(A_2B_2, J = 8 Hz, $\Delta\nu$ = 22 Hz, 4 H).

(-)-(***S***)-**12e**: R_f (50/50 Et_2O/hexane) 0.65; mp k 43 s 63 c 67 i; $[\alpha]^{22}_D$ -0.6° (c 0.6, $CHCl_3$); IR ($CHCl_3$) 1652, 1603 cm^{-1}; NMR ($CDCl_3$) δ 0.8-2.5 (m, 20 H with t at 1.20, J = 7 Hz, 3 H), 2.68 (t, J = 7 Hz, 2 H), 3.30 (d, J = 5 Hz, 2 H), 3.50 (q, J = 7 Hz, 2 H), 3.70 (m, 1 H), 6.70 (s, 1 H), 7.45 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 17 Hz, 4 H), 7.88 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 21 Hz, 4 H).

(-)-(***S***)-**12f**: R_f (50/50 Et_2O/hexane) 0.66; mp k 65 c 124 i; $[\alpha]^{22}_D$ -3.9° (c 0.2, $CHCl_3$); IR ($CHCl_3$) 1655, 1608 cm^{-1}; NMR ($CDCl_3$) δ 0.7-2.60 (m, 19 H), 3.60 (m, 1 H), 3.87 (s, 3 H), 6.70 (s, 1 H), 7.33 (A_2B_2, J = 10 Hz, $\Delta\nu$ = 37 Hz, 4 H), 7.90 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 23 Hz, 4 H).

(+)-(***R***)-**12g**: R_f (50/50 Et_2O/hexane) 0.55; mp k 102 s_A 123 i; $[\alpha]^{19}_D$ +2.5° (c 0.2, $CHCl_3$); IR ($CHCl_3$) 1652, 1605 cm^{-1}; NMR ($CDCl_3$) δ 0.87-2.5 (m, 26 H with t and 1.18, J = 7 Hz, 3 H), 3.27 (d, J = 5 Hz, 2 H), 3.48 (q, J = 7 Hz, 2 H), 3.65 (m, 1 H), 4.00 (t, J = 6 Hz, 2 H), 6.70 (s, 1 H), 7.30 (A_2B_2, J = 9 Hz, $\Delta\nu$ = 36 Hz, 4 H), 7.87 (A_2B_2, $\Delta\nu$ = 22 Hz, 4 H).

(-)-(***S***)-**12h**: R_f (50/50 Et_2O/hexane) 0.56; mp k 102 s 113 c 135 i; $[\alpha]^{21}_D$ -4.4° (c 0.6, $CHCl_3$); IR ($CHCl_3$) 2230, 1676, 1658, 1609 cm^{-1}; NMR ($CDCl_3$) δ 0.8-2.5 (m, 19 H), 3.60 (m, 1 H), 6.70 (s, 1 H), 7.77 (s, 4 H), 7.88 (A_2B_2, J = 8 Hz, $\Delta\nu$ = 24 Hz, 4 H).

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Registry No. **2a**, 94110-63-1; **2b**, 94110-64-2; **2c**, 94110-65-3; **2d**, 94110-66-4; **2e**, 94110-67-5; **2f**, 94110-68-6; **2g**, 94136-09-1; **2h**, 94110-69-7; **2i**, 94110-70-0; **6a**, 51638-45-0; **6b**, 94110-77-7; **7a**, 94110-78-8; **7f**, 82492-51-1; **7i**, 94110-79-9; **8b**, 97974-03-3; (*R*)-**9a**, 97974-04-4; (*R*)-**9b**, 94110-80-2; (*R*)-**9c**, 94110-81-3; (*R*,*R*)-**10a**, 97974-05-5; (*R*,*R*)-**10b**, 97974-07-7; (*R*,*R*)-**10c**, 97974-08-8; (*R*,*R*)-**10d**, 97974-09-9; (*R*,*R*)-**10e**, 97974-10-2; (*R*,*R*)-**10f**, 97974-11-3; (*R*,*R*)-**10g**, 97974-12-4; (*R*,*R*)-**10h**, 97974-13-5; (*S*,*R*)-**11a**, 97974-06-6; (*S*,*R*)-**11b**, 98048-31-8; (*S*,*R*)-**11c**, 98048-32-9; (*S*,*R*)-**11d**, 98048-33-0; (*S*,*R*)-**11e**, 98048-34-1; (*S*,*R*)-**11f**, 98048-35-2; (*S*,*R*)-**11g**, 98048-36-3; (*S*,*R*)-**11h**, 98048-37-4; (-)-(*S*)-**12b**, 94110-71-1; (+)-(*R*)-**12c**, 94110-72-2; (+)-(*R*)-**12d**, 94110-73-3; (-)-(*S*)-**12e**, 94110-74-4; (-)-(*S*)-**12f**, 94110-75-5; (+)-(*R*)-**12g**, 97974-18-0; (-)-(*S*)-**12h**, 94110-76-6; **13c**, 97974-14-6; **13d**, 97974-17-9; **13e**, 97996-90-2; **13h**, 97996-89-9; **14**, 98048-38-5; **15**, 97974-16-8; **16**, 97974-15-7; **17f**, 94110-68-6; **17h**, 97974-01-1; **17i**, 97974-02-2.

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

Judith E. Porter and Gary B. Schuster*

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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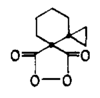
The preparation and thermal chemistry of 4-methyl-4-(1-propenyl)malonyl peroxide (**3**) is described. Thermolysis in acetonitrile at 84 °C gives 2,4-dimethylbut-2-en-4-olide in 45% yield and an oligomeric ester derived from an intermediate α-lactone in 55% yield. The reaction of **3** can be catalyzed 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 organisms[1] 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 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 peroxide is weakly chemiluminescent. The investigation of **3** reveals clear mechanistic limits to light generation by the CIEEL route.



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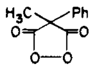

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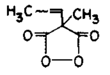

3

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(1) "Bioluminescence and Chemiluminescence"; DeLuca, M. A., McElroy, W. D., Eds.; Academic Press: New York, 1981. "Chemical and Biological Generation of Excited States"; Adam, W., Cilento, G., Eds.; Academic Press: New York, 1982.

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

(3) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 6107.

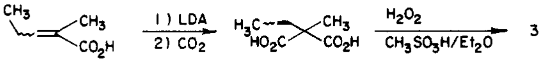
(4) Darmon, M. J.; Schuster, G. B. *J. Org. Chem.* **1982**, *47*, 4658.

(5) Porter, J. E.; Schuster, G. B. *J. Org. Chem.* **1983**, *48*, 4944.

0022-3263/85/1950-4068$01.50/0

Results

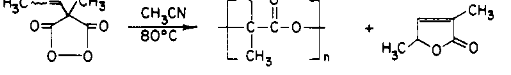
Synthesis of Peroxide 3. No malonyl peroxides have been reported that include olefinic functional groups as part of their structure.[6] The predictable sensitivity of the double bond to the usual acid-catalyzed oxidative cyclization conditions probably served to inhibit attempts to prepare these compounds. Indeed, we are 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 acid[7] is outlined in eq 1. Details of these reactions are given in the Experimental Section.



(1)

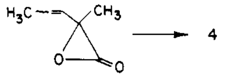
Peroxide **3** is isolated by column chromatography on silica gel at −20 °C as a mixture of cis and trans isomers. The ^{1}H NMR spectrum shows that the two isomers of **3** are present in a ca. 1:1 ratio. All attempts to separate these isomers were unsuccessful. The mixture was used in the subsequent 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 × 10^{-3} M) at 84 °C for 1 h gives a white solid identified as oligomeric ester **4** ($n \simeq 5$) in 55% yield and 2,4-dimethylbut-2-en-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 a 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.



3 4 5

(2)



6

(3)

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 × 10^{-3} M) gives products **4** and **5** in unchanged yields and easily detected, low intensity 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 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 I. 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

$$k_{\mathrm{obsd}} = k_1 + k_{\mathrm{CAT}}[\mathrm{ACT}] \qquad (4)$$

also are summarized in Table I. 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 II. There is much less light formed from 9,10-dibromoanthracene (DBA) than from 9,10-diphenylanthracene (DPA). 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 fro 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 $E_{\mathrm{a}}^{\mathrm{CAT}}$. The temperature dependence of the chemiluminescence intensity ($E_{\mathrm{a}}^{\mathrm{CHL}}$) contains contributions not only from the rate-limiting step ($E_{\mathrm{a}}^{\mathrm{CAT}}$) but also from a term(s) that reflects the partitioning of an intermediate between a path ultimately leading to light ($E_{\mathrm{a}}^{\mathrm{light}}$) and one not giving a photon as a

Table I. Kinetics of Thermal Reaction[a] of 3

perylene (M)	k_{obsd}(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 × 10^{-4} s^{-1} (IR;	6.0 × 10^{-4} s^{-1} (CHL)
k_{CAT} = 1.9 M^{-1} s^{-1} (IR);	1.6 M^{-1} s^{-1} (CHL)

[a] In acetonitrile; 84 °C; [**3**] = 8 × 10^{-1} M. [b] CHL indicates rate monitored by the decay of the chemiluminescence. [c] IR indicates rate measured by monitoring the decay of the infrared absorption of **3**.

Table II. Relative Chemiluminescence Yields[a]

[**3**], M	ACT[b]	$I^{\mathrm{corr}\ c}$
0.0100	perylene	3.1 × 10^6
0.0080	perylene	2.6 × 10^6
0.0053	perylene	1.9 × 10^6
0.0040	perylene	1.3 × 10^6
0.0027	perylene	1.1 × 10^6
0.0020	perylene	7.8 × 10^5
0.0013	perylene	4.8 × 10^5
0.0010	perylene	2.8 × 10^5
0.0080	DPEA (0.003 M)	3.3 × 10^6
0.0080	DPA (0.003 M)	0.9 × 10^6
0.0080	DBA (0.003 M)	<0.001 × 10^6

[a] In acetonitrile; 84 °C. [b] [ACT] = 1.0 × 10^{-3} M. [c] Total chemiluminescence intensity corrected for the fluorescence efficiency of ACT in arbitrary units.

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[6] (a) Adam, W.; Rucktaschel, R. *J. Am. Chem. Soc.* **1971**, *93*, 557. (b) Adam, W.; Rucktaschel, R. *J. Org. Chem.* **1978**, *43*, 3886. (c) Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriguez, O.; Rucktaschel, R. *J. Am. Chem. Soc.* **1972**, *94*, 1365. (d) Adam, W.; Liu, J.-C.; Rodriguez, O. *J. Org. Chem.* **1973**, *38*, 2269.

[7] Lucan, N. J.; Prater, A. N. *J. Am. Chem. Soc.* **1937**, *59*, 1682. Goldberg, A. A.; Linstead, R. P. *J. Chem. Soc.* **1928**, 2343.

[8] Gorewit, B.; Rosenblum, M. *J. Org. Chem.* **1973**, *38*, 2257.

[9] Vassil'ev, R. F. *Prog. React. Kinet.* **1967**, *4*, 305.

[10] Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.

Table III. 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

[a] In acetonitrile containing 3 = 8×10^{-3} M. [b] From the intercept of a plot of k_{obsd} vs. perylene concentration; eq 4. [c] From the slope of a plot of k_{obsd} vs. perylene concentration; eq 4. [d] Initial chemiluminescence intensity (before significant 3 is consumed in arbitrary units).

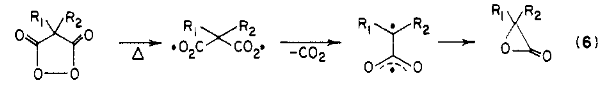
product (E_a^{dark}). This is expressed mathematically in eq 5. Thus, if E_a^{CHL} is greater than E_a^{CAT}, there is an intermediate in the reaction sequence leading to light, and this intermediate must proceed over a higher barrier to stay on the "light-path" than to get off of it.

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

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 III. The value of E_a^{CAT} with perylene as ACT in acetonitrile is 10 ± 1 kcal/mol and that of E_a^{CHL} is 14 ± 1 kcal/mol. Thus, this analysis 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.

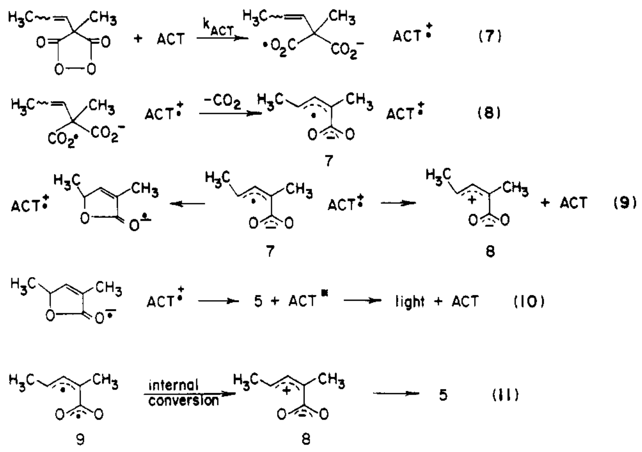
Discussion

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,

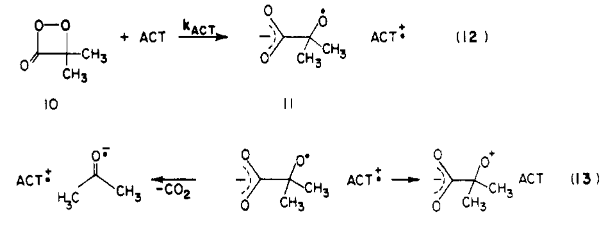


estimated by using Benson group equivalents,[11] is ca. 30 kcal/mol. This is not a sufficiently exothermic process to generate a photon of visible light in high yield. Catalyzing this reaction by electron transfer within the CIEEL mechanism simply lowers the activation energy and makes light generation 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/mol,[11] 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 uncatalyzed 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 of excited states from 3 must represent a mechanistic limitation.

Scheme I



Scheme II



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 configurations for 7. The one shown in Scheme I 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 4 ultimately observed is set by the configuration of the intermediate during decarboxylation.

Radical anion 7 can partition between two paths, eq 9. One of these, closure to the radical anion of butenolide 5, leads eventually to light, eq 10. The other, back electron transfer to $ACT^{+\bullet}$, 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.

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 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 genera-

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(11) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(12) Schmidt, S. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 7100.

tion 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 $ACT^{+\cdot}$ 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 light sources by the CIEEL mechanism.

Experimental Section

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-brand stopcock. The cuvette was placed in an electrically heated cell holder. After thermal equilibration (4–6 min) 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-(diethylphosphono)propionate was prepared by adding the phosphorus compound[14] (46 g, 0.19 mol) slowly to a slurry of excess NaH (13 g of 50% oil dispersion, 0.27 mol) in dimethoxyethane (400 mL) while maintaining the temperature below 20 °C with an ice bath. After 1 h of stirring at room temperature, propionaldehyde (14.5 g, 0.25 mol) 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 and then diluted with 200 mL of H_2O. The aqueous mixture was extracted 4 times with 75 mL of ether, the organic layers were combined and dried over $MgSO_4$, and the solvent was removed in vacuo. Distillation of the residue yielded 12.8 g of the ester (0.09 mol, 47.5%): bp 60–65 °C (18 mm) (lit.[15] bp 60–63 °C (18 mm)); NMR ($CDCl_3$) δ 6.75 (t, 1 H), 4.20 (q, 3 H), 2.20 (m, 2 H), 1.88 (s, 3 H), 1.34 (t, 3 H), 1.13 (t, 3 H).

2-Methyl-2-pentenoic Acid. The ethyl pentenoate (6.84 g, 0.048 mol was added to a solution of KOH (5.6 g, 0.10 mol) in 150 mL of MeOH and 150 mL of H_2O. The mixture was heated at reflux for 0.5 h, cooled, poured over 100 g of ice, and washed twice with 100-mL portions of ether. The ether washes were extracted with 50 mL of 10% aqueous NaOH, and the basic, aqueous wash was added to the aqueous reaction solution. The reaction solution mixture was then acidified to pH 3 with 6 M aqueous HCl and then extracted 4 times with 50-mL portions of ether. The organic layers were combined and dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was distilled to yield 4.2 g of the acid (0.037 mol, 77%): bp 70–73 °C (1 mm) lit.[16] bp 106.5 °C (10 mm)); NMR ($CDCl_3$) δ 6.86 (t, 1 H), 2.21 (m, 2 H), 1.84 (s, 3 H), 1.06 (t, 3 H).

2-Methyl-2-(1-propenyl)malonic Acid. A solution of LDA was prepared by adding 235 mL of 1.5 M *n*-BuLi in hexane (2 equiv) to a dry THF solution (500 mL, Na benzophenone) of diisopropyl amine (17.68 g, 0.350 mol, 2 equiv) at 0 °C. 2-Methyl-2-pentenoic acid (20.0 g, 0.175 mol) was dissolved in 50 mL of dry THF, and the solution was 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/CO_2 bath. Dry CO_2 was bubbled through the solution for 45 min at −78 °C and 30 min at 0 °C. The reaction solution was diluted with 200 mL of H_2O, acidified to pH 3 with 6 M HCl, and extracted 3 times with 150 mL of ether. The organic layers were combined and extracted 3 times with 100 mL of 10% aqueous NaOH. The combined basic layers were acidified to pH 3 with 6 M HCl and extracted with three 100-mL portions of ether. These final ether layers were combined and dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was recrystallized from 1:4 ethyl ether/pentane to yield 11.8 g of the malonic acid (0.075 mol, 43%): mp 137–139 °C; NMR (CD_3CN) δ 5.71 (m, 2 H), 1.70 (d, 3 H), 1.52 (s, 3 H).

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.33. Found: C, 53.61; H, 6.78.

4-Methyl-4-(1-propenyl)malonyl Peroxide (3). The malonic acid (1.0 g, 0.0063 mol) was added to a solution of 3 mL of CH_3SO_3H in 15 mL of ether at 0 °C under N_2. Hydrogen peroxide (90%, 3 mL, 0.011 mol) 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 50 g of crushed ice, diluted with 50 mL of aqueous saturated $(NH_4)_2SO_4$, and extracted 4 times with 25-mL portions of ether. The organic layers were combined and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was chromatographed on silica gel with 10% ether/pentane at −20 °C. This gave 75.8 mg of a clear liquid show to be a mixture of the cis and trans isomers of malonyl peroxide **3** (0.49 mmol, 7.8%): NMR ($CDCl_3$) δ 5.93 (d of q, 1 H), 5.44 (d of d, 1 H), 1.79 (d of d, 3 H), 1.62 (s, 3 H); IR (ethyl ether) $\nu_{C=O}$ 1804 cm^{-1}. Decoupling experiments show that the vinylic resonances at δ 5.93 and 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 $C_7H_8O_4$: 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** (0.090 g, 0.58 mmol) was added to 50 mL of dry CH_3CN, and the solution was heated at 84 °C for 4 h. The solution was cooled and the solvent was removed in vacuo to yield butenolide **5** (45% by GC) and 60 mg (55% by weight) of **4**: NMR ($CDCl_3$) δ 5.86 (br, 2 H), 1.79 (br, 3 H), 1.55 (br, 3 H); IR ($CHCl_3$) $\nu_{C=O}$ 1710 cm^{-1}.

Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.28; H, 7.14. Found: C, 64.81; H, 7.70; molecular weight (osmometry) 550 ($n \simeq 5$).

2,4-Dimethylbut-2-en-4-olide (5). This compound was prepared according to the method of Gorewit and Rosenblum:[8,17] bp 30 °C (0.07 mm) (lit.[8] bp 30 °C (0.05 mm)); NMR ($CDCl_3$) δ 7.05 (m, 1 H), 4.90 (m, 1 H), 1.93 (t, 3 H), 1.40 (d, 3 H).

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[13] Smith, J. P.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 1041.

[14] Dolby, L. J.; Riddle, G. N. *J. Org. Chem.* **1967**, *32* (1), 3481.

[15] Slougui, N.; Rousseau, G.; Conia, J.-M. *Synthesis* **1982**, 58.

[16] Lucan, N. J.; Prater, A. N. *J. Am. Chem. Soc.* **1937**, *59*, 1682. Goldberg, A. A.; Linstead, R. P. *J. Chem. Soc.* **1928**, 2343.

[17] Morel, T. H.; Verkade, P. E. *Recl. Trav. Chem. Pays-Bas* **1949**, *68*, 619.