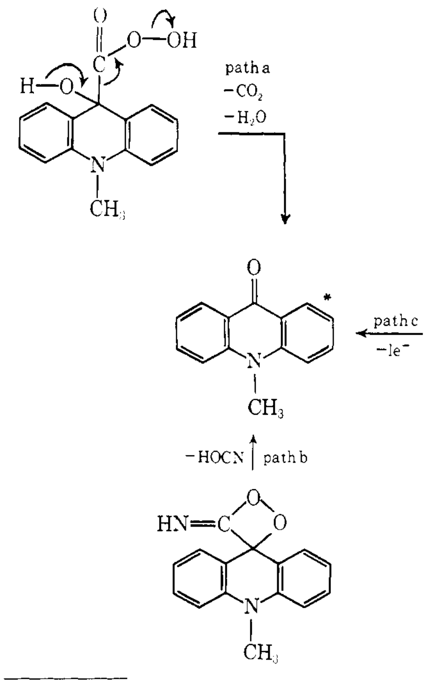
Chemiluminescence of Certain Aldehydes, Ketones, and Peroxides

Eliezer Rapaport, Malcolm W. Cass, and Emil H. White*

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received June 16, 1971*

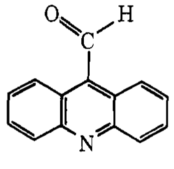
Abstract: Two aldehydes [9-formylacridine (**1**) and 9-formyl-10-methylacridinium methosulfate (**2**)] and two ketones [9-benzoylacridine (**7**) and 9-(4-nitrobenzoyl)acridine (**8**)] have been prepared and shown to chemiluminesce brightly in dimethyl sulfoxide solution with base and oxygen. Compounds **1** and **2** with potassium hydroxide and **7** and **8** with potassium *tert*-butoxide lead to light emission from electronically excited acridone. A mechanism based on the autoxidation of a reactive carbanion intermediate followed by electron transfer is suggested. Di-9-anthranoyl peroxide (**11**) has been synthesized. It reacts with the radical anion of naphthalene in dimethoxyethane to give light emission from excited anthranolate (**12**), presumably *via* a similar mechanism.

The acridine system is often selected for chemiluminescence studies because of the high fluorescence efficiency of most derivatives and their relatively easy synthesis. Several chemiluminescent reactions of these compounds are known in which *N*-methylacridone is formed and is believed to be the light emitter.[1,2] Three reaction mechanisms have been suggested for these examples of chemiluminescence. In one mechanism (path a), a pseudobase is formed (in aqueous solutions) followed by concerted multiple bond cleavage leading to excited acridone as a product.[2] In the second (path b), a dioxetane is proposed as an intermediate followed by its concerted decomposition to yield excited acridone.[1] Light emission from excited *N*-methylacridone has also been observed from the oxidation of corresponding ketyl (path c),[3a] and the third general mechanism for chemiluminescence, namely electron transfer, was proposed for this reaction.[3a] A version of this latter mechanism has been used to account for the formation of excited 9-acridinecarboxylate by the autoxidation of the corresponding hydrazide catalyzed with potassium *tert*-butoxide in dimethyl sulfoxide.[4] We now report on the chemiluminescence of two aldehydes [9-formylacridine (**1**) and 9-formyl-10-methylacridinium methosulfate (**2**)] and two ketones [9-benzoylacridine (**7**) and 9-(4-nitrobenzoyl)acridine (**8**)], which appear to luminesce *via* a similar mechanism.



Results and Discussion

Chemiluminescent Reaction of Aldehydes 1 and 2 with Hydroxide Ion. 9-Formylacridine (**1**) and 9-formyl-10-methylacridinium methosulfate (**2**) react with potassium hydroxide and oxygen in aprotic solvents to give bright chemiluminescent emissions. The emission spectra under these conditions match the fluorescence emission spectra of the spent reaction mixtures and the fluorescence emission spectra of acridones **5a** (anion) and **6**, respectively (Table I). Acridone (**5**) and 9-acridinecarboxylic acid (**9**) are the only detectable products of the chemiluminescent reaction of **1**, and they are obtained in a ratio of about 1:2. The chemiluminescent reaction of **2** under the same conditions yields *N*-methyl-9-acridinecarboxylate (**10**) and *N*-methylacridone as the only detectable products (by tlc). The above data suggest that light emission under these conditions stems essentially from the electronically excited acridones (Figure 1).



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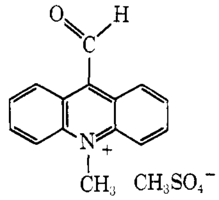

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The cleavage of formyl groups by hydroxide ion to give carbanions occurs in aqueous[5] and in aprotic (dimethyl sulfoxide)[6] media. The deformylation of 2,6-

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(1) (a) F. McCapra and D. G. Richardson, *Tetrahedron Lett.*, 3167 (1964); (b) F. McCapra, D. G. Richardson, and Y. C. Chang, *Photochem. Photobiol.*, **4**, 1111 (1965).

(2) M. M. Rauhut, D. Sheehan, R. A. Clarke, B. G. Roberts, and A. M. Semsel, *J. Org. Chem.*, **30**, 3587 (1965).

(3) (a) E. A. Chandross and F. I. Sontag, *J. Amer. Chem. Soc.*, **88**, 1089 (1966); (b) E. A. Chandross, *Trans. N. Y. Acad. Sci., Ser. II*, **31**, 571 (1969).

(4) E. Rapaport, M. W. Cass, and E. H. White, *J. Amer. Chem. Soc.*, **94**, 3153 (1972).

(5) J. F. Bunnett, J. H. Miles, and K. H. Nahabedian, *ibid.*, **83**, 2512 (1961).

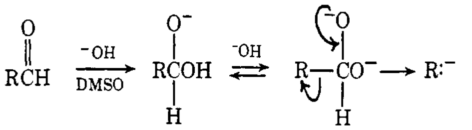
Table I. Chemiluminescence and Fluorescence Wavelengths[a]

Compound	Wavelength maxima, nm Chemiluminescence emission	 Fluorescence of spent reaction mixture	 Fluorescence[b]
9-Formylacridine (**1**)	469, 498, 530 (sh)[c]	469, 498, 527 (sh)	
	473, 499, 530 (sh)[d]	472, 498, 530 (sh)	
9-Formyl-10-methylacridinium methosulfate (**2**)	420, 432, 464, 497, 531 (sh)[c]	419, 432, 465, 497, 531 (sh)	
	420, 432[d]	420, 432	
9-Benzoylacridine (**7**)	473, 498, 530 (sh)[c]	473, 499, 531 (sh)	
9-(4-Nitrobenzoyl)acridine (**8**)	473, 499, 529 (sh)[c]	473, 499, 530 (sh)	
9(10*H*)-Acridone (**5**)			473, 498, 531 (sh)[c,d]
N-Methylacridone (**6**)			420, 432
9-Acridinecarboxylic acid (**9**)			467, 497, 531 (sh)[c,d]
N-Methyl-9-acridiniumcarboxylate (**10**)			465, 497, 532 (sh)[c,d]
Di-9-anthranoyl peroxide (**11**)	575[e]	425, 443 (sh), 578	
Anthrone (**12**)			580[c,e]
9-Anthracenecarboxylic acid (**13**)			425, 440 (sh)[c,e]

[a] All concentrations 10^{-4} *M* in dry dimethyl sulfoxide. [b] In the case of **5** the 498-nm peak is slightly higher than the 473-nm peak, while **7** shows a very weak maxima at 497 nm (almost a shoulder as compared with the 467-nm peak). [c] With potassium *tert*-butoxide. [d] With powdered potassium hydroxide. [e] With the radical anion of naphthalene in dry dimethoxyethane.

dihalobenzaldehydes with aqueous base was reported[5] to proceed through a doubly charged intermediate **4** which was in equilibrium with the initial addition product of hydroxide ion and the aldehyde group (**3**; eq 1). This process in our case would lead to a reactive carbanion (eq 1) as an intermediate in the light reaction.

There is evidence that reactive carbanions react with molecular oxygen in dimethyl sulfoxide to give radicals and superoxide ion.[7,8] These radicals would in turn give peroxy radicals in the presence of oxygen (eq 2).[9a]

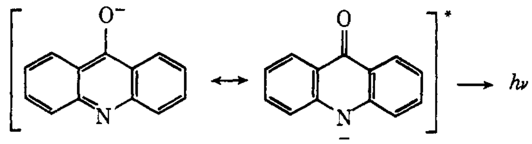


$$\mathrm{RCH{=}O} \xrightarrow[\text{DMSO}]{^{-}\text{OH}} \mathrm{RC(O^-)(H)OH} \overset{^{-}\text{OH}}{\rightleftarrows} \mathrm{R{-}C(O^-)(H)O^-} \longrightarrow \mathrm{R{:}^-} \qquad (1)$$

1 or 2 3 4

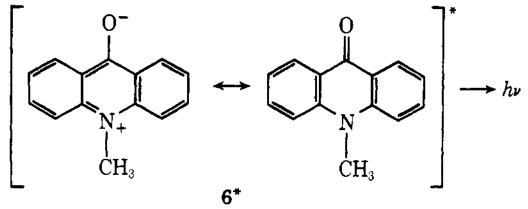
$$\mathrm{R{:}^-} \xrightarrow[\text{DMSO}]{\mathrm{O_2}} \mathrm{R\cdot} \xrightarrow{\mathrm{O_2}} \mathrm{ROO\cdot} \longrightarrow \mathrm{ROOOOR} \longrightarrow 2\mathrm{RO\cdot} + \mathrm{O_2} \qquad (2)$$

$$\mathrm{RO\cdot} \xrightarrow[+1e]{} \mathrm{RO^{-*}} \equiv$$



5a*

or (3)



6*

Dimerization of the peroxy radicals and loss of oxygen (eq 2) would lead to the corresponding oxy radicals.[9b] Electron transfer to these oxy radicals is proposed to result in the formation of electronically excited states of acridone anion **5a*** and *N*-methylacridone (**6***), respectively (eq 3).

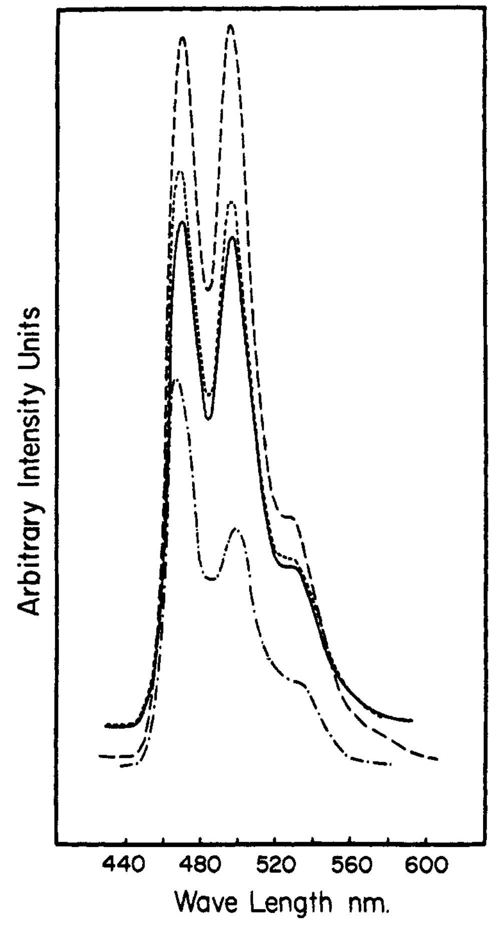


Figure 1. The chemiluminescence emission spectrum of 10^{-4} *M* **1** in dimethyl sulfoxide with sodium hydroxide (——), fluorescence emission spectrum of the spent reaction mixture (- - - - -), fluorescence emission spectrum of acridone (**5**) (— — — —), and 9-acridinecarboxylic acid (**9**) (–·–·–·–·); the latter two are 10^{-4} *M* in dimethyl sulfoxide with sodium hydroxide present as the base.

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(6) G. Belluci, B. Macchia, and F. Macchia, *Tetrahedron Lett.*, 3239 (1969).

(7) G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4153 (1962).

(8) G. A. Russell and A. G. Bemis, *ibid.*, **88**, 5491 (1966).

(9) (a) W. A. Pryor in "Free Radicals," McGraw-Hill, New York, N. Y., 1966; (b) J. A. Howard and A. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 1057 (1968).

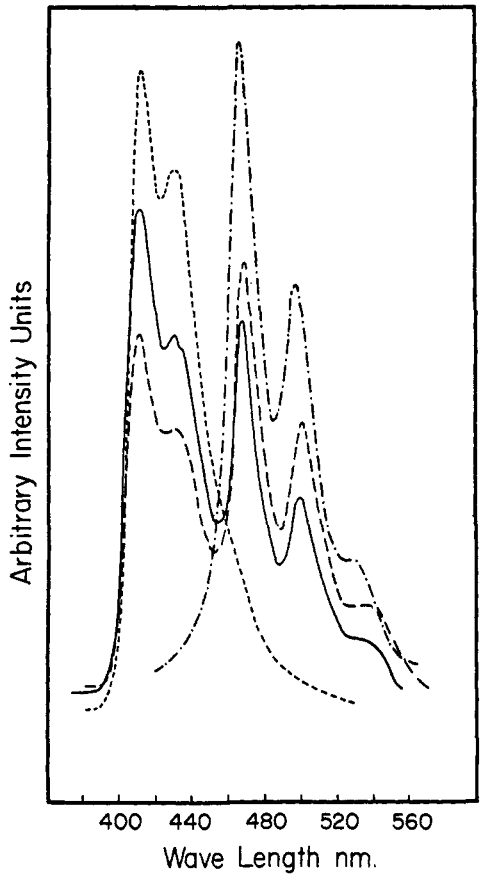


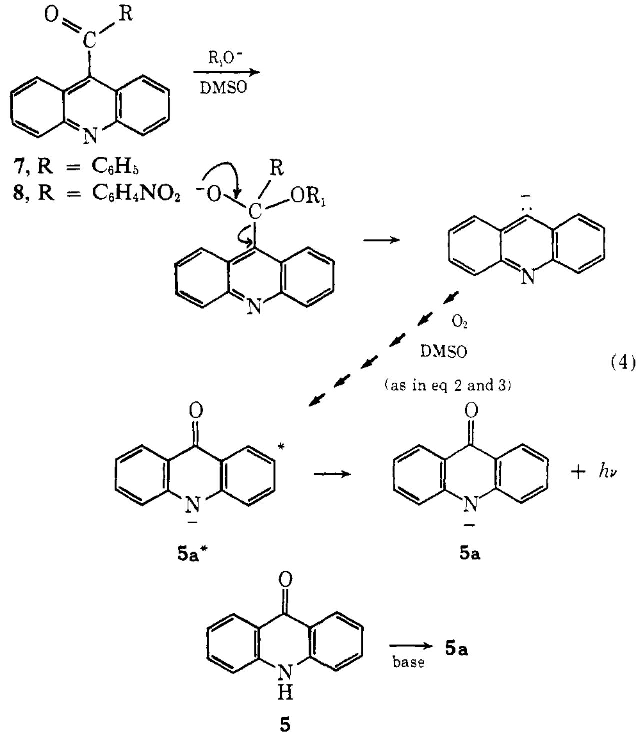
Figure 2. The chemiluminescence emission spectrum of 10^{-4} *M* **2** in hexamethylphosphoric triamide with potassium *tert*-butoxide (——), fluorescence emission spectrum of the spent reaction mixture (– – – –), fluorescence emission spectrum of *N*-methylacridone (**6**) (- - - - -), and *N*-methyl-9-acridiniumcarboxylate (**10**) (–·–·–·–); the latter two are 10^{-4} *M* in hexamethylphosphoric triamide with potassium *tert*-butoxide present as the base.

Radical anions of aromatic hydrocarbons have been reported to produce chemiluminescence upon oxidation.[3] Recombination of radical anions and radical cations also leads to light emission *via* a similar mechanism initiated by a one-electron transfer from the radical anion to the electron acceptor.[3,10–12] Similar mechanisms have been suggested recently to account for several cases of chemiluminescence where the electron donor is not a radical anion.[13] Hercules, *et al.*,[13a] have demonstrated that rubrene radical cation produced chemiluminescence upon reduction with electron donors such as water, *n*-butylamine, or triethylamine, and attributed light emission to the formation of electronically excited rubrene. They further reported[13b] that a one-electron reduction of a ruthenium complex brought about by aqueous base led to light emission from the reduced complex. The overall reaction was written as

$$\mathrm{RuL_3}^{3+} \xrightarrow{^{-}\mathrm{OH}} \mathrm{RuL_3}^{2+} + h\nu$$

where L was one of several suitable ligands. The conditions for chemiluminescence in these reactions include an electron donor which can provide the acceptor with an electron *via* the π^* orbital system.[14] The reactive carbanions present in solution in our case can serve as electron donors and the 9-oxyacridinyl radical (RO·) as the electron acceptor (eq 3). It was pointed out by Hercules, *et al.*,[13] that if electron transfer from a donor (*e.g.*, $\mathrm{R{:}^-}$) to an acceptor (RO·, eq 3) follows the excitation pathway $\mathrm{R{:}^- + RO\cdot \rightarrow R\cdot + RO^{-*}}$, which requires the loss of small amounts of energy, then the alternative pathway $\mathrm{R{:}^- + RO\cdot \rightarrow R\cdot + RO^-}$ would require a greater energy loss and hence will be slower.[13] This general mechanism for the excitation in the present case is strongly supported by the fact that compounds **7** and **8** which lead to the same reactive carbanion chemiluminesce brightly in dimethyl sulfoxide on reaction with potassium *tert*-butoxide and oxygen.

Chemiluminescent Reaction of Ketones 7 and 8 with *tert*-Butoxide. 9-Benzoylacridine (**7**) and 9-(4-nitrobenzoyl)acridine (**8**) were prepared following literature procedures.[15,16] Diphenylamine, phenylacetic acid, and zinc chloride were heated to 200° (the Bernthsen reaction) to give 9-benzylacridine[15a] which in turn was oxidized to give **7**,[15b] or nitrated and oxidized to give **8**.[16] These ketones chemiluminesce brightly in dimethyl sulfoxide with potassium *tert*-butoxide and oxygen. The quantum yield for emission is 1×10^{-3} for **7** and about half that value for **8**. The chemiluminescence emission spectra of **7** and **8** match the fluorescence emission spectra of the spent reaction mixtures and the fluorescence emission spectrum of acridone (Table I). Acridone was also found to be the major reaction product and no 9-acridonecarboxylic acid could be detected in either case (by tlc). These data suggest that acridone **5a** in its electronically excited



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(10) G. N. Lewis and J. Bigeleisen, *J. Amer. Chem. Soc.*, **65**, 2424 (1943).

(11) G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

(12) For a recent review on chemiluminescence from electron transfer reactions see D. M. Hercules, *Accounts Chem. Res.*, **2**, 301 (1969).

(13) (a) D. M. Hercules, R. C. Lansbury, and D. K. Roe, *J. Amer. Chem. Soc.*, **88**, 4578 (1966); (b) D. M. Hercules and F. E. Lytle, *ibid.*, **88**, 4745 (1966).

(14) For a more complete discussion of similar cases see ref 4 and 13.

(15) (a) H. Decker and T. Hock, *Chem. Ber.*, **37**, 1564 (1904); (b) K. Lehmstedt and F. Dostal, *ibid.*, **72**, 804 (1939).

(16) E. H. Huntress and E. N. Shaw, *J. Org. Chem.*, **13**, 674 (1948).

state is the light emitter. Thus, a nucleophilic addition of the base to the carbonyl group followed by elimination to give the reactive carbanion intermediate is a likely mechanism (eq 4).

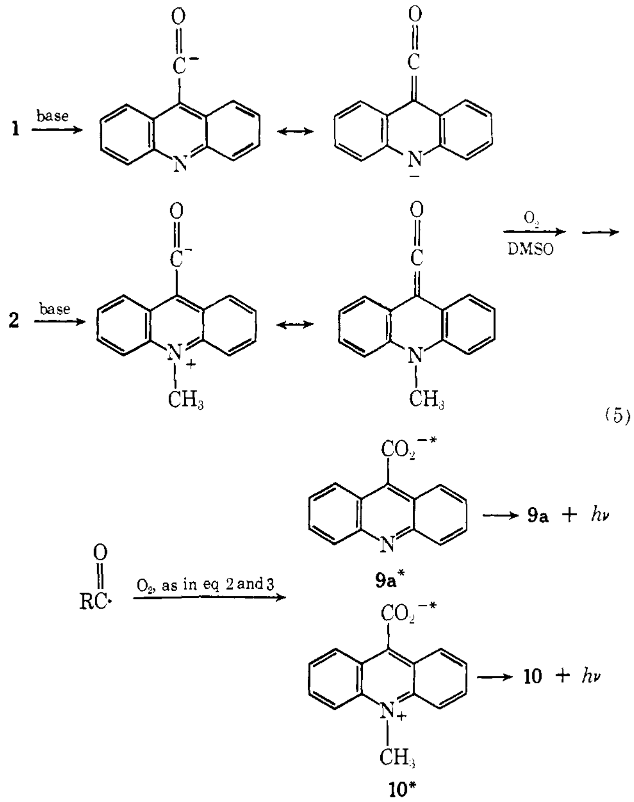
This carbanion is expected to react as described in eq 2 and 3 to give electronically excited acridone followed by light emission. Although **8** should be more reactive than **7** toward the initial nucleophilic addition, its quantum yield for emission was found to be lower than that for **7**. This observation is consistent with the proposed mechanism since it is known that electron transfer between carbanions and electron acceptors such as nitro aromatics occurs readily.[17] This process would reduce the concentration of the reactive carbanions and by favoring other reaction pathways could lower the quantum yield.

Chemiluminescent Reaction of Aldehydes 1 and 2 with *tert*-Butoxide. Aldehydes **1** and **2** react with potassium *tert*-butoxide and oxygen in dimethyl sulfoxide to give bright emissions, both with quantum yields of about 2 × 10^{-4}. The chemiluminescence emission spectrum of **1** matches the fluorescence emission spectrum of the spent reaction mixture and the fluorescence emission spectrum of a mixture of the acid anion **9a** and acridone anion **5a**. The chemiluminescence emission spectrum of **2** matches the fluorescence emission spectrum of the spent reaction mixture and the fluorescence emission spectrum of a mixture of the anion of acid **10** and *N*-methylacridone (**6**) (Figure 2). Since the fluorescence efficiency of *N*-methylacridone (~0.8) is much higher than the fluorescence efficiency of *N*-methyl-9-acridinecarboxylate (**10**) (~0.01) while their contribution to the chemiluminescent emission is comparable (Figure 2), it seems that the chemiluminescent reaction leads mainly to the excited state of the corresponding acid. As will be apparent from eq 5 (*vs.* eq 1), this implies that direct proton abstraction from the aldehyde[18] initiates the main light reaction.

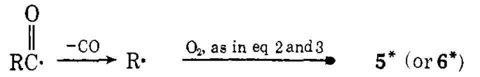
When 9-formylacridine (**1**) was allowed to react under the chemiluminescent reaction conditions, the products were acridone (**5**) (32% yield), acridine (14%), and 9-acridinecarboxylic acid (**9**) (21%). Carbon monoxide was identified as a product. When the reaction of **1** in dimethyl sulfoxide with potassium *tert*-butoxide was carried under degassed conditions no light emission was observed and acridine and 9-acridinecarboxylic acid (**9**) were the only products (the formation of **9** under degassed conditions can be accounted for by a Cannizzaro reaction). To eliminate the possibility of any steric effect by the use of *tert*-butoxide as base we showed that sodium *n*-propoxide and sodium methylsulfinylmethide gave rise to the same chemiluminescent emission.

We do not consider that energy transfer from the excited acids to the acridones, or *vice versa*, can account for the double emission (Figure 2) since the reaction of aldehydes **1** and **2** with hydroxide ion leads to emission exclusively from the excited acridones although the corresponding acids are also present in solution. In a previous paper[4] we reported emission mainly from the excited acid **9a** in mixtures also containing acridone (**5a**). The chemiluminescent reaction of **1** with potassium *tert*-butoxide is similar in its emission spectrum and products to the reported reaction of 9-acridinecarboxylic acid hydrazide under the same conditions.[4] The aldehyde was eliminated from being a necessary intermediate in the hydrazide chemiluminescence because of its lower quantum yield for chemiluminescence emission.

The formation of the excited acid is proposed to proceed *via* an acyl anion (eq 5) and a reaction mechanism developed for the chemiluminescence of the hydrazide[4] in which the acid anion is the emitter. The small amount of electronically excited acridone which was formed can be accounted for by a process outlined in eq 6. It can also be produced by a reaction sequence similar to the one described for ketones **7** and **8** (eq 4).



(5)



$$\overset{\displaystyle O}{\overset{\|}{RC\cdot}} \xrightarrow{-CO} R\cdot \xrightarrow{O_2,\ \text{as in eq 2 and 3}} 5^*\ (\text{or } 6^*) \qquad (6)$$

Chemiluminescent Reaction of Di-9-anthranoyl Peroxide (11) with the Radical Anion of Naphthalene. To test the validity of the proposed mechanism involving electron transfer we examined the following chemiluminescent reaction. Di-9-anthranoyl peroxide (**11**) was synthesized by treating 9-anthracenecarboxylic acid (**13**) with anhydrous hydrogen peroxide and dicyclohexylcarbodiimide according to the method of Greene and Kazan.[19] Di-9-anthranoyl peroxide (**11**) in dimethoxyethane gave a bright yellow chemiluminescent emission upon injection of a solution of naphthalene radical anion in dimethoxyethane. The chemiluminescence emission spectrum matches the fluorescence emission spectrum of anthrone in dimethoxyethane with base. The fluorescence emission spectrum of the spent reaction mixture matches the fluorescence emission spectrum of anthrone and 9-anthracenecarboxylic acid in

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(17) G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4143 (1962).

(18) A similar deformylation with strong base, the conversion of mesitaldehyde to mesitylene, has been communicated to us by Professor R. M. Stiles (University of Michigan).

(19) F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

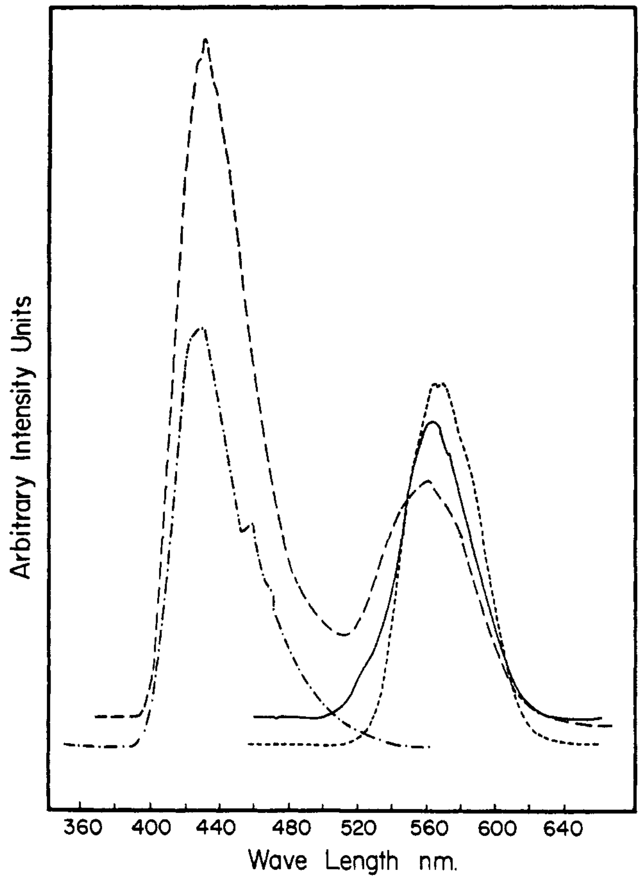
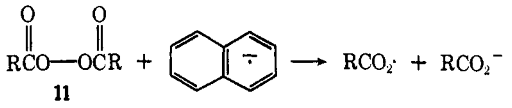


Figure 3. The chemiluminescence emission spectrum of 10^{-4} *M* **11**, in dimethoxyethane with the radical anion of naphthalene 10^{-2} *M* in dimethoxyethane (——), fluorescence emission spectrum of the spent reaction mixture (- - - -), fluorescence emission spectrum of 9-anthracenecarboxylic acid (**13**) (–·–·–·–), and anthrone (**12**) (- - - - -); the latter two are 10^{-4} *M* in dimethoxyethane with the radical anion of naphthalene in dimethoxyethane 10^{-2} *M*, or with potassium *tert*-butoxide in dimethoxyethane as bases.

peak position (Figure 3). The fluorescence emission spectrum of the latter two was determined in dimethoxyethane with base. The fluorescence emission peak of 9-anthracenecarboxylate has a shoulder which is not observed in the fluorescence emission of the spent reaction mixture (Figure 3). The latter emission is broader, a result, probably, of the emission by impurities (which could also obliterate the shoulder). These spectral data indicate that anthrone (in its anthranolate form) is the light emitter in the chemiluminescence.

Three major products were isolated from the neutralized spent reaction mixture by column chromatography: 9-anthracenecarboxylic acid (162% yield), anthraquinone (20%), and anthrone (8%). The formation of anthraquinone is attributed to base autoxidation of anthrone, as the autoxidation of anthrone to anthraquinone in an aprotic solvent with base is well known.[20] The addition of the radical anion of naphthalene in dimethoxyethane to di-9-anthranoyl peroxide (**11**) in dimethoxyethane under degassed conditions did not produce any observable light emission, and neither anthrone nor anthraquinone could be identified as reaction products.

The following electron transfer mechanism[3] is proposed for the formation of anthranolate in an electronically excited state (eq 7–9).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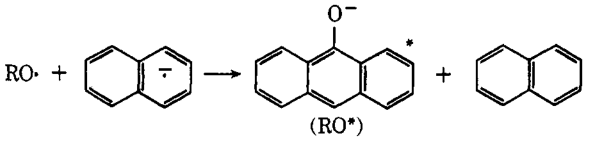
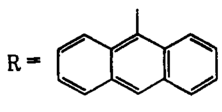
(7)

$$RCO_2\cdot \xrightarrow{-CO_2} R\cdot \xrightarrow[\text{as in eq 2}]{O_2} R\text{—}O\cdot \qquad (8)$$


(RO*)
12

(9)



Equation 7 is analogous to the reported reaction of benzoyl peroxide and the radical anion of 9,10-diphenylanthracene,[3a] which was suggested to lead to benzoate radical and benzoate anion. An electron transfer from naphthalene radical anion to the oxy radical of anthracene is proposed to give the enolate form of anthrone in an electronically excited state (eq 9). Presumably, it is the antibonding electron of naphthalene radical anion which is transferred directly to the antibonding level of 9-oxyanthracene radical to give an electronically excited anthranolate and ground state naphthalene.[12] We feel that an energy transfer mechanism from excited naphthalene to anthranolate to account for the excited anthranolate is unlikely. It seems probable that the conversion of an activated complex (as in eq 9) into products, one of which is in an excited electronic state, would result in the excitation being localized in the molecule having the lowest lying level before the complex breaks up.[3] The energy required for the formation of electronically excited naphthalene is 3.87 eV, while the energy requirement for excited anthranolate is about 2.3 eV. The oxidation potential of anthranol (anthrone) to 9-oxyanthracene radical was determined as 0.693 V *vs.* nhe.[21] The potential of the reversible naphthalene–radical anion couple was reported as −2.254 V *vs.* nhe.[22] The electron transfer reaction between 9-oxyanthracene radical (as acceptor) and the radical anion of naphthalene (as donor) would provide 2.947 eV, which is sufficient for emission from excited anthranolate. To explain the fact that light emission from excited 9-anthracenecarboxylate could not be detected, we assume that the decarboxylation of the carboxy radical (eq 8) is fast and that it occurs before electron transfer from the radical anion to the carboxy radical takes place. A similar mechanism was proposed to account for the formation of 9-acridinecarboxylate (see above)[4] with the assumption of a longer lifetime for 9-acridinecarboxylate radical compared to that of 9-anthracenecarboxylate radical.

Chemiluminescence from Aldehydes and Imines. Although aldehydes are known to be involved in Latia[23] and bacterial[24] bioluminescence, the present report is

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[20] G. A. Russell, *et al.*, *Advan. Chem. Ser.*, No. **75**, 209 (1968).

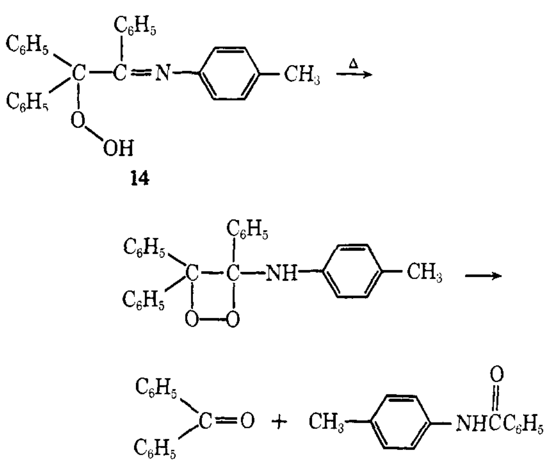
[21] L. F. Fieser, *J. Amer. Chem. Soc.*, **52**, 5204 (1930).

[22] F. E. Lytle and D. M. Hercules, *Photochem. Photobiol.*, **13**, 123 (1971).

[23] O. Shimomura and F. H. Johnson, *Biochemistry*, **7**, 1734 (1968).

the first concerning the direct chemiluminescence of an aldehyde. It is a possibility that in biological systems the reactions leading to excited states (followed by energy transfer) are similar to those discussed above, although pathways leading to Schiff bases and dioxetanes[25,26] appear more likely at the moment.

It was shown recently that a Schiff's base can produce chemiluminescence in solution with base and oxygen, and this type of reaction was suggested to account for bioluminescence where aldehydes are the substrates.[26] The Schiff's base formed from diphenylacetaldehyde and *p*-anisidine[27a] was shown several years ago to decompose upon exposure to air to benzophenone and formyl-*p*-anisidine.[27] Attempts to isolate a hydroperoxy intermediate have failed.[27b] We prepared a known stable imine hydroperoxide (**14**)[28] hoping that its decomposition would lead to a dioxetane intermediate and excited carbonyl products (eq 10). Heating **14** in benzene or toluene solution resulted in its decomposition which was accompanied by a weak bluish emission with a maximum at 490 ± 20 nm. Because of its weakness the emission could not be measured accurately. The only decomposition products were benzophenone and benz-*p*-toluidide isolated in 90 and 93% yields, respectively. In order to determine whether electronically excited benzophenone was formed, we carried out several experiments under conditions where excited benzophenone is known to give photoproducts. For example, the thermal decomposition of **14** in degassed benzene in the presence of benzhydrol should have yielded benzopinacol if excited benzophenone were formed;[29] benzopinacol was not detected in our experiment, however. The decomposition of **14** in 2-propanol with isopropoxide as base under degassed conditions also failed to produce any photoproduct, and its thermal decomposition in benzene in the presence of biacetyl or benzil did not lead to any photosensitized phosphorescence.[30] It seems likely therefore that the thermal decomposition of **14** does not follow a heterolytic route in which a dioxetane intermediate would be expected to form. Another possible explanation is that the decomposition of **14** leads to triplet states, which are quenched by oxygen. Oxygen may be a minor decomposition product as has been observed in the decomposition of the hydroperoxide of lophine.[31]


14

(10)

Experimental Section

Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories (Knoxville, Tenn.). Infrared spectra were determined on a Perkin-Elmer Model 337 instrument. Ultraviolet and visible spectra were determined on a Cary Model 14 instrument. Proton magnetic resonance spectrum (pmr) were determined on a Varian Associates A-60 instrument. Chemical shifts are reported in τ units relative to tetramethylsilane (TMS). Solvents except where stated were reagent grade and used as received. Mass spectra were determined on a Hitachi Model RMU 6E instrument.

Materials. Potassium *tert*-butoxide (MSA Research Corp.) was used as received. Dimethyl sulfoxide (Matheson Coleman and Bell) was stirred overnight over crushed potassium hydroxide, decanted and distilled from potassium *tert*-butoxide. 1,2-Dimethoxyethane (Aldrich Chemicals Co.) was distilled from sodium hydride.

Acridone. Commerical material was purified by vacuum sublimation at 0.1 Torr and crystallized from a 2:5 mixture of aniline–acetic acid to give yellow needles, mp 350–352° (lit.[32] 348–352°). *N*-Methylacridone was obtained as an analytically pure sample from Dr. D. F. Roswell.[33]

Sodium *N*-Propoxide. Sodium metal was dissolved in *n*-propyl alcohol and the solvent was evaporated to dryness. The solid residue was heated (80°) under vacuum for 5 hr and used without further purification.

Sodium Methylsulfinylmethide. This base was prepared according to Corey and Chaykovsky.[34] Sodium hydride was added to dimethyl sulfoxide and the mixture was warmed to 70–80° under nitrogen until hydrogen evolution stopped.

9-Formylacridine (1). This compound was prepared following a literature procedure.[35a] It was purified before use by preparative thin-layer chromatography (silica gel with chloroform): mp 144–145° (lit.[35] 145–146°); uv (95% ethanol) 359 nm (log ϵ 3.90) and 247 (4.74).

9-Formyl-10-methylacridinium Methosulfate (2). 9-Formylacridine (372 mg, 1.71 mmol) was heated in a sealed tube at 100° with dimethyl sulfate (2 ml) for 15 min. The solution was cooled and filtration gave a brown crystalline product which was washed with ether (396 mg, 1.16 mmol, 69%). Recrystallization from acetonitrile–ether gave a pure product: mp 170–180° depending on the rate of heating; ir (KBr) 3200 and 1685 cm^{-1}; uv (95% ethanol) 414 (log ϵ 3.57), 395 (3.57), 358 (4.05), 345 (sh) (3.76), 280 (3.68), and 260 nm (4.81).

Anal. Calcd for $C_{16}H_{15}NO_5S$: C, 57.66; H, 4.54; N, 4.20. Found: C, 57.47; H, 4.53; N, 4.27.

9-Carboxy-*N*-methylacridinium Chloride (10). This compound was prepared according to the procedure given by Rauhut, *et al.*[2] The compound yielded the following analysis: mp 206–208° dec (lit.[2] 205°) depending on the rate of heating; uv (water) 419 (log ϵ 3.61), 399 (3.62), 358 (4.29), 340 (3.97), and 259 nm (4.89); uv (0.1 *N* aqueous sodium hydroxide) 330 (sh) (log ϵ 3.85), 285 (4.26), and 252 nm (3.91).

9-Benzoylacridine (7). A solution of 9-benzylacridine[15] (2.0 g, 7.2 mmol) in glacial acetic acid (40 ml) containing sodium dichromate (2.5 g) was refluxed for 2 hr. Water (40 ml) was added and a yellow product precipitated upon cooling. The crude product was collected (1.16 g, 4.1 mmol, 56%) and recrystallized twice from

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ethanol: mp 215–217° (lit.[15b] 214–216°); ir ($CHCl_3$) 1670 cm^{-1}; uv (95% ethanol) 384 (log ϵ 3.70), 359 (4.00), and 344 nm (3.89).

Anal. Calcd for $C_{20}H_{13}NO$: C, 84.78; H, 4.62; N, 4.94. Found: C, 84.56; H, 4.58; N, 4.80.

9-(4-Nitrobenzoyl)acridine (8). 9-(4-Nitrobenzyl)acridine[16] was oxidized using exactly the same procedure as for the oxidation of 9-benzylacridine. The crude product was recrystallized twice from ethanol to give pure material in 59% yield: mp 227–229° (lit.[15] 226–228°); ir ($CHCl_3$) 1680 and 1625 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}N_2O_3$: C, 73.17; H, 3.68; N, 8.53. Found: C, 72.96; H, 3.71; N, 8.24.

Product Analysis of the Chemiluminescent Reaction of 9-Formylacridine with Potassium *tert*-Butoxide in Dimethyl Sulfoxide. 9-Formylacridine (50 mg, 0.24 mmol) was dissolved in dimethyl sulfoxide (15 ml) and potassium *tert*-butoxide (150 mg, 2.02 mmol) in dimethyl sulfoxide (15 ml) was added with vigorous stirring. The blue emission stopped after about 5 min and 5% aqueous sodium bicarbonate solution (25 ml) was added. The solvent was evaporated *in vacuo* and the dry residue was extracted with three portions of chloroform (150 ml). The chloroform extracts were dried and evaporated to dryness. The ultraviolet spectrum of the dry residue showed it to contain acridine (5.37 mg, 0.03 mmol, 14%) and acridone (15.8 mg, 0.081 mmol, 32%). Quantitative determination of acridine was based on its 339-nm (log ϵ 3.74) absorption, and of acridone was based on its 398-nm (log ϵ 3.93) absorption. An authentic solution of acridine (5.37 mg) and acridone (15.8 mg) gave the same ultraviolet spectrum. Thin-layer chromatography of the dry residue (silica gel:10% methanol in chloroform) compared with authentic samples showed acridine (R_f 0.62) and acridone (R_f 0.35) to be the only products.

The chloroform insoluble material was dissolved in water and shown by the ultraviolet spectrum [356 nm (log ϵ 3.97)] to be 9-acridinecarboxylic acid (11.2 mg, 0.05 mmol, 21%). A qualitative experiment showed acridine to be oxidized to acridone in dimethyl sulfoxide with potassium *tert*-butoxide in the presence of oxygen.

Product Analysis of the Chemiluminescent Reaction of 9-Formylacridine with Potassium *tert*-Butoxide under Degassed Conditions. 9-Formylacridine (53 mg, 0.25 mmol) was dissolved in dimethyl sulfoxide (25 ml) in a three-necked flask. The flask was connected by means of a side arm to a round-bottomed flask containing potassium *tert*-butoxide (450 mg, 6 mmol) in dimethyl sulfoxide (25 ml). The whole system was degassed (six freeze–pump–thaw cycles) and the two solutions were mixed; no light emission was observed. The combined solution was stirred *in vacuo* for 20 hr and decomposed with degassed water distilled directly into the reaction flask. The solution was evaporated to dryness *in vacuo* and product analysis was carried by ultraviolet spectra as described above. Acridine (14 mg, 0.08 mmol, 32%) and 9-acridinecarboxylic acid (26 mg, 0.12 mmol, 49%) were shown to be the only detectable products.

Product Analysis of the Chemiluminescent Reaction of 9-Formylacridine with Sodium Hydroxide (Powder) in Dimethyl Sulfoxide. 9-Formylacridine (50 mg, 0.25 mmol) was dissolved in dimethyl sulfoxide (30 ml) and powdered sodium hydroxide (100 mg, 2.5 mmol) was added. Light emission was observed for 5 min, then water (50 ml) was added as soon as light emission stopped. The solvent was evaporated *in vacuo* and the residue was analyzed by ultraviolet spectrum as described before. The only products detected were acridone (14.8 mg, 0.075 mmol, 32%) and 9-acridinecarboxylic acid (39.6 mg, 0.18 mmol, 70%).

Gas–Liquid Chromatography of Gaseous Reaction Products. 9-Formylacridine (50 mg, 0.25 mmol) was dissolved in dimethyl sulfoxide (15 ml) in a 25-ml, two-necked, round-bottomed flask where the side arm was closed with a rubber septum. Potassium *tert*-butoxide (100 mg, 0.85 mmol) was added and the flask was closed tightly. The reaction flask was shaken until light emission stopped and a gas sample (5 cm^3) was drawn with a syringe. Carbon monoxide was identified as a product on a molecular sieve 5-Å column at room temperature with a thermal conductivity detector. It was identical in retention time with an authentic sample of carbon monoxide (Matheson Chemicals, Inc.).

Product Analysis of the Chemiluminescent Reaction of 9-Benzoylacridine (7) and 9-(4-Nitrobenzoyl)acridine (8) with Potassium *tert*-Butoxide in Dimethyl Sulfoxide. Each of these chemiluminescent materials (20 mg) was dissolved in dimethyl sulfoxide (25 ml) and potassium *tert*-butoxide (100 mg) in dimethyl sulfoxide (15 ml) was added with vigorous stirring. Both solutions were allowed to stir in the presence of oxygen for 30 min after light emission stopped. Aqueous sodium bicarbonate (5%, 25 ml) solution was added and the mixture was evaporated to dryness. The dry residue was extracted with chloroform (100 ml) and the chloroform solution was dried and evaporated to dryness. The dry residue was shown by tlc to contain acridone with a trace of impurity of acridine (silica gel with chloroform). The ultraviolet spectrum of the material extracted by chloroform was essentially identical with that of acridone [λ_{max}^{EtOH} 398, 380, and 362 (sh) nm]. Thin-layer chromatography of the acidic material not extracted by chloroform (cellulose, ethanol–water–ammonia, 8:1:1) did not show any 9-acridinecarboxylic acid when compared with an authentic sample of the acid.

Di-9-anthranoyl Peroxide (11). *N,N'*-Dicyclohexylcarbodiimide (2.06 g, 9.06 mmol) was weighed as a liquid and dissolved in ether (15 ml). A solution of 98% hydrogen peroxide (1.7 g, 50 mmol) in ether (20 ml) was dried over magnesium sulfate, and the two solutions were then mixed at 0°. The combined solution was stirred at 0° while 9-anthracenecarboxylic acid (2.0 g, 9 mmol) was added followed immediately by cold methylene chloride (35 ml). The reaction solution from which dicyclohexylurea began to precipitate after 10 min was stirred at 0° for 30 hr. It was followed by tlc (silica gel with hexane–ether, 6:4), and the product appeared at R_f 0.91 while 9-anthracenecarboxylic acid stayed at the origin. At the end of the reaction, the solution was filtered through a sintered glass funnel and the precipitate was washed twice with cold methylene chloride. Ether (50 ml) was added to the organic solution, and it was washed with two 90-ml portions of cold saturated ammonium sulfate solution and two 90-ml portions of cold saturated sodium chloride solution. The organic solution was then dried over magnesium sulfate and the solvent removed *in vacuo* at room temperature. The dry residue was recrystallized twice from chloroform–methanol to give a pure product (1.4 g, 3.1 mmol, 62%), mp 194–197° dec. The product gave a positive iodine test:[36] uv ($CHCl_3$) 385 (log ϵ 3.55), 367 (3.55), 344 (3.43), 273 (sh) (4.22), and 252 nm (4.91); ir ($CHCl_3$) 1800, 1740, and 1680 cm^{-1}. (The infrared spectrum of 9-anthracenecarboxylic acid shows absorptions at ν ($CHCl_3$) 1710 and 1690 cm^{-1}, and the acid chloride absorbs at ν ($CHCl_3$) 1800 and 1760 cm^{-1}.)

Anal. Calcd for $C_{30}H_{18}O_4$: C, 81.44; H, 4.10. Found: C, 81.33; H, 4.26.

Preparation of Naphthalene Radical Anion in Solution. The preparation was carried out by the same method used by Scott, *et al.*[37] A solution of naphthalene (1.28 g, 0.01 mol) in dry dimethoxyethane (200 ml) was stirred under nitrogen and small pieces of freshly cut potassium (0.433 g, 0.011 g-atom) were carefully added. The solution was kept at 10°, and a dark blue color appeared after 1 hr. Aliquots of the radical anion solution were drawn after an additional 2 hr.

Product Analysis of the Chemiluminescent Reaction of Di-9-anthranoyl Peroxide with the Radical Anion of Naphthalene. The chemiluminescent reaction was carried on di-9-anthranoyl peroxide (1.0 g, 2.2 mmol) in dimethoxyethane (200 ml) with a solution of naphthalene radical anion in dimethoxyethane (10^{-1} *M*). The radical anion solution was injected into the stirred peroxide solution in the presence of oxygen until light emission could not be observed. The resulting solution was immediately neutralized with glacial acetic acid. The solution showed three major spots on tlc (alumina, petroleum ether–benzene, 1:1). The reaction solution was then evaporated to dryness and the residue absorbed on basic alumina which was put on the top of an alumina column (100 g, Alcoa F-20). The column was eluted with increasing amounts of benzene in petroleum ether (up to 50%), and 50-ml fractions were collected. The first compound to come off the column was naphthalene which was followed by anthrone, a mixture of anthrone and anthraquinone, and anthraquinone. The fraction containing anthrone (33 mg, 0.17 mmol, 8%) was identified by its infrared spectrum; ν ($CHCl_3$) 3000–3080 (broad), 1660, 1640 (sh), 1600, and 970 cm^{-1}. This spectrum matched the infrared spectrum of an authentic sample of anthrone. The yellowish needles collected from the column melted at 154–156° and did not decrease the melting point of an authentic sample 155–156°: uv (MeOH) 304 (sh) (log ϵ 3.66), 295 (sh) (3.82), and 260 nm (4.27), very similar to the reported spectrum of anthrone;[38] mass spectrum (70 eV) *m/e* (rel intensity) 194 (P) (100), 195 (P + 1) (25), 166 (P − 28) (87). The next fraction contained a mixture of anthrone and an-

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thraquinone and was followed by a fraction identified as anthraquinone (92 mg, 0.44 mmol, 20%), mp 280–282°, mixture melting point with an authentic sample of anthraquinone 284–286°; tlc (basic alumina, petroleum ether–benzene, 1:1) showed one spot R_f 0.43 the same as for an authentic sample; mass spectrum (70 eV) m/e (rel intensity) 208 (P) (100), 209 (P + 1) (33), 180 (P − 28) (71), 152 (P − 28 − 28) (32); the spectrum is very similar to the published spectrum of anthraquinone.[39] The top of the column was scraped off and the alumina was extracted with ether–acetic acid (8:2). The solvent was removed *in vacuo* and the residue was identified as 9-anthracenecarboxylic acid (0.811 g, 3.7 mmol, 162%). The compound was identified by mp 213–215° and mixture melting point 212–214° with an authentic sample. The infrared spectrum in chloroform (3010–3030, 1710, 1690, and 1200 cm^{-1}) matched the infrared spectrum of an authentic sample of 9-anthracenecarboxylic acid.

Reaction of Di-9-anthranoyl Peroxide with the Radical Anion of Naphthalene under Degassed Conditions. Di-9-anthranoyl peroxide (**11**) (22 mg, 0.05 mmol) was dissolved in dimethoxyethane (50 ml) making a 10^{-3} *M* solution. The flask was connected by means of a side arm to another round-bottomed flask containing a solution of naphthalene radical anion in dimethoxyethane (30 ml of 10^{-1} *M*). The system was degassed (three freeze–pump–thaw cycles) and the radical anion solution was added to the peroxide solution. No light emission was observed and thin-layer chromatography after neutralization of the solution (basic alumina, petroleum ether–benzene, 1:1) did not show any anthrone or anthraquinone as products. A control experiment carried out under the same conditions with the same concentrations in the presence of oxygen gave yellow emission upon mixing of the two solutions. In this case anthrone and anthraquinone were identified by thin-layer chromatography as compared to authentic samples.

α,α-Diphenyl-α-hydroperoxyacetophenone *p*-Tolylimine (14). Phenylmagnesium bromide was allowed to react with diphenylketene-*p*-tolylimine[28] in ether according to Stevens and Gasser.[28] The crude product was washed several times with cold pentane to give pure material in 61% yield: mp 111–113° (lit.[26] 112–113.5°); nmr (carbon tetrachloride) τ 0.2 (1 H, broad singlet), 2.35–3.60 (19 H, multiplet), 7.83 (3 H, singlet); ir (KBr) 3440 and 1655 cm^{-1}; chemiluminescent emission (10^{-3} *M* in benzene), $\lambda_{\max}$ 490 ± 20 nm (full width at half-maximum intensity 95 ± 10 nm). Addition of benzoyl peroxide does not enhance the emission; no increase in intensity is observed when the decomposition is carried in a sealed degassed tube.

Decomposition of 14 in Benzene in the Presence of Benzhydrol. α,α-Diphenyl-α-hydroperoxyacetophenone *p*-tolylimine (**14**) (400 mg, 0.001 mol) and benzhydrol (1.84 g, 0.01 mol) were dissolved in 15 ml of benzene in a tube which was degassed (five freeze–pump–thaw cycles) and sealed. The sealed tube was heated to 100° for 10 min, and opened, and the solvent removed by evaporation. The residue was chromatographed on a silica gel (Davison Grade 62) column using increasing concentrations (1–15%) of ether in petroleum ether as eluent. The first compound collected was identified as benzophenone (0.180 g, 0.89 mmol, 89%) by ultraviolet absorption and thin-layer chromatography compared with an authentic sample. The next compound to come off the column was identified as benzhydrol by its mp, 64–65°, and mmp, 64–65°, and also by tlc compared with an authentic sample. Eluting the column with 15% ether in petroleum ether gave benz-*p*-toluidide (mp 156–158° and mmp) which was identical on tlc with a synthetic sample (0.165 g, 0.8 mmol, 80%).

The synthetic sample was prepared by adding slowly a solution of benzoyl chloride in ether to a solution of *p*-toluidine and triethylamine in ether. The resulting suspension was allowed to stand overnight, filtered, and evaporated to dryness. The residue was recrystallized from ethanol to give benz-*p*-toluidide, mp 156–157° (lit.[28] 156–157°). Some of the fractions that contained benzhydrol and benzophenone were rechromatographed on a dry column (silica gel, Davison Grade 62) and proven by thin-layer chromatography to contain only benzhydrol and benzophenone.

Decomposition of 14 in Toluene. A solution of the hydroperoxide **14** (0.3 g, 0.75 mmol) in toluene was degassed (five freeze–pump–thaw cycles) in a tube which was sealed *in vacuo* and heated at 100° for 10 min. Evaporation of the solvent and chromatography on a silica gel column exactly as in the previous experiment resulted in the isolation and identification of benzophenone and benz-*p*-toluidide in 90 and 93% yield, respectively. No other compound could be identified by thin-layer chromatography of each fraction.

Decomposition of 14 with Potassium *tert*-Butoxide in Toluene. A solution of **14** (700 mg, 1.75 mmol) in toluene (70 ml) in a three-necked flask was degassed together with potassium *tert*-butoxide (75 mg, 6.9 mmol) in a separate round-bottomed flask connected by a side arm. Six cycles of freeze–pump–thaw were performed and the *tert*-butoxide was added with vigorous stirring. After 5 min, the solution was exposed to air and washed with water, hydrochloric acid (5%), and again with water, and evaporated to dryness. Petroleum ether was added and the mixture was stirred for 12 hr and then filtered. The insoluble solid was identified by thin-layer chromatography to be benz-*p*-toluidide (0.320 g, 1.55 mmol, 89%) containing a trace of benzophenone (benz-*p*-toluidide was also identified by mp 155–156° (lit.[28] 156–157°) and mixture melting point. The petroleum ether solution was evaporated to dryness and the oily residue crystallized upon standing to give benzophenone (0.300 g, 1.50 mmol) in 87% yield.

The decomposition of **14** was carried out in the same manner while an isopropoxide solution in 2-propanol was added to the hydroperoxide in 2-propanol under degassed conditions. The work-up of the reaction was done in the same way. The identification of benzophenone and benz-*p*-toluidide was by thin-layer chromatography using authentic samples of benzophenone, benz-*p*-toluidide, benzpinacol, and benzhydrol. The product mixture did not contain even a trace of the last two (by tlc).

Emission Spectra. Fluorescence and chemiluminescence emission spectra were determined on a Hitachi Model MPF-2A recording spectrophotofluorimeter. Spectra are not corrected for phototube sensitivity, instrumental distortion or source intensity fluctuation. Chemiluminescence spectra were obtained by addition of the base to a 10^{-4} *M* solution of the active compound and running the spectrophotofluorimeter with the source off.

Total Light Emission Studies. Chemiluminescence relative efficiencies were determined using a RCA IP21 phototube, biased by a Fluke Model 4128 dc power supply. The output of the phototube was amplified and the signal was collected on a capacitor and recorded for total light yields. All determinations (under strictly anhydrous conditions) were performed relative to luminol[40] and no correction was made for phototube sensitivity since all the measured emissions and that of luminol are within 70 nm. The fluorescence efficiency of *N*-methyl-9-acridiniumcarboxylate (**8**) was determined on a Hitachi MPF-2A recording spectrophotofluorimeter. The determination was based on ϕ = 0.8 for *N*-methylacridone.

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