Chemiluminescence of Organic Peroxides: Intramolecular Electron-Exchange Luminescence from a Secondary Perester

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The reaction of an aminocoumarincarboxylic acid chloride (Coumarin 343) with 1-phenethyl hydroperoxide results in light emission that is easily detected with the unaided eye. This reaction proceeds through a secondary perester intermediate. Intramolecular electron exchange, modeled after the analogous process in the bioluminescence of the firefly, is proposed as the mechanism for light generation. Attempts to carry out this reaction under conditions where the coumarin acid is recycled were not successful.

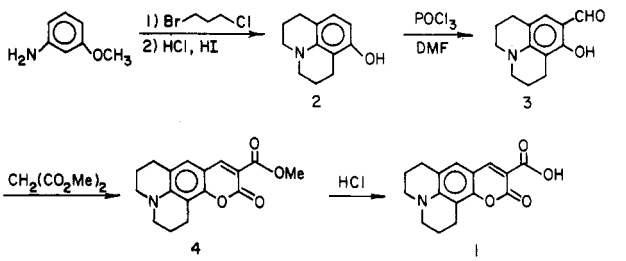
Efficient chemical generation of light is an important goal that has been only partly realized with the discovery[1] and development[2] of oxalate ester based chemiluminescent reactions. Numerous other light-producing reactions are known, but these generally suffer low efficiencies or the use of unstable, sometimes treacherous, reagents.

On the other hand, Nature has developed several bioluminescent reactions that are both efficient and apparently convenient to use. Among the most familiar of these is that of the North American firefly.[3] The mechanism of this reaction has been studied in great detail and is now known to involve the formation of a four-membered ring peroxide. A key to understanding the high efficiency (ca. 90%) of the firefly reaction was the realization that an intramolecular version of the mechanism we identified as chemically initiated electron-exchange luminescence (CIEEL)[4] could account for the high yield and the predominance of singlet excited states produced.[5]

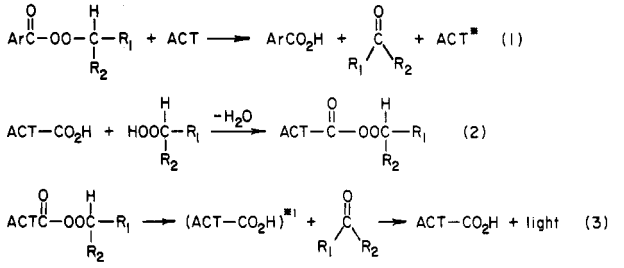
The success of the intramolecular CIEEL reaction depends on the simultaneous operation of several difficult-to-achieve conditions. First, a high-energy content functional group (a peroxide almost without exception) must be prepared. Second, this functional group must be linked to a fragment (ACT) that is capable of facile electron donation to the peroxide oxygen–oxygen bond. Third, the electron transfer must initiate a reaction that ultimately raises the potential of the transferred electron so that when back electron transfer (ion annihilation) occurs, sufficient energy is released to form an excited singlet state of the product. Fourth, the excited state formed must fluoresce with high efficiency. Finally, if the process is to have more than academic value, then it should operate in a cyclic manner in which some readily available reagent is consumed as light is produced.

Despite the impressive array of conditions mounted in opposition, our discovery that secondary peresters can generate light by the CIEEL process,[6,7] eq 1, provided some hope that we could uncover a reaction that would satisfy all of these requirements. This hope is based on the assumption that it is possible to prepare a perester from an easily oxidized, fluorescent carboxylic acid and a secondary

Scheme I



hydroperoxide. Operation of the intramolecular CIEEL reaction would then convert the hydroperoxide (a consumable reagent) to a ketone and, after emission of light from the excited state, regenerate the carboxylic acid. These reactions are shown schematically in eq 2 and 3.



Results and Discussion

A key to the successful development of an efficient intramolecular CIEEL reaction as described above is the proper choice of the "activated" carboxylic acid. We chose to examine 2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]-benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid (1) an aminocoumarin laser dye available from Eastman Kodak under the tradename Coumarin 343. This compound fluoresces with high efficiency under a wide range of conditions, and a recent report by Jones and co-workers[8] indicates that coumarins of this general structure are easily and reversibly oxidized to their radical cations. We expected that 1 could be converted to a perester under a variety of conditions that would preserve the amino-coumarin functional group.

Despite the commercial availability of 1, its synthesis has not been reported in the open literature. Its high cost as a laser dye makes its purchase prohibitive. Thus we developed the synthesis outlined in Scheme I. Each of the steps described has precedent in the literature. The overall yield of 1 from *m*-methoxyaniline is 22%. The details for preparation of 1 are presented in the Experimental Section.

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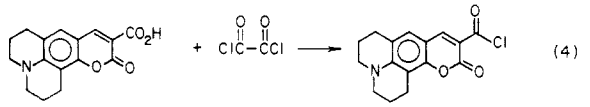
Table I. Reaction of Acid Chloride 5 with Hydroperoxides

hydroperoxide[a]	light yield[b]
$PhCH(CH_3)OOH$	100
$CH_3(CH_2)_3OOH$[19]	2.0
$CH_3CH(OOH)CH_2CH_3$[19]	1.7
$(CH_3)_3COOH$[20]	<0.1

[a] Reactions were carried out in chloroform solution at room temperature. [b] Relative to 1-phenethyl hydroperoxide (6) which is set at 100.

Conversion of 1 to a perester requires its prior activation so that the dehydration can be carried out under mild conditions. The first method we chose to activate 1 was conversion to the acid chloride 5 by reaction with oxalyl chloride, eq 4. Acid chloride 5 is a stable, moisture-sensitive, orange solid.



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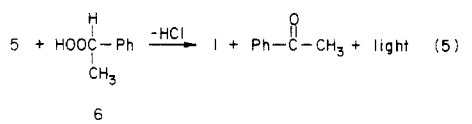
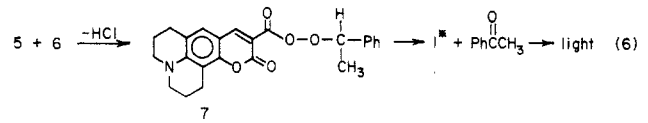


(5)

Treatment of a chloroform solution of 5 (ca. 5×10^{-3} M) at room temperature with 1-phenethyl hydroperoxide[9] (6) gives acetophenone (65–80%, depending on conditions), regenerates acid 1, and produces chemiluminescence that is visible to the unaided eye even in a dimly lit room, eq 5. The chemiluminescence emission spectrum from this reaction is identical with the fluorescence of 1 under these conditions. This observation identifies the emitting excited state as 1*. We presume that this is the initially formed excited state as well (i.e., no energy transfer from a preceding excited state to 1).

The time-dependent behavior of the chemiluminescent reaction of 5 with hydroperoxide 6 is quite simple. After a period of rapid intensity growth due to thermal equilibration and mixing, the light intensity decreases following a first-order rate law. The half-life of this decline is essentially independent of the concentration of 5 and of 6. We interpret this behavior to be indicative of the rapid combination of the acid chloride with the hydroperoxide to form secondary perester 7, followed by the slower unimolecular conversion of 7 to 1, acetophenone, and light, eq 6. Some confirmation of this assertion comes from the



(6)

observation that reaction of 5 with *tert*-butyl hydroperoxide (which cannot be converted to a ketone) does not generate a significant yield of chemiluminescent light.

The quantum efficiency for light generation from the reaction of acid chloride 5 with phenethyl hydroperoxide was determined by comparison with the chemiluminescence of luminol. The yield of light from the acid chloride reaction is disappointingly low. Measurement of the total integrated (over wavelength and time) chemiluminescence yield shows that it has about 5% of the efficiency of luminol.[10] Evidently, some intermediate is being diverted from the light-producing route to one that also gives acetophenone but reforms the acid in its ground electronic state. At the present time we do not know which step in the sequence is responsible for the low yield of excited states.

Table II. Effect of TsOH and Pyridine Concentrations on the Light Yield in the Reaction of Hydroperoxide 6 with Acid 1 and DCC[a,b]

[DCC]	[PhCH-(CH_3)-OOH]	[TsOH]	[pyridine]	light yield[c]
0.1	0.1			44 093
0.1	0.1	1×10^{-3}		55 517
0.1	0.1	1×10^{-3}	1×10^{-3}	57 325
0.1	0.1		1×10^{-3}	78 276

[a] Acid 1, 5×10^{-4} M, chloroform solution, 57 °C. [b] Reaction of acid chloride, 5, 5×10^{-4} M, with hydroperoxide 6 (0.01 M) in chloroform solution at 60 °C gives 36 362 counts. [c] Light yield in arbitrary units.

We briefly investigated the effect of the structure of the hydroperoxide on the yield of light from the reaction of 5. The results are summarized in Table I. Fundamentally, the highest light yield is obtained with those secondary hydroperoxides that have the weakest α-carbon–hydrogen bond.

It is still conceivable, despite the low chemiluminescent yield, that acid 1 could be an important chemiluminescent regent if it were activated perpetually. Thus, even though each turn through the cycle giving secondary perester would give only a few photons, many turns could still give a high light yield (based on the amount of 1 present at the start). We investigated several routes for continual reactivation of acid 1 under chemiluminescent conditions.

A common and often successful strategy for the formation of esters from acids and alcohols utilizes dicyclohexylcarbodiimide (DCC) as a dehydrating agent.[11] This reagent also finds widespread use in the synthesis of peresters and diacylperoxides.[12] It was hoped that DCC would activate acid 1 in the presence of a secondary hydroperoxide and thereby perpetuate the chemiluminescent reaction passing through perester 7.

Chemiluminescence is observed when a solution of acid 1, hydroperoxide 6, and DCC is prepared in chloroform at 90 °C. The emission spectrum is exactly the same as that obtained from reaction of the acid chloride, but the kinetic behavior of the reaction is different. The light intensity rises rapidly as in the reaction between 5 and 6, but the rate of decay is dependent on the concentrations of both DCC and the hydroperoxide. At low hydroperoxide concentrations (0.01–0.05 M), the rate of light intensity decay increases with increasing DCC concentration, whereas at high hydroperoxide concentrations (0.1, 0.2 M), the rate of decay is essentially independent of initial DCC concentrations. In addition, the light yields from these solutions increase with increasing hydroperoxide concentration, but are largely independent of initial DCC concentrations. In all cases, acid 1 is consumed as is evidenced by a blue shift in the optical absorption spectrum from 445 nm (characteristic of acid 1) to 375 nm as the reaction proceeds.

If acid 1 were being recycled through the chemiluminescent reaction initiated by DCC, then the total light yield could be much higher than it is in the direct reaction of acid chloride 5 with the hydroperoxide. Direct comparison

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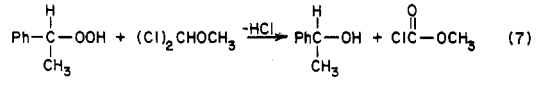
of these two procedures under a wide range of temperature, solvent, and concentration conditions (Table II) reveals that the light yield from the DCC-mediated reaction of 1 is never more than ca. twice that of the direct reaction of 5. Thus if the hoped for recycling is operating, its efficiency is so low that it barely overcomes the irreversible destruction of 1 that occurs under these conditions. We did not identify the ultimate fate of 1 in this reaction.

Another reagent useful for the in situ activation is 1,1-dichloromethyl methyl ether (DCE),[13] which converts acids to acid chlorides. We studied the reactions of DCE with acid 1 and hydroperoxide 6 under a range of conditions.

When DCE is added to a chloroform solution of 1, only slow conversion to 5 is observed by IR spectroscopy. However, the rate of this reaction is greatly accelerated by inclusion of the nonnucleophilic base 2,6-lutidine. When hydroperoxide 6 is added to the solution of 5 formed from reaction of 1 with excess DCE and lutidine, a burst of chemiluminescence is observed that rapidly decays to a much lower but longer lived level. The total light intensity obtained by this procedure is approximately the same as that from the reaction of an equivalent amount of independently prepared 5. Thus it appears that neither DCE nor lutidine interferes in the formation of 7 or its chemiluminescent reaction.

Attempts to cycle 1 through the chemiluminescent reaction path with DCE were not successful. The total light yield from this reaction is no greater than that from reactions under comparable conditions with preformed acid chloride 5. The reason for this is apparent from the examination of the reaction products. The two major coumarin-containing products obtained are the phenethyl ester, 8, and the methyl coumarin acid carbonic anhydride. These products reasonably result from reaction of the acid 1 or acid chloride 5 with the products of the reaction of DCE and hydroperoxide 6, eq 7. Clearly, once the ester or anhydride is formed, acid 1 is removed from the reaction cycle and perpetuation of the chemiluminescent reaction is stopped. It was shown independently that phenethyl alcohol is formed from the reaction of hydroperoxide 6 with DCE, eq 7. The bimolecular rate constant for reaction of 6 with DCE is nearly the same as that for formation of 5, but the much higher concentration of the hydroperoxide under the chemiluminescent conditions insures that little recycling will occur.



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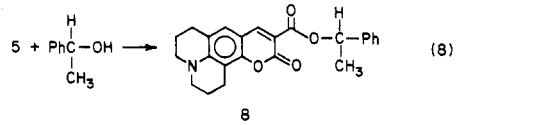

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Conclusions

One objective of this investigation was the attempt to mimic the intramolecular CIEEL reaction believed to be responsible for light production in bioluminescence. This has been accomplished. The chemiluminescence observed in the reaction of 5 with 6 can be neatly explained within this context. The aminocoumarin functions as the electron donor and the perester as the electron acceptor. Unfortunately, the yield of excited states formed in this reaction is not nearly as high as in the biological model. The reason for this is not at all clear and will be revealed only through additional experimentation.

A second objective of this investigation was to cycle the carboxylic acid repeatedly through the chemiluminescent process. This was not accomplished. Competing reactions of the acid with DCC and of the hydroperoxide with DCE short-circuited the efficient reuse of the acid. This problem might be overcome if a carboxylic acid with higher reactivity toward DCE were used. Attempts to find an acid with this property that also gives a greater chemiluminescence yield are under way.

Experimental Section

General Methods. Fluorescence spectra were recorded on a Farrand Mark I spectrofluorometer. All chemiluminescence data were obtained with standard photon-counting techniques. Light emission was detected by an EMI 9813B or 9816B photomultiplier tube. Spectral resolution was accomplished by using a Jarrel-Ash 0.25 M monochromator. Chemiluminescence cell temperatures were regulated to within 0.1° by an electrically heated jacket. Chloroform (Burdick and Jackson Distilled in Glass) was distilled from P_2O_5 before use. Dicyclohexylcarbodiimide (Aldrich) was distilled under reduced pressure. All other materials were used as received.

8-Methoxyjulolidine.[14] 3-Methoxyaniline (0.10 mol, 11 mL, 12.3 g), 1-bromo-3-chloropropane (160 mL, 1.5 mol, 235 g), and anhydrous sodium carbonate (0.4 mol, 42.7 g) were combined in a 500-mL three-necked round-bottomed flask equipped with an overhead mechanical stirrer, thermometer, and a pressure-equalizing addition funnel packed with 10 g of 4-Å molecular sieves. The top of the addition funnel was fitted with a condensor. The mixture was warmed to 70 °C for 1 h and 100 °C for 2 h and then heated at reflux for 11 h. The progress of the reaction was monitored by ^1H NMR spectroscopy. When the conversion of the aromatic resonances (6.2, 7.0 ppm) to two doublets (6.15, 6.75 ppm) and the growth of the multiplets (1.95, 2.65, and 3.05 ppm) representing the alkyl side chains ceased, the reaction was stopped. The mixture was cooled to room temperature and 150 mL of concentrated HCl and 50 mL of water were slowly added. Upon dissolution of all solids, the phases were separated and the organic layer was washed with 10% HCl to remove remaining product. This washing was added to the aqueous phase, which was washed with ether to remove 1-bromo-3-chloropropane. The aqueous phase was made basic with 50% aqueous sodium hydroxide and extracted with ether until the organic phase was no longer colored. The ethereal solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting brown oil was distilled (0.5–1 mm, 110–114 °C), yielding 13 g (64%) of a viscous yellow oil which turned red on exposure to air: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.94 (m, 4 H), 2.68 (m, 4 H), 3.08 (m, 4 H), 3.75 (s, 3 H), 6.14 (d, 1 H, J = 8), 6.72 (d, 1 H, J = 8); IR (neat film) cm^{-1} 1615, 1502, 1318, 1140, 1070, 780. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.54; H, 8.17; N, 6.82.

8-Hydroxyjulolidine (2). 8-Methoxyjulolidine (10 g, 50 mmol) was dissolved in a solution consisting of 50 mL of 47% HI, 80 mL of concentrated HCl, and 200 mL of H_2O. This solution was heated at reflux and the progress of the reaction was followed by TLC on silica gel using 10% ethyl acetate in benzene as eluant. After 15 h another 50-mL portion of concentrated HCl was added to the reaction. The reflux was stopped when starting material was no longer present by TLC (about 60 h). The solution was cooled in an ice bath and neutralized to pH 6 first using 50% NaOH and then phosphate buffer (6.9 g of $NaH_2PO_4 \cdot H_2O$ and 1.4 g of Na_2HPO_4 in 100 mL of H_2O). The product was extracted with methylene chloride, the organic phase was washed with brine and dried over Na_2SO_4, and the solvent was removed at aspirator pressure. The ^1H NMR spectrum of the brown solid (7.98 g, 86%) showed a small singlet at 3.70 ppm, presumably due to remaining methoxy compound, so the crude product was taken up in

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methylene chloride and extracted into 10% NaOH until the aqueous phase remained colorless. The organic phase was then acidified, dried, and extracted, and the solvent was removed as above. This process yields 6.24 g (67%) of a tan solid: mp 126–130 °C;[15] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.95 (m, 4 H), 2.70 (m, 4 H), 3.01 (m, 4 H), 4.3 (br s, 1 H, dissappears D_2O), 6.05 (d, 1 H, J = 8), 6.65 (d, 1 H, J = 8).

9-Formyl-8-hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizine (3).[16] 8-Hydroxyjulolidine (5.0 g, 26.4 mmol) was dissolved in 5 mL of dry DMF and the resulting solution was added dropwise to a cold solution of $POCl_3$ (29.1 mmol, 4.46 g, 2.66 mL) in 10 mL of DMF which had been stirring for 15 min. After 30 min at room temperature, the solution was heated over a steam bath (N_2 atmosphere) for an additional 30 min and was then cooled to room temperature. A 25-mL portion of water was added with stirring and a blue-green solid formed slowly. The precipitate was filtered, washed with water, and dried in a vacuum dessicator overnight. The solid was dissolved in benzene/5% ethyl acetate and filtered through a ca. 3-cm bed of silica gel. The product was collected and solvent was removed, leaving 4.87 g (87%) of a yellowish oil which solidified on standing: mp 71.5–73 °C (lit.[16] mp 70–72 °C). Recrystallization from hexane gives glistening yellow prisms: mp 73–74 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.92 (m, 4 H), 2.66 (t, 4 H, J = 6), 3.27 (m, 4 H), 6.84 (s, 1 H), 9.37 (s, 1 H), 11.8 (s, 1 H).

2,3,6,7-Tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano-[6,7,8-*ij*]quinolizine-10-carboxylic Acid, Methyl Ester (Coumarin 343 Methyl Ester) (4). Attempts to prepare the desired carboxylic acid by reaction of 3 with malonic acid in the presence of pyridine as described in the literature[17] yielded only starting material. The following modified procedure was found to be successful.

Dimethyl malonate (2.74 g, 2.4 mL, 20.7 mmol), 3 (3.0 g, 13.8 mmol), and piperidine (3.53 g, 4.10 mL, 41.5 mmol, distilled from KOH prior to use) were dissolved in a solution of 50 mL of acetonitrile and 100 mL of benzene. A blue fluorescence was visible immediately. The solution was heated at reflux for 3 h and then slowly distilled. Methanol and water produced by the condensation reaction distilled first as an azeotrope; then benzene was added and the acetonitrile was removed by azeotropic distillation. The remaining solution was cooled to room temperature and yellow crystals formed (3.07 g, 75.0%). The crystals were isolated by filtration, washed with pentane, and dried: mp 230–232 °C (sealed tube); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.97 (m, 4 H), 2.75 (t, 2 H, J = 6), 2.86 (t, 2 H, J = 6), 3.32 (m, 4 H), 3.90 (s, 3 H), 6.92 (s, 1 H), 8.34 (s, 1 H). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72; N, 4.68. Found: C, 68.47; H, 5.73; N, 4.82.

2,3,6,7-Tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano-[6,7,8-*ij*]quinolizine-10-carboxylic Acid (Coumarin 343) (1). A portion (2.0 g, 6.7 mmol) of coumarin ester 4 was dissolved in 100 mL of concentrated HCl and kept at room temperature overnight. The reaction mixture was cooled in an ice bath and 40–50 mL of concentrated NH_4OH was added slowly with stirring. The orange solid that precipitated was removed by filtration and washed with water. The filtrate was treated with additional NH_4OH and the resulting precipitate was suspended with the first crop in 150 mL of water. NaOH (10%) was added dropwise to the suspension until no more solid went into solution (about 5 mL). The orange solution was filtered and slowly reacidified with 10% HCl. The precipitated carboxylic acid was filtered on a large Buchner funnel, washed with water, air-dried for 1 h, and finally dried under vacuum (crude yield 1.63 g, 85%). Recrystalization from acetonitrile/Me_2SO gave fine orange needles: mp 253 °C (sealed tube) dec; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.00 (m, 4 H), 2.79 (t, 2 H, J = 6), 2.88 (t, 2 H, J = 6), 3.40 (m, 4 H), 7.00 (s, 1 H), 8.48 (s, 1 H), 12.5 (s, 1 H, dissappears with D_2O); UV–vis (ethanol) λ_{max} nm (lit.[18] 446 nm); MS, m/e 285, 257 (CO), 256 (COH), 241 (CO_2), 240 (CO_2H), 213 (CO, CO_2), 212 (CO, CO_2H), 184 (CO_2H, C_2O_2). Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.03; H, 5.35; N, 4.88.

Coumarin 343 Acid Chloride 5. An oven-dried, 100-mL, pear-shaped flask with a side arm and a condensor set for reflux was charged with 100 mg of acid 1 (0.35 mmol) and 15 mL of warm, dry $CHCl_3$. The reaction mixture was kept under a nitrogen atmosphere. Oxalyl chloride (0.150 mL, 225 mg, 1.75 mmol) was added by syringe through the side arm followed by 15 μL of DMF. Gas evolution ensued for about 5 min during which time the solution darkened from orange to red. After 20 min, the solution was heated and 50 mL of dry cyclohexane was added slowly while maintaining reflux. The solution was cooled to room temperature and stored overnight. Cooling for several hours in an ice bath gave fine red needles. The solvent was decanted under an atmosphere of dry N_2, and the crystals were collected and dried under vacuum: 81.9 mg (77%), mp 209–211 °C (sealed tube) dec; IR ($CHCl_3$) cm^{-1} 1774.7, 1524, 1312, 1624, 1586, 1174. Anal. Calcd for $C_{16}H_{14}NO_3Cl$: C, 63.27; H, 4.65; N, 4.61; Cl, 11.67. Found: C 63.40; H, 4.62; N, 4.74; Cl, 11.70.

Chemiluminescence of Acid Chloride 5. A 60-μL portion of a stock solution of 5 (7×10^{-3} M) in $CHCl_3$ was injected into an oven-dried Pyrex cuvette equipped with a Teflon stopcock. To this solution was added 2.8 mL of $CHCl_3$ and 120 μL of a 0.1 M $CHCl_3$ stock solution of hydroperoxide 6. The final concentrations of 5 and 6 were 1.4×10^{-4} M and 4.0×10^{-3} M, respectively. The stopcock was closed, and the cuvette was shaken once and placed in a cell holder which was prewarmed to 66 °C. The chemiluminescent decay was recorded in 128 registers each with a 20-s dwell time. A first-order rate constant for decay of the chemiluminescent emission of 1.9×10^{-3} s^{-1} was obtained by a linear least-squares analysis of this data. The total chemiluminescent intensity (arbitrary units) was determined by integration of the area under the decay curve and subtraction of a small background level.

Chemiluminescence from 1 with DCC. To a Pyrex cuvette equipped with a Teflon stopcock was added 2.7 mL of a 6.6×10^{-3} M $CHCl_3$ stock solution of acid 1, 0.3 mL of a 1.00 M stock solution of DCC, and 21 μL (0.150 mmol) of 6. The final concentrations were 1, 5.9×10^{-4} M; 6, 5×10^{-2} M; DCC, 0.1 M. The cuvette was placed in a cell holder which had been prewarmed to 90 °C. Data were recorded in 128 registers with 20-s dwell times each. The total integrated intensity and observed first-order decay rate were calculated as described above.

Chemiluminescence from 1 with DCE. Method 1. A 250-μL portion of a 0.01 M stock solution of 1 in $CHCl_3$ was added to a Pyrex cuvette equipped with a Teflon stopcock. Next, 27 μL of DCE (34.2 mg, 0.3 mmol) and 150 μL of a 0.1 M stock solution of 2,6-lutidine in $CHCl_3$ and 300 μL of a 0.1 M stock solution of 6 in $CHCl_3$ were added. The chemiluminescent emission was recorded as described above.

Method 2. A 30-μL portion of a 0.01 M stock solution of 1 in $CHCl_3$, 68 μL (86.4 mg, 0.75 mmol) of DCE, and 3.2 μL (2.9 mg, 0.028 mmol) of lutidine was kept at 60 °C for 45 min. Then 1.4 mL of $CHCl_3$ and 2.1 μL (2.0 mg, 0.015 mmol) of 6 were added to the cuvette. The chemiluminescent emission was recorded as described above.

Quantum Yields. The luminol reaction was performed as described by Lee.[10] A 1.5×10^{-5} M solution of luminol was prepared in 0.1 M K_2CO_3 (pH 11.6). A 150-μL portion of the luminol solution was injected into a 1-mm pathlength cell (to minimize self-absorption) and purged with oxygen for 10 min. The cell was placed in the photon counter and the chemiluminescence was recorded under standard conditions described. The total integrated emission intensity was calculated as above and averaged over several runs. The chemiluminescence emission intensity from luminol was compared with that of a solution of acid chloride 5.

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