3.77×10^5

[a] Determined at 98 °C in deoxygenated *p*-xylene. [b] Wavelength monitored to determine chemiluminescence intensity. [c] Determined by cyclic voltammetry relative to SCE in CH_3CN with tetrabutylammonium perchlorate as supporting electrolyte. [d] Corrected for fluorescence efficiency of the activator and the spectral response of the chemiluminometer.

the chemiluminescence is shown in Figure 6.

Quenching of Diketone Formation from 1 with Dimethylmaleic Anhydride. Solutions of endoperoxide **1** (1.5×10^{-3} M) and dimethylmaleic anhydride (3.0×10^{-3} to 1.5×10^{-2} M) and eicosane (internal standard for gas chromatographic analysis) in *p*-xylene were degassed by freeze-pump-thaw techniques and sealed in individual glass ampules. The ampules were heated at 112 °C for 12 h. The yield of diketone **3** was determined by gas chromatography (see above). The data are shown on Figure 3.

Isolation and Identification of 1,3-Diphenylisobenzofuran 6 from the Thermolysis of Peroxide 1. A solution of peroxide **1** (120 mg) in 1.0 mL of *p*-xylene was deoxygenated by purging with dry Argon in a Pyrex test tube fitted with a Teflon stopcock. The solution was heated at 112 °C for 65 min at which time the maximum amount of yellow color had developed. The components of the thermolysis solution were separated by preparative HPLC on silica gel eluting with hexane-0.1% CH_3CN. The fraction that absorbed strongly at 390 nm was collected and the solvent evaporated, leaving a yellow residue (2 mg). The mass and ^1H NMR spectra of this residue and its melting point correspond with those of authentic (Aldrich) 1,3-diphenylisobenzofuran.

Acknowledgment. This work was support by the Office of Naval Research and by the National Science Foundation. We thank Mr. John Hurst of this department for the use of his computer programs.

Registry No. 1, 25994-58-5; **2**, 17023-28-8; **3**, 1159-86-0; **5**, 66819-90-7; **7**, 66819-89-4; maleic anhydride, 108-31-6; dimethylmaleic anhydride, 766-39-2; acridine orange, 65-61-2; 9-dimethylamino[*b*]benzophenazine, 80294-18-4; 7-dimethylamino-2-methylphenazine, 4661-61-4; **6**, 5471-63-6; rubrene, 517-51-1; tetracene, 92-24-0; DPET, 18826-29-4; perylene, 198-55-0; DPEA, 10075-85-1; DPA, 1499-10-1.

Effects of Substituents and Generation Methods on Insertion-Addition Selectivities of "Arylcarbene" in Alcohol-Olefin Binary Mixtures. Intervention of Reaction of Diazo Compounds Masquerading as Carbenes

Hideo Tomioka,* Shinji Suzuki, and Yasuji Izawa

Contribution from the Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan. *Received May 5, 1981*

Abstract: A Hammett study of the insertion-addition selectivity (k_i/k_a) and cyclopropanation stereoselectivity (k_c/k_t) of "arylcarbene" generated either photolytically or thermally in 2-propanol-ethyl vinyl ether binary mixtures showed that ρ values are highly sensitive to the generation method. Thus, plots of k_i/k_a and k_c/k_t vs. σ (σ^+) in the photolytic run gave ρ values of -0.96 ($r = -0.96$) and -0.15 ($r = -0.95$), respectively, whereas similar values are $+1.4$ ($r = 0.93$) and -1.1 ($r = -0.96$) in the thermal run. The results along with the effects of precursor, temperature, and sensitizer on the product distributions are interpreted as indicating that, while free carbene is involved in the photolytic run, the ground-state diazo compound is masquerading as carbene in its thermal reaction with the olefin.

In view of the many cases in which formal carbenic products have been obtained in the photolysis and thermolysis of diazo compounds, the intermediacy of free carbenes in these experiments has been widely accepted.[1] However, as Kirmse stated in his book,[1b] "the long-lasting fascination of the carbene concept for organic chemists appears to have emotional rather than empirical grounds". Conceivably, excited precursor molecules may act as carbenoid species, mimicking free carbene in their reactions. In fact, a recent product analysis[2] as well as spectroscopic[3] studies revealed that carbene-mimicking reactions of excited diazo compounds are involved in the photochemical processes of several α-diazocarbonyl compounds. For example, it has been shown that the photochemical Wolff rearrangement to form ketene takes place directly from the singlet excited state of the *s-Z* conformer whereas the excited state of the *s-E* conformer dissociates nitrogen to

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