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CIEEL mechanism to 3 reveals an important limitation to light generation by this path. *CVE* *...* *...* *...*

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by

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**Thermolysis of 4-Methyl-4-(1-propenyl)malonyl Peroxide:
Mechanistic Limits to Chemiluminescence Efficiency**

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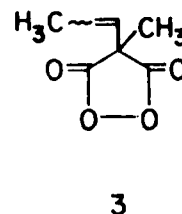
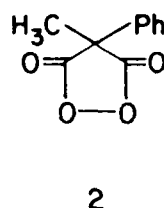
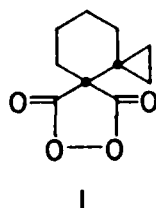
Abstract: The preparation and thermal chemistry of 4-methyl-4-(1-propenyl)-malonyl peroxide (**3**) is described. Thermolysis in acetonitrile at 84°C gives 2,4-dimethylbut-2-ene-4-olide in 45% yield and an oligomeric ester derived from an intermediate α -lactone in 55% yield. The reaction of **3** can be catalyzed by aromatic hydrocarbons such as perylene. Under these conditions weak chemiluminescence results. The mechanism for light generation is identified as chemically initiated electron-exchange luminescence (CIEEL). Application of the CIEEL mechanism to **3** reveals an important limitation to light generation by this path.

Chemical reactions that generate visible light often arouse interest. This phenomenon is observed to occur naturally in bioluminescent organisms¹ and it can be created synthetically in the laboratory.² The organic substances that are known to exhibit chemiluminescence with measurable efficiency are limited to structures containing a peroxide linkage. This constraint is related directly to the energy required to generate light. The exothermic conversion of the oxygen-oxygen bond of the peroxide to some other functional group is one of the few transformations capable of releasing sufficient energy to generate a visible photon.

Satisfaction of the energy requirement outlined above is a necessary but not a sufficient criterion for the design of an efficient chemiluminescent reaction. Successful routing of the released energy to the creation of an electronically excited state product must also occur. The details of this routing are revealed by studying the mechanism of chemiluminescent reactions. Our previous efforts in this regard have revealed a general pathway we identified as chemically initiated electron-exchange luminescence (CIEEL).³

Malonyl peroxides are endowed with many of the features required for the efficient generation of chemical light by the CIEEL path.⁴ In their simplest form, these substances lack an efficient path for energy release. Recently, we reported investigations of the chemiluminescence of cyclopropyl-substituted malonyl peroxide **1**⁴ and 4-methyl-4-phenylmalonyl peroxide (**2**)⁵. Both of these high-energy compounds do generate light by the CIEEL route. Herein we report our investigation of the thermal and chemiluminescent properties of 4-methyl-

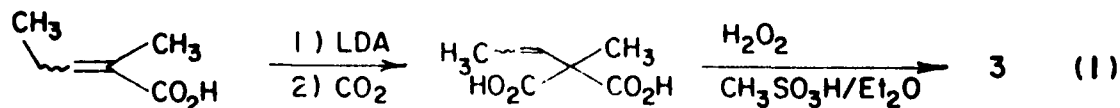
4-(1-propenyl)malonyl peroxide (3). This compound also is weakly chemiluminescent, and its investigation reveals clear mechanistic limits to light generation by the CIEEL route.



Results

Synthesis of Peroxide 3.

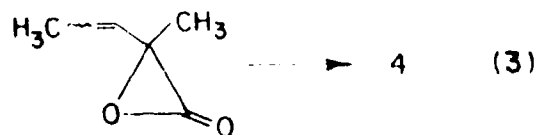
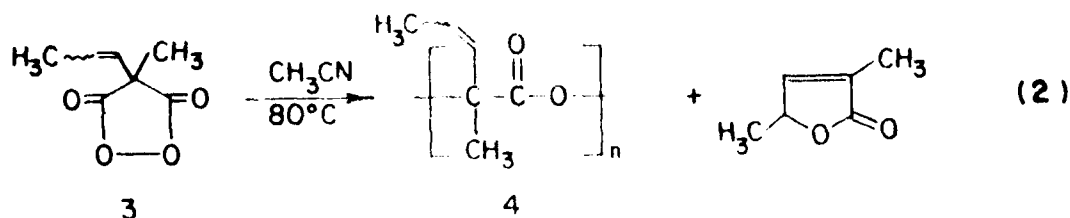
No malonyl peroxides have been reported that include olefinic functional groups as part of their structure.⁶ The predictable sensitivity of the double bond to the usual acid-catalyzed oxidative cyclization conditions probably served to inhibit attempts to prepare these compounds. Indeed, we were unable to develop a synthesis of 4-methyl-4-(2-styryl)malonyl peroxide. However, the synthesis of 3 proceeds smoothly, but in relatively low yield, under these conditions from the malonic acid. The preparation of 3 from a mixture of cis- and trans-2-methyl-2-pentenoic acid⁷ is outlined in eq. 1. Details of these reactions are given in the Experimental section.



Peroxide **3** is isolated by column chromatography on silica gel at -20°C as a mixture of cis- and trans- isomers. The ^1H NMR spectrum shows that the two isomers of **3** are present in a ca. 1:1 ratio. All attempts to separate these isomers were unsuccessful. The mixture was used in the subsequent investigation of the thermal and chemiluminescent properties of this peroxide.

Thermolysis of Malonyl Peroxide **3**.

The thermal reactions of **3** were investigated under a range of conditions. Heating a nitrogen purged acetonitrile solution ($8 \times 10^{-3}\text{M}$) at 84°C for 1 h gives a white solid identified as oligomeric ($n \approx 5$) ester **4** in 55% yield and 2,4-dimethylbut-2-ene-4-olide (**5**) in 45% yield, eq. 2. Based on the behavior of other malonyl peroxides,^{6c} we presume that the oligomeric ester is derived from α -lactone **6**, which is the primary product formed by decarboxylation of **3**, eq. 3. The butenolide (**5**) was identified by comparison with an authentic



sample prepared by the procedure of Gorewit and Rosenblum.⁸ Oligomeric ester **4** was characterized spectroscopically and by its molecular weight (osmometric). There is no detectable chemiluminescence from the reaction of **3** under these conditions.

The CIEEL mechanism relies on an initial electron transfer from an activator (ACT, typically an aromatic hydrocarbon) to the peroxide for initiation. Thermolysis of **3** in acetonitrile containing perylene ($3 \times 10^{-3} \text{M}$) gives products **4** and **5** in unchanged yields and low intensity, but easily detected, chemiluminescence. The chemiluminescence emission spectrum is identical with perylene fluorescence. Similar results are obtained in benzene solution (the yields of light and **5** are lower) and in the presence of O_2 .

The rate of reaction of peroxide **3** was studied, in part, to confirm that it is the source of the observed chemiluminescence. The thermal reaction was monitored both by infrared spectroscopy and by chemiluminescence. The rate of consumption of **3** (IR, 1804 cm^{-1}) is the same as the rate of chemiluminescence decay, Table 1. Moreover, it was observed, as expected from the CIEEL mechanism,³ that perylene (and other ACT) accelerate the reaction of **3** according to the kinetic law displayed in eq. 4. These data also are

$$k_{\text{obsd}} = k_1 + k_{\text{ACT}} [\text{ACT}] \quad (4)$$

summarized in Table 1. The chemiluminescence intensity is directly proportional to the concentration of malonyl peroxide **3** and depends inversely on the one-electron oxidation potential of ACT. The data are displayed in Table 2.

There is much less light formed from 9,10-dibromoanthracene than from 9,10-diphenylanthracene. This result helps exclude mechanisms requiring energy transfer from an initially formed excited state of **5** or **6** to the ACT.⁹

The temperature dependence of the ACT catalyzed chemiluminescence of **3** is particularly helpful in analyzing this reaction. Chemiluminescent reactions provide the unique opportunity to measure both the temperature dependence of the consumption of the peroxide and the instantaneous rate of formation of the excited product.¹⁰ The first is determined from conventional analysis of the temperature dependence of the reaction of **3** and corresponds to the activation energy for the rate-determining-step in the mechanism. For the ACT catalyzed process, the rate limiting step is characterized by k_{CAT} and its temperature dependence gives E_a^{CAT} . The temperature dependence of the chemiluminescence intensity (E_a^{CHL}) contains contributions not only from the rate-limiting-step (E_a^{CAT}), but also from a term(s) that reflects the partitioning of an intermediate between a path ultimately leading to light (E_a^{light}) and one not giving a photon as a product (E_a^{dark}). This is expressed mathematically in eq. 5. Thus, if E_a^{CHL} is greater than E_a^{CAT} ,

$$E_a^{CHL} = E_a^{CAT} + (E_a^{light} - E_a^{dark}) \quad (5)$$

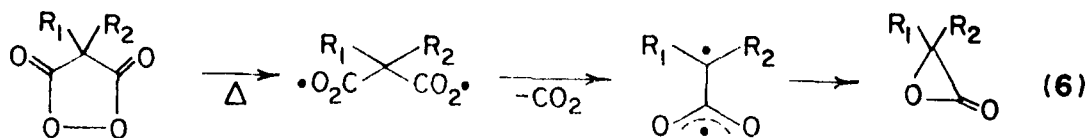
there is an intermediate in the reaction sequence leading to light, and this intermediate must proceed over a higher barrier to stay on the "light-path" than to get off of it.

The activation energies E_a^{CAT} , and E_a^{CHL} were determined by measuring the temperature dependence of k_{CAT} and the chemiluminescence intensity. The data are summarized in Table 3. The value of E_a^{CAT} for perylene in acetonitrile is

10±1 kcal/mol and that of E_a^{CHL} is 14±1 kcal/mol. Thus, analysis within the model described above shows that there is an intermediate in this reaction that can proceed to give light by a path that has a barrier ca. 4 kcal/mol higher than one leading only to ground state products. This helps to explain the low yield of light obtained from malonyl peroxide 3.

Discussion

The chemistry of simply substituted malonyl peroxides is well understood. Thermolysis leads to oxygen-oxygen bond cleavage, decarboxylation, and 1,3-closure to give an α -lactone, eq. 6.⁶ The heat of reaction for this



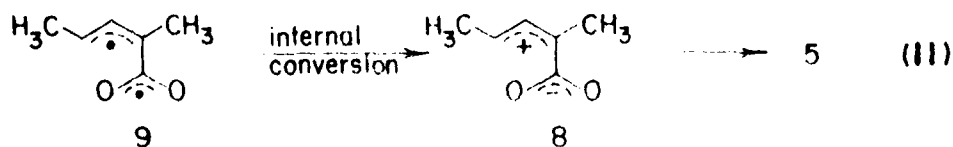
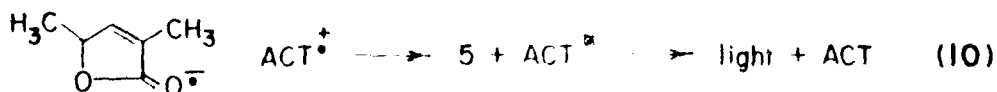
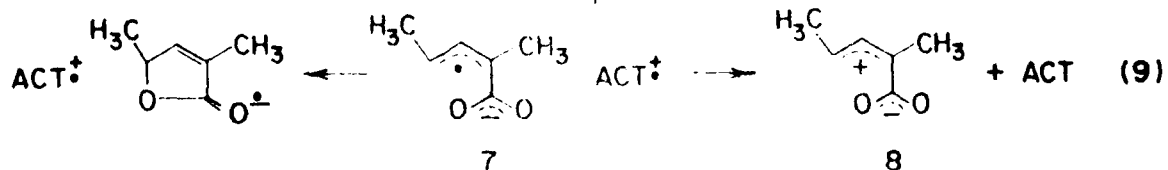
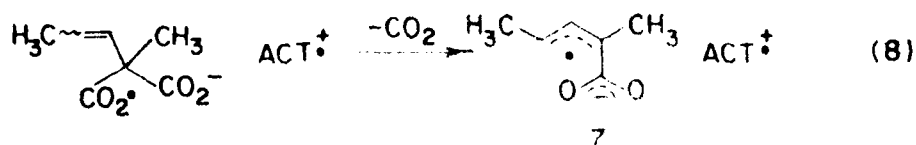
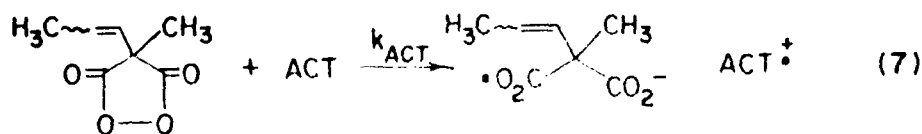
sequence, estimated using Benson group equivalents,¹¹ is ca. 30 kcal/mol. This is not a sufficiently exothermic process to generate a photon of visible light in high yield. Catalyzing this reaction by electron transfer within the CIEEL mechanism simply lowers the activation energy and makes light generation even less probable. Inspection of eq. 6 readily reveals that much of the energy of potential use for excited state formation from the malonyl peroxide is used up instead as strain in the three membered ring lactone. Our investigation of malonyl peroxide 3 was undertaken with the hope that its reaction to form butenolide 5, which is exothermic by ca. 60 kcal/mol¹¹, would forestall the "energy-wasting" formation of α -lactone 6. Indeed, this does occur. The yield of 5 is ca. 50% in acetonitrile in both the un-catalyzed and the perylene catalyzed reaction. However, the yield of light in these reactions is still

dissappointingly low. We did not measure the chemiluminescence quantum yield, but, by comparison with other reactions, we can conclude with certainty that it is considerably less than 1%. Since the energy requirement for efficient chemiluminescence is satisfied, the low yield from **3** must represent a mechanistic limitation.

Scheme I is the mechanism we propose for the ACT-catalyzed reaction of malonyl peroxide **3**. It is consistent with all of the results reported above, with the behavior of other malonyl peroxides, and with other chemiluminescent reactions known to proceed by the CIEEL path.

The first step in the proposed mechanism is the thermally activated transfer of an electron from ACT to the peroxide eq. 7. This probably occurs during the cleavage of the oxygen-oxygen bond and is followed rapidly by (in concert with ?) loss of CO_2 to give radical anion **7**. There are two

Scheme I



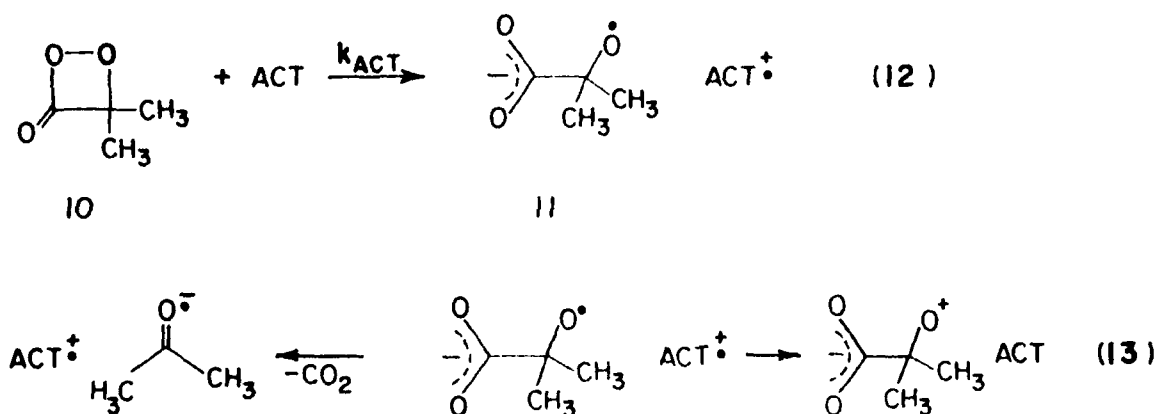
configurations for 7. The one shown in Scheme 1 has a cis-allyl structure and can close to give the butenolide. The alternative structure has a trans-allyl geometry and cannot close to 5. These isomers probably do not interconvert during the lifetime of 7 (or 8, or 9) and the ratio of 5 to 6 ultimately observed is set by the conformation of the intermediate during decarboxylation.

Radical anion 7 is in its electronic ground state. As outlined in eq. 9, it can partition between two paths. One of these, closure to the radical anion of butenolide 5 leads eventually to light, eq. 10. The other, back electron transfer to ACT^{\ddagger} , leads to zwitterion 8 and is a step off the light path. Consideration of the values of E_a^{CAT} and E_a^{CHL} leads to the conclusion that the back electron transfer has a barrier which is ca. 4 kcal/mol less than the closure to the butenolide radical anion. This competition limits the yield of light, and points to an important criterion that must be satisfied in order to generate light efficiently by the CIEEL route. We will return to this point below, but first it is interesting to consider biradical 9 in a little more detail. The uncatalyzed thermolysis of peroxide 3 can reasonably be thought of as generating biradical 9. It is likely that 9 is an electronically excited state. The ground state of this structure is reasonably represented as the zwitterion 8. It is not possible to estimate easily the energy difference between 8 and 9, but we feel confident that 8 is lower. With this conclusion in mind, the formation of 9 is a chemiexcitation. That is, a ground-state species reacts to form an electronically excited state product. However, this excited state is useless if light generation is the goal. It does not emit, and its lifetime is probably too short (9→8, fast) to permit energy transfer to

an emitter even in the unlikely event that its excitation energy ($\Delta E_{9 \rightarrow 8}$) is great enough to create a visible photon. Thus, malonyl peroxide **3** does form an excited state (**9**), but the characteristics of the state prohibit luminescence.

Finally, it is instructive to compare the reaction of dimethyldioxetanone (**10**), a peroxide known to generate light efficiently by the CIEEL route,¹² with malonyl peroxide **3**. A partial mechanism for the chemiluminescence of **10** is shown in Scheme II. The first step in the sequence, eq. 12, is exactly

Scheme II



analogous to eq. 7 in the reaction of **3**. However, back electron transfer from radical anion **11**, eq. 13 is probably endothermic (oxidation of an alkoxy radical) and cannot compete with the decarboxylation of **11**. Comparison of this step with the competition outlined in eq. 9 pinpoints the mechanistic limitation to light generation from **3**, and, by extrapolation, from all malonyl peroxides. The required rapid decarboxylation, eq. 8, generates a carbon centered radical that can be oxidized by ACT^\dagger and thus removed from the light

path. This feature is endemic to malonyl peroxides. So, with this knowledge, we can conclude with some certainty that, despite a great deal of promise,⁴ malonyl peroxides are not useful as chemiluminescent reagents.

Experimental

General. Proton magnetic resonance spectra were recorded on a Varian Associates EM-390 or XL-200 using tetramethylsilane as the internal standard. IR spectra were recorded on a Nicolet 7199 FT-IR or a Perkin-Elmer 1320 instrument. Gas chromatographic analyses were done on a Hewlett Packard 5790A or a Varian 3700 gas chromatograph both equipped with a flame ionization detector. UV-Vis absorption spectra were recorded on a Perkin-Elmer 552 spectrometer. Fluorescence spectra were recorded on a Farrand Mark I Spectrofluorometer or by photon counting to permit direct comparison with chemiluminescence emission spectra. Elemental analyses, active oxygen, and molecular weight determinations were performed by the Analysis Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois.

Chemiluminescence Measurements. Chemiluminescence measurements were performed as described previously.¹³ Sample temperature was regulated to within 0.1°C by means of an electrically heated cell holder. In a typical experiment, a solution of peroxide and ACT was placed in a Pyrex cuvette equipped with a Teflon stopcock. The cuvette was placed in an electrically heated cell holder. After thermal equilibration (4-6 minutes) the chemiluminescence decay was monitored at the fluorescence maximum of the activator. The rate constant was determined by least squares analysis. The kinetics were found to be strictly first-order and independent of peroxide concentration in all cases.

Ethyl 2-Methyl-2-pentenoate. A solution of the anion of ethyl α -diethylphosphonopropionate was prepared by adding the phosphorus compound ¹⁴ (46g, 0.19mol) slowly to a slurry of excess NaH (13g of 50% oil dispersion, 0.27mol) in dimethoxyethane (400mL) while maintaining the temperature below 20°C with an ice bath. After stirring for 1 h at room temperature, propionaldehyde (14.5g, 0.25mol) was slowly dripped into the reaction mixture while maintaining the temperature below 35°C with the ice bath. The mixture was stirred at room temperature for 20 min, then diluted with 200mL H₂O. The aqueous mixture was extracted 4 times with 75mL of ether, the organic layers combined, dried over MgSO₄, and the solvent removed in vacuo. Distillation of the residue yielded 12.84g of the ester (0.09mol, 47.5%): bp 60-65°C (18mm) (lit.¹⁵ = 60-63°C (18mm)); NMR (CDCl₃), δ 6.75 (t, 1H), 4.20 (q, 3H), 2.20 (m, 2H), 1.88 (s, 3H), 1.34 (t, 3H), 1.13 (t, 3H).

2-Methyl-2-pentenoic Acid. The ethyl pentenoate (6.84g, 0.048mol) was added to a solution of KOH (5.6g, 0.10mol) in 150mL MeOH and 150mL H₂O. The mixture was heated at reflux for 0.5 h, cooled, poured over 100g ice, and washed twice with 100mL portions of ether. The ether washes were extracted with 50mL 10% aqueous NaOH and the basic, aqueous wash added to the aqueous reaction solution. The reaction solution mixture was then acidified to pH 3 with 6M aqueous HCl, then extracted four times with 50mL portions of ether. The organic layers were combined, dried over MgSO₄, the solvent removed in vacuo, and the residue distilled to yield 4.2g of the acid (0.037mol, 77%): bp 70-73°C (1mm) (lit.¹⁶ bp 106.5°C (10mm)); NMR (CDCl₃), δ 6.86 (t, 1H), 2.21 (m, 2H), 1.84 (s, 3H), 1.06 (t, 3H).

4-Methyl-4-(1-Propenyl)Malonic Acid. A solution of LDA was prepared by adding 235mL of 1.5M n-BuLi in hexane (2 eq) to a dry THF solution (500mL, Na, benzophenone) of diisopropyl amine (17.68g, 0.350mol, 2 eq) at 0°C. 2-Methyl-2-pentenoic acid (20.0g, .175mol) was dissolved in 50mL dry THF and the solution added slowly to the LDA solution at 0°C. The solution was stirred for 1.5 h at 0°C and then cooled to -78°C with an IPA/CO₂ bath. Dry CO₂ was bubbled through the solution for 45 min at -78°C and 30 min at 0°C. The reaction solution was diluted with 200mL H₂O, acidified to pH 3 with 6M HCl, and extracted three times with 150mL ether. The organic layers were combined and extracted three times with 100mL of 10% aqueous NaOH. The combined basic layers were acidified to pH 3 with 6M HCl and extracted with 3 100mL portions of ether. These final ether layers were combined, dried over MgSO₄, the solvent removed in vacuo, and the residue recrystallized from 1:4 ethyl ether/pentane to yield 11.85g of the malonic acid (0.075mol, 43%): mp 137-139°C; NMR (CD₃CN), δ5.71 (m, 2H), 1.70 (d, 3H), 1.52 (s, 3H).

Anal. Calcd for C₇H₁₀O₄: C, 53.16; H, 6.33. Found: C, 53.61; H, 6.78.

4-Methyl-4-(1-propenyl)malonyl Peroxide. (3) The malonic acid (1.0g, 0.0063mol) was added to a solution of 3 mL CH₃SO₃H in 15 mL of ether at 0°C under N₂. Hydrogen peroxide (90%, 3mL, 0.011mol) was added dropwise to the cold solution at a rate that kept the temperature below 10°C. The reaction solution was stirred at room temperature for 4 h, poured over 50g of crushed ice, diluted with 50mL of aqueous saturated (NH₄)₂SO₄, and extracted four times with 25 mL portions of ether. The organic layers were combined, dried over MgSO₄, and the solvent removed in vacuo. The residue was chromatographed on silica gel with 10% ether/pentane at -20°C. This gave 75.8mg of malonyl peroxide 3 as a mixture of the cis and trans isomers (0.49mmol, 7.8%): NMR

(CDCl₃), δ 5.93 (d of q, 1H), 5.44 (d of d, 1H), 1.79 (d of d, 3H), 1.62 (s, 3H); IR (ethyl ether) $\nu_{C=O}$ 1804cm⁻¹. Decoupling experiments show that the vinylic resonances at δ 5.93 and δ 5.44 come from the different isomers of 3. Integration of these absorptions shows that the cis and trans isomers of 3 are present in approximately equivalent amounts.

Anal. Calcd for C₇H₈O₄: C, 53.85; H, 5.13; Active Oxygen, 10.26; Molecular Weight, 156. Found: C, 53.85; H, 5.23; Active Oxygen, 9.77; Molecular Weight (Osmometry), 162.

Oligomeric Ester 4. Malonyl peroxide 3 (0.090g, 0.58mmol) was added to 50mL dry CH₃CN and the solution was heated at 84°C for 4 h. The solution was cooled and the solvent removed in vacuo to yield butenolide 3 (45% by GC) and 60mg (55% by weight) of 4: NMR (CDCl₃), δ 5.86 (br, 2H), 1.79 (br, 3H), 1.55 (br, 3H); IR (CHCl₃) $\nu_{C=O}$ 1710cm⁻¹.

Anal. Calcd for (C₆H₈O₂)_n: C, 64.28; H, 7.14. Found: C, 64.81; H, 7.70; Molecular Weight (Osmometry) 550 (n \approx 5).

2,4-Dimethylbut-2-ene 4-olide 5. This compound was prepared according to the method of Gorewit and Rosenblum:^{8,17} bp 30°C (0.07mm) (lit.⁸ 30°C (0.05mm)); NMR (CDCl₃) δ 7.05 (m, 1H), 4.90 (m, 1H), 1.93 (t, 3H), 1.40 (d, 3H).

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Table 1 - Kinetics of **3** Thermal Reaction^a

Perylene (M)	k_{obs} (s^{-1})(Method)
4.7×10^{-4}	1.6×10^{-3} (CHL) ^b
6.3×10^{-4}	1.4×10^{-3} (CHL)
6.3×10^{-4}	1.2×10^{-3} (IR) ^c
9.4×10^{-4}	2.3×10^{-3} (CHL)
1.3×10^{-3}	2.3×10^{-3} (CHL)
1.9×10^{-3}	4.4×10^{-3} (CHL)
3.8×10^{-3}	5.4×10^{-3} (CHL)
5.0×10^{-3}	9.7×10^{-3} (CHL)
$k_1 = 8.0 \times 10^{-4} s^{-1}$ (IR); $6.0 \times 10^{-4} s^{-1}$ (CHL)	
$k_{ACT} = 1.9 M^{-1} s^{-1}$ (IR); $1.6 M^{-1} s^{-1}$ (CHL)	

^aIn acetonitrile; 84°C; $[3] = 8 \times 10^{-1} M$.

^bCHL indicates rate monitored by the decay of the chemiluminescence.

^cIR indicates rate measured by monitoring the decay of the infrared absorption of **3**.

Table 2. - Relative Chemiluminescence Yields.^a

[3]M	ACT ^b	I_{corr} ^c
0.0100	Perylene	3.1×10^6
0.0080	"	2.6×10^6
0.0053	"	1.9×10^6
0.0040	"	1.3×10^6
0.0027	"	1.1×10^6
0.0020	"	7.8×10^5
0.0017	"	4.8×10^5
0.0010	"	2.8×10^5
0.0080	DPEA	1.5×10^6
0.0080	DPA	1.2×10^6

^aIn acetonitrile; 34°C

^b[ACT] = 1.0×10^3 M

^cTotal chemiluminescence intensity corrected for the fluorescence efficiency of ACT in arbitrary units.

Table 3. - Temperature Dependence of the Thermal, Catalyzed, and
Chemiluminescent Reactions of **3**^a

T (°C)	k_1^b (s ⁻¹)	k_{CAT}^c (M ⁻¹ s ⁻¹)	I_{CHL}^d
44	2.1×10^{-4}	0.12	465
54	2.2×10^{-4}	0.34	300
62	2.5×10^{-4}	0.56	950
74	3.6×10^{-4}	1.2	2200
84	5.7×10^{-4}	1.6	4225
94	1.8×10^{-3}	2.1	8400

^aIn acetonitrile containing **3** = 8×10^{-3} M,

^bFrom the intercept of a plot of k_{obsd} vs. perylene concentration; eq. 4.

^cFrom the slope of a plot of k_{obsd} vs. perylene concentration; eq. 4.

^dInitial chemiluminescence intensity (before significant **3** is consumed in arbitrary units.

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