in that an enone concentration of 2.5 M in IPA was utilized, and the internal standard for GLC analysis, 0.0127 M 2-acetonaphthone, was added following irradiation. The photodimers **5** and **6** had been isolated and identified previously by Nũnez.[13] The GLC analysis for **5** and **6** was done on a 6 ft × $^1/_8$ in. aluminum column of 5% QF-1 and 1% Carbowax 20M on Chromasorb G (AW/DMCS treated) at an oven temperature of 160 °C and with the detector set at 250 °C.

Preparation of Photoadducts of Enone 1 and Cyclohexene. In these experiments, 2.3 g of **1** and 24 g of cyclohexene in 125 mL of hexane was irradiated for 24 h by using the Rayonet apparatus without the merry go round. The crude mixture was analyzed by GC/MS, which indicated two components of mass 206, corresponding to adducts of **1** and cyclohexene. The mixture was chromatographed on Davison silica gel (60–200 mesh) with 0–8% ether in hexane as the eluent. The collected fractions were analyzed by gas chromatography (GC), and those showing only a single component were also analyzed by GC/MS. Two different fractions, representing major and minor products, were found which possessed a molecular ion of mass 206 but which otherwise had different mass spectra. The ^{1}H NMR and IR spectra of both fractions and the ^{13}C NMR spectrum of the major product were taken. The IR spectra showed carbonyl absorption at 1710 cm^{-1} for the minor component and at 1705 cm^{-1} for the major component; neither spectrum showed C=C absorption. Both components showed complex ^{1}H NMR spectra in the range 0.5–2.6 ppm. The major product had methyl resonances at 0.89 and 1.05 ppm in addition to two much smaller peaks (<10% of the above) at 0.94 and 1.00 ppm, while the minor product had methyl resonances at 0.85 and 0.95 ppm. The ^{13}C NMR spectrum of the major component in $CDCl_3$ (chemical shifts relative to Me_4Si) was as follows: 214.7 (s), 49.1 (d), 47.8 (d), 37.3 (d of t), 34.8 (d), 34.5 (t), 34.2 (d), 31.0 (s), 28.5 (t), 26.8 (d of q), 23.4 (t), 21.8 ppm (t).

Both adducts were treated with 15% NaOH in methanol at room temperature for 72 h to see if they would undergo isomerization, under conditions previously used to isomerize trans-fused to cis-fused cycloadducts. The NMR spectrum of the major component after base treatment showed that the small peaks at 0.94 and 1.00 ppm had disappeared, suggesting that a small amount of a trans-fused adduct may have been present and was converted by base to the corresponding cis-fused cycloadduct. Similar treatment of the minor component produced no change in its IR spectrum and its GC retention time.

Synthesis and Characterization of Photodimers of 4,4-Dimethylcyclohex-2-en-1-one (1). Irradiation of neat enone **1** with 350-nm lamps in a Rayonet Reactor for 17 h yielded a yellow oil containing suspended crystalline material. This mixture was chromatographed on silica gel by elution with mixtures of ether and hexane. In addition to pure enone **1**, a white crystalline material (dimer A, mp 154–156 °C) was eluted with 5% ether. A second dimeric product, present in trace amounts in later fractions, was detected by GC analysis. The amount did not allow structural studies, except that it was noted that upon standing in acetonitrile for prolonged periods of time, this material isomerized to dimer A. A third product was eluted with 40% ether, and this material also crystallized (dimer C, mp 96–98 °C). The mass spectra of A and C, as well as their IR, UV, ^{1}H NMR, and ^{13}C NMR spectra, indicated they were [2 + 2] dimers of enone **1**.[13] Since their ^{13}C NMR spectra showed only eight signals, unsymmetrical structures for dimers A and C can be ruled out. On steric as well as mechanistic grounds, structures with two trans cyclobutane ring junctions can also be eliminated. On the basis of the crowding seen in models, cis–syn–cis dimers also appear to be unlikely. Dimer A is assigned the anti head-to-tail structure **6** and dimer C the anti head-to-head structure **5** on the following grounds. A downfield signal at 3.01 ppm (d, $J = 9$ Hz) seen for C is not present in the spectrum of A and is assigned to bridgehead protons α to the carbonyl; a head-to-tail structure would not be expected to give a sharp doublet. The more polar dimer **5** would be expected to be retained on a silica gel column compared with the less polar structure **6**,[26] while the lower melting point of C compared to that of A is consistent with a less symmetrical structure (note that structure **6** has a center of symmetry, allowing tighter packing in the crystalline state). Other arguments to support these assignments are given in ref 13. Dimer B is tentatively concluded to be epimeric to **6** at one of the carbons α to the carbonyls, i.e., it may be a trans-fused cyclo dimer.

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Registry No. **1**, 1073-13-8; **5**, 37402-51-0; **6**, 37165-47-2; **7**, 57166-80-0; **8**, 86118-06-1; DEE, 2678-54-8; cyclohexene, 110-83-8; methyl vinyl ketone, 78-94-4; isobutyraldehyde, 78-84-2; bromoacetaldehyde diethyl acetal, 2032-35-1; naphthalene, 91-20-3.

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[26] See: Gioia, B.; Ballabio, M.; Beccalli, E. M.; Cecchi, R.; Marchesini, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 560.

Chemiluminescence from the Reaction of 2-Methylene-3-acetyloxazoline-4,5-dione with Hydrogen Peroxide

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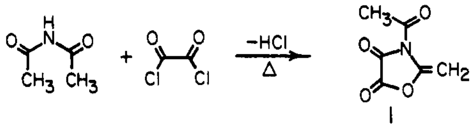
Chemical reactions that generate visible light have been actively investigated for the past 50 years.[1] Recent research has revealed important details of the chemical and physical transformations required for efficient light generation from these processes.[2] Typically these reactions involve, as the starting material or as a key intermediate, an organic peroxide. Conversion of the weak oxygen–oxygen bond of the peroxide to a much stronger carbon–oxygen double bond in a product carbonyl group in most cases supplies much of the energy required to form the requisite electronically excited state. The mechanism for conversion of the chemical potential energy of the peroxide to visible light depends on the details of the structure of the peroxide. One of the most efficient chemiluminescent systems yet discovered is based on the reaction of hydrogen peroxide with certain derivatives of oxalic acid in the presence of a suitable fluorescer.[3,4] This reaction can generate light with an efficiency approaching 35%[5] and forms the basis for the popular Cyalume light sticks. For these reasons we were attracted to the recent report by Richter and Temme[6] of a new reaction of aliphatic imides with oxalyl chloride to give oxazolidinediones (eq 1). We have examined the chemiluminescent reaction of this "derivative" of oxalic acid with hydrogen peroxide.



(1)

Oxazolidinedione **1** was prepared according to the published procedure[6]. When a solution of dione **1** in dimethyl phthalate containing 9,10-diphenylanthracene (DPA) is treated with hydrogen peroxide, the blue chemilumines-

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[1] Albrecht, H. O. *Z. Phys. Chem.* **1928**, *136*, 321.

[2] Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187.

[3] Chandross, E. A. *Tetrahedron Lett.* **1963**, 761.

[4] Rauhut, M. M. *Acc. Chem. Res.* **1969**, *2*, 80.

[5] Tseng, S.-S.; Mohan, A. G.; Haines, L. G.; Vizcarra, L. S.; Rauhut, M. M. *J. Org. Chem.* **1979**, *44*, 4113.

[6] Richter, R.; Temme, G. H. *J. Org. Chem.* **1981**, *46*, 3015.

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Table I. Chemiluminescence of Dione 1[a]

run	[2,6-lutidine], M	$[H_2O_2]$,[b] M	k_{obsd},[c] s^{-1}	CHL intensity counts[d] × 10^{-7}
1	2.6×10^{-3}	0.038	8.2×10^{-4}	3.0
2	5.2×10^{-3}	0.038	2.1×10^{-3}	2.4
3	2.5×10^{-2}	0.038	1.3×10^{-2}	0.45
4	5.2×10^{-2}	0.038	2.5×10^{-2}	0.27
5	5.2×10^{-3}	0.020	8.4×10^{-3}	3.6
6	5.2×10^{-3}	0.036	2.2×10^{-3}	3.5
7	5.2×10^{-3}	0.073	5.2×10^{-3}	2.6
8	5.2×10^{-3}	0.12	8.5×10^{-3}	2.2
9	5.2×10^{-3}	0.20	1.6×10^{-2}	1.4

[a] The concentration of 1 is 5.5×10^{-4} M; the activator is 9,10-diphenylanthracene (3.5×10^{-4} M). The solvent is dimethyl phthalate, and all experiments are at room temperature. [b] Calculated from the amount of 95% H_2O_2 added to the reaction. [c] The observed pseudo-first-order rate constant for decay of the chemiluminescence. [d] Integrated chemiluminescence output for ca. 4 half-lives.

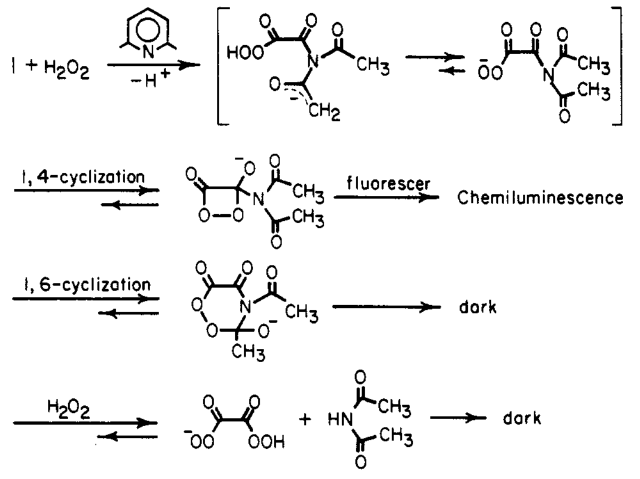
cence characteristic of DPA fluorescence can be seen easily in a darkened room with the unaided eye. Control experiments showed that all three ingredients are required to generate light. Thus dione 1 is capable of generating chemiluminescence.

The rate of the chemiluminescent reaction of 1 is increased by added bases. We explored several potential catalysts for the reaction of 1 with hydrogen peroxide and found that 2,6-lutidine gives clean and reproducible results. Addition of the lutidine to the reaction mixture has two effects on the chemiluminescent process (Table I runs 1–4). First, as the lutidine concentration is increased, the observed pseudo-first-order rate constant for decay of the chemiluminescent reaction increases. Second, increasing the lutidine concentration leads to a decrease in the total chemiluminescent intensity obtained by a factor of about 10. Thus the base must be affecting two parts of the reaction sequence that leads eventually to light. Evidently, lutidine increases the rate of the slow step and diverts a key intermediate away from the eventual generation of light. It should be noted that lutidine does quench the fluorescence of DPA in dimethyl phthalate, but this process alone is not sufficient to account for the decrease in light intensity observed.[7]

In a similar fashion we examined the effect of hydrogen peroxide concentration on the rate of the chemiluminescent reaction of 1 and its light-generating efficiency (Table I, runs 5–9). This study revealed that the hydrogen peroxide and the base have similar affects. Increasing the hydrogen peroxide concentration increases the rate of reaction while simultaneously decreasing the light output.

Changing the fluorescer structure reveals some additional details about the light-generating process. The aromatic hydrocarbon fluorescers such as DPA, rubrene, perylene, and 9,10-diphenyl-1-ethynylanthracene all give reasonably intense chemiluminescence. However, 9,10-dibromoanthracene (DBA), which has been shown to be useful in the detection of triplet excited states,[8] yields no meaningful chemiluminescence above the low background level. This observation, similar to one we made earlier for diphenoyl peroxide chemiluminescence,[9] is indicative of the operation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism.[2]

Scheme I



Investigations of the chemiluminescence of some other oxalic acid derivatives has revealed that the fluorescer catalyzes the decomposition of a metastable intermediate.[4] Thus addition of the fluorescer to the reaction mixture some time after the other reagents have been mixed still yields nearly as much light as is obtained when the fluorescer is present from the outset. Similar attempts to detect a metastable intermediate from dione 1 were unsuccessful. Late addition of the fluorescer did not generate any light above that anticipated to result from residual dione 1 based on the known rate of its consumption.

The results of this investigation support the mechanism for the chemiluminescence of dione 1 shown in Scheme I. This mechanism is modeled after a similar proposal made by Rauhut for the chemiluminescence of oxalate esters.[4] The first step is the rate-limiting addition of hydroperoxide anion to the oxazolinedione which eventually opens the ring to give first an enolate anion and then the peroxycarboxylate anion. The fate of the ring-opened intermediate probably determines the chemiluminescence yield. Three reasonable alternative reactions are suggested: (i) 1,4-cyclization leading to a dioxetane intermediate is the precedented route to the observed chemiluminescence; (ii) 1,6-cyclization; (iii) base-catalyzed addition of a second molecule of hydrogen peroxide. The last two paths thus compete with the dioxetane route and do not lead to light. The effect of lutidine and hydrogen peroxide concentration on the reaction rate and inhibition of chemiluminescence are consistent with this proposal. Also, the absence of a metastable intermediate is reasonably accounted for since reversal of the 1,4-cycloaddition gives the dark routes another opportunity to consume the intermediate. Finally, the intermediate peroxycarboxylate anion formed from 1 and hydroperoxide (Scheme I) should also be formed in the analogous reaction of hydroperoxide with the appropriate oxamide. Rauhut and co-workers report[10] that tetrabenzoyloxamide gives no light under conditions where dione 1 is clearly chemiluminescent. We suspect that this difference may be related to either acceleration of the rate of initial reaction of 1 with hydroperoxide or steric congestion inhibiting 1,4-cyclization of the benzoyl analogue of the peroxycarboxylate anion compared to addition of a second molecule of hydrogen peroxide.

We have qualitatively measured the light-generating efficiency of the reaction of 1 and find it to be several

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(7) The lifetime of DPA is ca. 9 ns; thus quenching would have to occur at a rate far above the diffusion limit for the lutidine to quench DPA fluorescence to the extent observed.

(8) Vassil'ev, R. F. *Prog. React. Kinet.* **1967**, *4*, 305. Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.

(9) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 6107; **1978**, *100*, 4496.

(10) Maulding, D. R.; Clarke, R. A.; Roberts, B. G.; Rauhut, M. M. *J. Org. Chem.* **1969**, *33*, 250.

orders of magnitude less than the most efficient oxalate esters. However, no attempt has been made to optimize the structure of the oxazolinedione to increase light output.

Experimental Section

General Methods. Solvents were purified by distillation before use. Fluorescers were chromatographed on alumina and then recrystallized. The chemiluminescence measurements were performed by the photo-counting method at room temperature by using the apparatus previously described.[11]

Typical Chemiluminescence Measurement. A solution of oxazolinedione 1 in dimethyl phthalate was added to a solution of the fluorescer and hydrogen peroxide, also in dimethyl phthalate, so that the final volume was ca. 2.0 mL. Typical concentrations of these reagents in this solution were as follows: 1, 5.5×10^{-4} M; fluorescer, 3.5×10^{-4} M; 95% H_2O_2, 0.4 M. For the lutidine-catalyzed runs, the base was included in the peroxide solution. The light output from these solutions was monitored for ca. 4 half-lives at room temperature.

Acknowledgment. This work was supported by the Office of Naval Research.

Registry No. 1, 77903-65-2; 9,10-diphenylanthracene, 1499-10-1; hydrogen peroxide, 7722-84-1; 2,6-lutidine, 108-48-5.

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(11) Smith, J. P.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 1041.

Bicyclic Dioxaphosphoranes. 3.[1] Spectral Evidence for the Conformation of a Phosphorane

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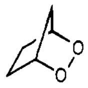
The insertion of a phosphine into the oxygen–oxygen bond of a peroxide to produce a phosphorane was first reported in 1964.[2] Since that initial report the reactions of phosphines with diacyl peroxides,[3] peresters,[4] dialkyl peroxides,[5] hydroperoxy endoperoxides,[6] ozonides,[7] and dioxetanes[8] have all been observed.

We have previously reported[1] that triarylphosphines and phosphites insert into the oxygen–oxygen bond of the prostaglandin endoperoxide model 2,3-dioxabicyclo[2.2.1]heptane (1). We presented spectral evidence that the products of these reactions were bicyclic dioxaphosphoranes which were undergoing rapid pseudorotation at room temperature. We report here the first example of the insertion of a phosphine into the peroxide linkage of 1 to produce at room temperature two noninterconverting phosphoranes kinetically isolated from each other by a high-barrier pseudorotation. The ^{13}C and ^1H NMR's of these phosphoranes further allow us to eliminate from consideration possible structures of these products and to estimate lower limits for the activation barriers necessary to place a bicyclo[3.2.1] structure and a four-membered ring in the equatorial–equatorial position of a trigonal bipyramid.



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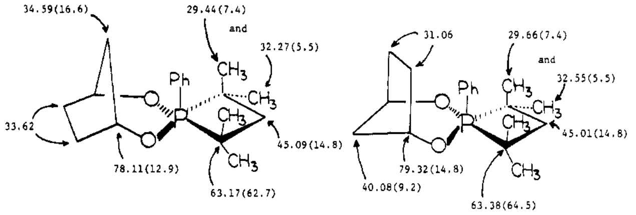
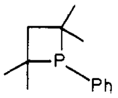


3 4

Figure 1. ^{13}C chemical shift assignments for the two phosphoranes. The carbon–phosphorus coupling constants are reported in hertz in parentheses following the chemical shift. The aromatic chemical shifts are reported in the Experimental Section.

A solution of phosphine 2[9] in dry benzene[10] was added to a serum-capped 10-mm NMR tube containing a solution of peroxide at −78 °C. Warming to room temperature resulted in the complete disappearance of 2 as indicated by the ^{31}P NMR peak at δ 49.08.[11] Concurrent with the disappearance of 2, two new peaks at δ −42.48 and −44.77 in an integrated ratio of 1.0:1.6, respectively, appeared in the ^{31}P NMR spectrum. We suggest that these two peaks are due to two structurally different and kinetically isolated phosphoranes. Consistent with this interpretation are the ^{13}C NMR spectral assignments presented in Figure 1. The ^{13}C NMR spectra are reminescent of those previously reported.[1b] Carbon–phosphorus coupling to C_5 but not $C_{7,8}$ is observed, indicative of a Karplus relationship. The assignments of the ^{13}C peaks were made with the aid of intensity measurements and the DEPT (Distortionless Enhancement of Polarization Transfer)[12] pulse sequence.



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The NMR indicated that the yields of the two phosphoranes were essentially quantitative as revealed by the absence of any peaks attributable to starting material, byproducts, or decomposition products. (The ^{13}C NMR is available as supplementary material; see the paragraph at the end of the paper for further details.)

The observation of two different methyls by ^{13}C NMR but only one quaternary carbon in the four-membered ring of both phosphoranes precludes any conformational pro-

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(1) For parts 1 and 2 see: (a) Clennan, E. L.; Heah, Poh Choo *J. Org. Chem.* **1981**, *46*, 4105. (b) *Ibid.* **1982**, *47*, 3329.

(2) Denney, D. B.; Relles, H. M. *J. Am. Chem. Soc.* **1964**, *86*, 3897.

(3) (a) Greenbaum, M. A.; Denney, D. B.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1956**, *78*, 2563. (b) Denney, D. B.; Greenbaum, M. A. *Ibid.* **1957**, *79*, 979.

(4) Denney, D. B.; Goodyear, W. F.; Goldstein, B. *J. Am. Chem. Soc.* **1961**, *83*, 1726.

(5) Denney, D. B.; Relles, H. M. *J. Am. Chem. Soc.* **1964**, *86*, 3897.

(6) Porter, N. A.; Funk, M. O.; Gilmore, D.; Isaac, R.; Nixon, J. *J. Am. Chem. Soc.* **1976**, *98*, 6000.

(7) Carles, J.; Fliszar S. *Can. J. Chem.* **1969**, *47*, 1113.

(8) Bartlett, P. D.; Baumstark, A. L.; Landis, M. E.; Lerman, C. L. *J. Am. Chem. Soc.* **1974**, *96*, 5267.

(9) De'Ath, N. J.; Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *J. Am. Chem. Soc.* **1976**, *98*, 768.

(10) The benzene was distilled from benzophenone ketyl and stirred over EDTA before use.

(11) All ^{31}P chemical shifts are reported relative to 85% H_3PO_4 by substitution. A negative shift is indicative of a peak appearing upfield of the reference.

(12) (a) Bendall, M. R.; Doddrell, D. M.; Pegg, D. T. 23rd Experimental Nuclear Magnetic Resonance Conference, Madison, WI, Apr 25–29, 1982. (b) Bendall, M. R.; Pegg, D. T.; Doddrell, D. M.; Thomas, D. M. *J. Magn. Reson.* **1982**, *18*, 1.

(13) DeBruin, K. E.; Neumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7031.

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