i.d., packed with 3% ethylene glycol succinate on silanized Chromosorb W 80–100 mesh; low isotherm 70 °C, temperature increment 6 °C/min, high isotherm 200 °C, evaporator and detector 200 °C, nitrogen flow 30 mL/min).

The incubation mixture was then diluted with methanol (20 mL), the protein fraction removed by centrifugation, the solution evaporated under reduced pressure, and the residue extracted five times with 3 mL of ethyl ether. Evaporation of the combined extracts followed by one crystallization of the residue from petroleum ether gave 8 mg of slightly impure *trans*-1,2-cyclohexanediol, $[\alpha]^{25}_D$ −26.4°. After a second crystallization, the optical rotation rose to $[\alpha]^{25}_D$ −36.5° (ee 78.7%).

In another experiment carried out under identical conditions but with an incubation time of 8.5 h, no unreacted epoxide was recovered by extraction with petroleum ether. The extraction with ethyl ether of the residue obtained by evaporation of the incubation mixture, after removal of the protein fraction, gave crude *trans*-1,2-cyclohexanediol which was purified by sublimation at 1 mm to give the pure diol, $[\alpha]^{25}_D$ −33.5° (ee 72%). Further extraction with ethyl acetate and sublimation yielded a second crop of diol with $[\alpha]^{25}_D$ −31.4° (ee 67.5%). Crystallization from petroleum ether of the combined products from the two extractions (65 mg) gave a sample of diol with $[\alpha]^{25}_D$ −32.8° (ee 70.5%), and a further crystallization changed the optical rotation to $[\alpha]^{25}_D$ −34.6° (ee 74.5%). These experiments indicate that the optical purity of the diol changes little with percent conversion. They also show that crystallization of the diol is accompanied by a slight increase in optical purity. We believe that the most reliable value is obtained by sublimation and therefore that the actual optical purity of the enzymatically formed diol is around 70 ± 2%.

B. *trans*- and *cis*-4-*tert*-Butylcyclohexene Oxides. The epoxide **6** or **8** (100 mg) was incubated as described above for cyclohexene oxide. The incubations were terminated by cooling after the times reported in Table I, and the mixtures were extracted three times with 30 mL of ethyl ether. The combined extracts were analyzed by GLC under the following conditions: 3-m glass column, 2-mm i.d., packed with 2% ethylene glycol succinate on silanized Chromosorb W 80–100 mesh; low isotherm 80 °C, high isotherm 200 °C, temperature increment 2.5 °C/min, evaporator and detector 200 °C, nitrogen flow 30 mL/min; relative retention times for **6** or **8**, 1, and **7**, 2.21. The percentage of hydrolysis, determined from the ratios of glycol produced to unreacted epoxide, is reported in Table I. Blank experiments carried out with artificial mixtures of epoxide and diol showed that the recovery was identical for both compounds, and no chemical hydrolysis occurred. The extracts were then evaporated, and the residues were crystallized from petroleum ether to give the pure (GLC) diol. No variation in optical purity occurred on crystallization, since two or more consecutive crystallizations gave products with unchanged optical rotations. Alternatively, the crude products of the incubations were taken up in cold petroleum ether in order to remove the unreacted epoxide, and the insoluble diol was sublimed at 1 mm. The optical purity of the same sample of diol was identical after crystallization or sublimation. The optical rotations and optical purities of the diols obtained by stopping the incubations at different times are reported in Table I.

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Registry No. **3**, 31062-01-8; **4**, 61062-50-8; **5**, 61062-49-5; (1*R*,2*S*,4*R*)-**6**, 71961-99-4; (1*S*,2*R*,4*S*)-**6**, 71962-00-0; (±)-**6**, 71962-01-1; (+)-**7**, 71962-02-2; (−)-**7**, 71962-03-3; (1*S*,2*R*,4*R*)-**8**, 35650-41-0; (1*R*,2*S*,4*S*)-**8**, 72274-34-1; (±)-**8**, 71962-04-4; *trans*-3-*tert*-butylcyclohexene oxide, 20887-61-0; *cis*-3-*tert*-butylcyclohexene oxide, 20887-60-9; *t*-3-*tert*-butylcyclohexane-*r*-1,*t*-2-diol, 25348-58-7; *c*-3-*tert*-butylcyclohexane-*r*-1,*t*-2-diol, 25348-59-8; cyclohexene oxide, 286-20-4; *trans*-1,2-cyclohexanediol, 1460-57-7.

Energy Sufficient α-Amino Peroxides as Potential Sources of Excited-State Carbonyls

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Products from the thermolysis of α-amino peroxides **2** and **3** reveal a normal di-*sec*-alkyl peroxide decomposition route rather than an intramolecular base-catalyzed elimination. With peroxide **2**, *N*-phenyl-*N*-methylformamide and benzophenone were produced in 92 and 97% yield, respectively. Peroxide **3** gave *N*-phenyl-*N*-methylformamide and 1-mesityl-3,3-diphenylpropane-1,2-dione in yields of 82 and 89%, respectively. From thermochemical calculations, it was deduced that peroxides **2** and **3** are energy sufficient to generate excited-state products upon thermolysis. Extremely low chemiluminescence quantum yields (Φ_{CL}) were observed for **3**, in both the absence and the presence of acceptors (9,10-dibromoanthracene, 9,10-diphenylanthracene, and rubrene). Luminescence from the thermolysis of **2** was too weak to obtain Φ_{CL} values. The lack of efficient excited-state product formation in these energy sufficient reactions is discussed. A proposed mechanism for bioluminescence in the flavin system is also considered in relationship to the thermolyses of **2** and **3**.

A necessary condition for the production of excited-state products in a chemical reaction is that there be sufficient energy. The energy requirement is such that the enthalpy of reaction plus some fraction of the activation energy be equal to or greater than the difference in energy between the ground-state and excited-state product.[1] This can be seen in Figure 1, as well as the need for a nuclear configuration of the two surfaces so that crossing occurs. In addition, the probability of crossing from one energy surface to the other is dependent on the difference between the slopes of the two surfaces near the crossing point.[2] A smaller difference between the slopes will favor crossing. Furthermore, the crossing will be facilitated by an increase in density of vibrational states of the two surfaces at the crossing point. These latter two factors will also be dependent on the relative placement of the two surfaces. Lastly, the probability of crossing to P* will depend on the total electronic spin states of the species associated with the two surfaces.

(1) (a) E. B. Wilson, *J. Am. Chem. Soc.*, **98**, 3387 (1976); (b) E Lissi, *ibid.*, **98**, 3386 (1976); H. E. O'Neal and W. H. Richardson, *ibid.*, **92**, 6553 (1970); **93**, 1828 (1971).

(2) L. D. Landau and E. M. Lifschitz, "Quantum Mechanics", Addison-Wesley, Reading, MA, 1958.

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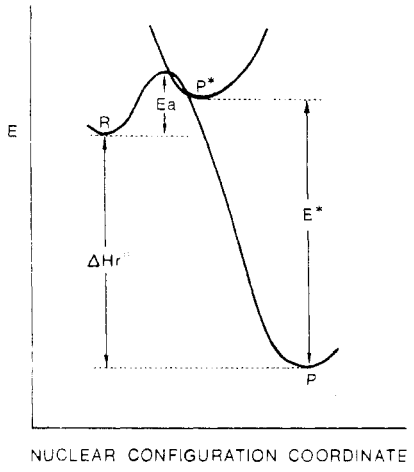
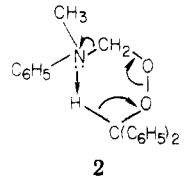


Figure 1. Energy vs. nuclear configuration coordinate for a reactant (R) proceeding to a product (P) where there is sufficient energy to produce the excited-state product (P*).

In order to survey reactions for potential excited-state product formation, it would be desirable to have a readily calculable parameter to evaluate the system. From thermochemical calculations, the necessary parameter of sufficient energy can be readily obtained. Unfortunately, the ease and accuracy of calculating the energy surfaces do not allow one to readily evaluate the relative placement of these surfaces in the energy vs. nuclear configuration coordinate diagram.[3]

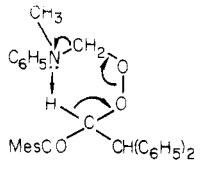
It did seem worthwhile to apply the one readily calculable parameter, i.e., the sufficiency of energy, to see if this could be used as a predictive tool for the production of excited-state products. We have used the thermochemical criterion with α-amino peroxides and found that they are most likely energy sufficient for the generation of excited-state products. Luminescence measurements were made to determine if excited-state carbonyl products were produced from two α-amino peroxides.

The thermolysis of α-amino peroxides is of interest as well with regard to bacterial luminescence.[4] Recently, a mechanism was proposed to explain this type of bioluminescence, which proceeded from an α-amino peroxide in the flavin system (Scheme I),[5] where R_1 = ribosyl. By analogy, the α-amino peroxides **2** and **3** could undergo such a cyclic base elimination process to generate excited-state products (eq 1 and 2; Mes = mesityl). We report here the



$\longrightarrow C_6H_5NHCH_3 + CH_2O + (C_6H_5)_2CO$ (1)

2

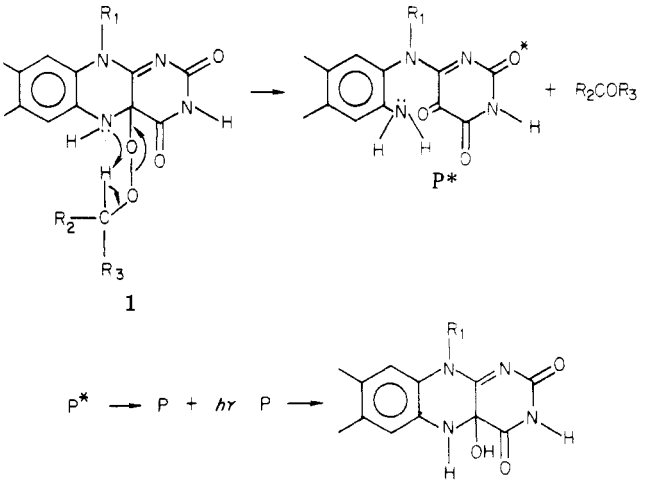


$\longrightarrow C_6H_5NHCH_3 +$

3

$CH_2O + MesCOCOCH(C_6H_5)_2$ (2)

Scheme I



measurement of luminescence and the products from α-amino peroxides **2** and **3**, along with thermochemical calculations for thermolysis reactions associated with these peroxides.

Results

Product Studies. Thermolysis of **2** in chlorobenzene in sealed capillary tubes at 110 °C was found to give *N*-phenyl-*N*-methylformamide (**4**) and benzophenone (**5**) in yields of 92 and 97%, respectively. The determination of yields and identification of products were accomplished by GLC. The presence of benzophenone was confirmed by TLC. Analysis by NMR revealed the presence of **4** (NCH_3, δ 3.13, s) and the absence of *N*-methylaniline (NCH_3, δ 2.68, s).

Thermolysis of **3** in carbon tetrachloride in sealed capillary tubes at 110 °C gave **4** and 1-mesityl-3,3-diphenylpropane-1,2-dione (**6**) in yields of 82 and 89%, respectively. The determination of yields and identification of products were accomplished by GLC. The presence of **4** and absence of *N*-methylaniline were determined by NMR as outlined before. The presence of **6** was confirmed by the $(C_6H_5)_2CH$ absorption (δ 6.00, s) in the NMR spectrum after thermolysis of **3**.

Light Emission Studies. Light emission measurements were carried out at 110 °C in xylene solvent. Chemiluminescence quantum yields (Φ_{CL}) were calculated from Φ_{CL} = In (einsteins)/mol of peroxide decomposition, where In is the integrated light intensity. Luminescence measurements for **2** and **3** were carried out in the absence of acceptors and in the presence of 9,10-dibromoanthracene (DBA), 9,10-diphenylanthracene (DPA), and rubrene (RB) as acceptors. The use of DBA and DPA for detecting triplets and singlets, respectively, has been previously reported.[6,7] The use of acceptors allows one to detect possible excited states that have low emission quantum yields.

Approximate efficiencies of generating excited states (%α) were calculated from $\Phi_{CL} = \alpha\Phi_{ET}\Phi_{fl}^{A}$, where Φ_{ET} is the quantum yield for energy transfer to the acceptor which is assumed to be 1.0 and Φ_{fl}^{A} is the fluorescence quantum yield of the acceptor.[6] The Φ_{fl}^{A} values for DBA (0.030) and DPA (0.38) at 110 °C were calculated with our

(3) See: (a) J. Michl, *Top. Curr. Res.*, **46**, 1 (1974); (b) C. D. Duncan, E. A. Halevi, and C. Trindle, *J. Am. Chem. Soc.*, **101**, 2269 (1979).

(4) See J. W. Hastings, A. Eberhard, T. O. Baldwin, M. Z. Nicoli, T. W. Cline, and K. H. Nealson, "Chemiluminescence and Bioluminescence", M. J. Cormier, D. M. Hercules, and J. Lee, Eds., Plenum Press, New York, 1973, p 369.

(5) C. Kemal and T. C. Bruice, *J. Am. Chem. Soc.*, **99**, 7064 (1977).

(6) W. H. Richardson, J. H. Burns, M. E. Price, R. Crawford, M. Foster, P. Slusser, and J. H. Anderegg, *J. Am. Chem. Soc.*, **100**, 7596 (1978).

(7) (a) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *J. Am. Chem. Soc.*, **96**, 1627 (1974); (b) W. Adam, O. Rodriguez, and K. Zinner, *J. Org. Chem.*, **43**, 4495 (1978).

Table I. Chemiluminescence Quantum Yields (Φ_{CL}) and Efficiencies (α) of Excited States from the Thermolysis of 3 at 110 °C in Xylene[a]

acceptor (conc, M)	Φ_{CL}	% α
	2.1×10^{-10}	
DBA (6.14×10^{-4})	3.6×10^{-10}	1.2×10^{-6}
DPA (5.9×10^{-4})	3.2×10^{-10}	8.4×10^{-8}
RB (5.8×10^{-4})	1.8×10^{-10}	$\sim 4.7 \times 10^{-8}$ [b]

[a] [3] = 2.92×10^{-2} M. [b] Approximate value calculated with $\Phi_{fl}^{A}(RB) = \Phi_{fl}^{A}(DPA) = 0.38$.

Table II. Enthalpies of Formation and Reaction for Reactions 1, 2, 3, and 4

reaction	ΔH_f° [a]	ΔH_r° [a]
1	2 (51.78) → 7[b] (20.82) + CH_2O (−27.7) + 5 (13.3)	−45.4
2	3 (15.43) → 7[b] (20.82) + CH_2O (−27.7) + 6 (−21.59)	−43.9
3	2 (51.78) → 4 (−14.28) + H_2 (0) + 5 (13.3)	−52.8
4	3 (15.43) → 4 (−14.28) + H_2 (0) + 6 (−21.59)	−51.3

[a] In kcal/mol. [b] 7 = $C_6H_5NHCH_3$.

previously reported activation parameters.[6] The Φ_{fl}^{A} for rubrene was assumed to be the same as that for DPA, so that an approximate efficiency could be calculated. The results of these measurements and calculations are given in Table I for 3. Light emission from 2 (1.27×10^{-2} M) was too weak to obtain Φ_{CL} values, in the presence or absence of DBA, DPA, or RB.

Thermochemical Calculations. The enthalpies of reaction (ΔH_r°) for reactions 1, 2, 3, and 4 were calculated from heats of formation of the reactants and products.[8] The results are given in Table II.

$$\underset{2}{} \rightarrow \underset{4}{C_6H_5N(CH_3)CHO} + H_2 + \underset{5}{(C_6H_5)_2CO} \quad (3)$$

$$\underset{3}{} \rightarrow \underset{4}{} + H_2 + \underset{6}{(C_6H_5)_2CHCOCOMes} \quad (4)$$

Discussion

As seen from the product studies, thermolyses of α-amino peroxides 2 and 3 do not proceed by intramolecular base elimination (eq 1 and 2). Instead, the products from 2 and 3 suggest that reactions 3 and 4 are the major decomposition routes. This type of reaction is well-known for di-*sec*-alkyl peroxides.[9,10]

In comparison to the decomposition of 1, the decompositions of 2 and 3 appear considerably slower. Overall rate coefficients for reaction of hydroperoxides (0.01 M) with the oxidized flavin (10^{-4} M) range from 6.7×10^{-5} s^{-1} at 30 °C with p-$CH_3C_6H_5CH_2OOH$ to 3.5×10^{-3} s^{-1} at 30 °C with $CH_3(CH_2)_8CH(OH)OOH$.[5] In contrast, the rate of decomposition of 2 is estimated to be about 10^{-4} s^{-1} at 110 °C by NMR. Since there was no evidence for the type of intramolecular base elimination as shown in Scheme I for 2 or 3, this reaction with 2 or 3 would even be slower. On the basis of the model α-amino peroxides 2 and 3, the intramolecular base elimination of 1 (Scheme I) appears questionable.

Chemiluminescence quantum yields (Φ_{CL}) and efficiencies of excited state product formation (α) are at very low levels for the thermolyses of 2 and 3. There is some question as to the facility of triplet–singlet energy transfer between benzophenone (E_{t_1} = 69 kcal/mol),[11] which could arise from 2, and DBA ($E_{s_1} \simeq 71$ kcal/mol, estimated). However, there should be no difficulty in singlet–singlet energy transfer between benzophenone (E_{s_1} = 75 kcal/mol)[11] and DPA (E_{s_1} = 73 kcal)[11] or RB (E_{s_1} = 54 kcal/mol).[12] Since no measurable light emission was observed with 2 and DPA or RB, extremely low efficiencies of singlet excited states must result from 2. Considering that the usual high range of $\alpha_{t_1}/\alpha_{s_1}$ ratios is about 200,[6,13] the triplet efficiencies must also be quite low. A similar problem in energy transfer between 6 ($E_{t_1} \simeq 62$ kcal/mol, $E_{s_1} \simeq 55$ kcal/mol, vide infra) and DBA and DPA can result. However, energy transfer between singlet (s_1) 6 and RB appears acceptable. With a ratio of $\alpha_{t_1}/\alpha_{s_1} = 200$[6,13] and with % $\alpha_{s_1} \simeq 4.7 \times 10^{-8}$ (Table I), the triplet efficiency is apparently very low (% $\alpha_{t_1} = 9.4 \times 10^{-6}$). In comparison, the triplet efficiencies for many 1,2-dioxetanes range from about 1 to 40%.[6,13] In fact, with such low yields of excited-state production from 2 and 3, the luminescence may result from spurious reactions.

A thermochemical analysis of reactions 3 and 4 for the α-amino peroxides 2 and 3 suggests that these processes are energy sufficient for the formation of excited-state products. Consider first the decomposition of 3 (eq 4). Although the excited-state energies of the α-diketone 6 are not reported, they should lie between those of benzil (E_{s_1} = 59.0 kcal/mol; E_{t_1} = 53.4 kcal/mol)[11] and biacetyl (E_{s_1} = 65.3 kcal/mol; E_{t_1} = 56.3 kcal/mol). A simple average of these energies would place the E_{s_1} and E_{t_1} values for 6 at approximately 62 and 55 kcal/mol, respectively. These energies exceed the heat of reaction 4 ($-\Delta H_r^\circ$ = 51.3 kcal/mol), but with some contribution from activation energy they can be readily reached. For example, the overall activation energy (E_a) for di-*sec*-butyl peroxide in toluene is 35.5 kcal/mol, while the E_a value for the hydrogen elimination process is calculated to be 31 kcal/mol.[9] On the basis of the latter E_a value, the singlet and triplet excited states of 6 could be reached with ΔH_r° plus 36 and 13% contributions from E_a, respectively. Considering next the decomposition of 2 (eq 3), the singlet and triplet energies of benzophenone are 75.4 and 68.6 kcal/mol, respectively.[11] In addition to ΔH_r° (−52.8 kcal/mol) for reaction 3, 73 and 51% of the activation energy (based on di-*sec*-butyl peroxide, E_a = 31 kcal/mol) would be required to reach the s_1 and t_1 states of benzophenone.

The lack of efficient (or possibly any) excited-state product formation from either 2 or 3 shows that energy considerations ($-\Delta H_r^\circ + E_a$) alone are insufficient to predict excited-state production. It appears that the relative placement of the energy surfaces for reactions 3 and 4 may not be correct for efficient crossing from one surface to the other. As a screening method, thermochemical calculations can readily eliminate reactions from consideration as sources of excited states. This may be the major value of this screening method, since the probability of predicting chemiluminescent reactions by ther-

(8) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.
(9) R. Hiatt, *Org. Peroxides*, 3, 1 (1972).
(10) R. Hiatt and S. Szelagyi, *Can. J. Chem.*, 48, 615 (1970).
(11) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.
(12) B. G. Dixon and G. B. Schuster, *J. Am. Chem. Soc.*, 101, 3116 (1979).
(13) (a) T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, 98, 1086 (1976); (b) E. J. H. Bechara, A. L. Baumstark, and T. Wilson, *ibid.*, 98, 4648 (1976); (c) N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, 33, 353 (1973); (d) K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.*, 53, 1103 (1975); (e) G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, 97, 7110 (1975); (f) M. A. Umbreit and E. H. White, *J. Org. Chem.*, 41, 479 (1976); (g) J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, 99, 5403 (1977).

mochemical calculations appears problematic.

Experimental Section[14]

2. A mixture of 90 μL (0.829 mmol) of freshly distilled *N*-methylaniline (BDH) and 62.5 μL (0.833 mmol) of 40% formalin solution (M & B) were allowed to stir for 20 min at 0 °C. A 167-mg (0.835-mmol) sample of benzylhydryl hydroperoxide[15] [NMR (60 MHz) δ 7.36 (s, 10 H, $(C_6H_5)_2$), 6.02 (s, 1 H, CH), 7.92 (s, 1 H, OOH); IR 3520 cm^{-1} (br, OOH)] was added to give a thick paste, which was partially stirred for an additional 6.0 h at 0 °C. The reaction mixture was transferred to a separatory funnel with petroleum ether (bp 40–60 °C) and benzene and then washed with five 2-mL portions of water. The organic extract was dried over sodium sulfate in the refrigerator and rotevaporated (water aspirator, room-temperature bath) to give 0.233 g of a viscous yellow oil. The resulting oil was chromatographed on silica gel with carbon tetrachloride as the eluent. The overall yield was 65%: NMR (60 MHz) δ 7.07 (m, 15 H, ArH), 5.75 (s, 1 H, $(C_6H_5)_2CH$), 5.00 (s, 2 H, N-CH_2), 2.88 (s, 3 H, NCH_3). It was estimated that about 26% decomposition occurred upon chromatography. The peroxide was placed in carbon tetrachloride solution and stored in the freezer (ca. −20 °C) prior to use.

3. To a stirred mixture of 120 mg (0.333 mmol) of 1-mesityl-3,3-diphenyl-2-(hydroperoxy)-1-propanone[16] [7: NMR (60 MHz) δ 7.25 (s, 10 H, $(C_6H_5)_2$), 6.80 (s, 2 H, $C_6H_2(CH_3)_3$), 5.54 (d, J = 4.5 Hz, 1 H, COCH), 4.67 (d, J = 4.5 Hz, 1 H, $(C_6H_5)_2CH$), 2.33 (s, 3 H, p-$CH_3C_6H_2(CH_3)_2$), 1.93 (s, 6 H, o-$(CH_3)_2C_6H_2CH_3$), 9.10 (s, 0.8 H, OOH); IR 3480 (br, OOH), 3090, 3060, 3030 (ArH), 2970, 2920 (aliphatic H), 1700 cm^{-1} (CO)] and 0.5 mL of benzene, cooled in an ice bath, was added 25 μL (0.333 mmol) of 40% formalin solution. A 37-μL (0.341 mmol) sample of *N*-methylaniline (BDH, freshly distilled) was then added, and the mixture was stirred for 6 h with cooling in an ice bath. The reaction mixture was transferred to a separatory funnel with petroleum ether (bp 40–60 °C) and benzene and washed with eight 5-mL portions of water. The organic extract was dried over magnesium sulfate, filtered, and then concentrated with a stream of nitrogen to give 0.121 g (76% yield) of a viscous yellow oil. Several attempts were made to chromatograph the product on silica gel with carbon tetrachloride and then benzene elution. In each case, decomposition on the column occurred, and no peroxide was obtained: NMR (60 MHz) δ 7.37 (s, 5 H, C_6H_5N), 7.25 (m, 10 H, $(C_6H_5)_2$), 6.73 (m, 4 H, $C_6H_2(CH_3)_3$), 5.42 (d, J = 4.5 Hz, 1 H, COCH), 4.87 (d, J = 4.5 Hz, 1 H, $(C_6H_5)_2CH$), 4.80 (s, 2 H, N-CH_2), 2.92 (s, 3 H, NCH_3), 2.34 (s, 3 H, p-$CH_3C_6H_2(CH_3)_2$), 1.92 (s, 6 H, o-$(CH_3)_2C_6H_2CH_3$).

6. The hydroperoxide 7 was reduced with potassium iodide in acetic acid to give 1-mesityl-3,3-diphenyl-2-hydroxy-1-propanone (8) in 84% yield: NMR (90 MHz) δ 6.94 (m, 10 H, $(C_6H_5)_2$), 6.50 (s, 2 H, $C_6H_2(CH_3)_2$), 5.00 (d, J = 5 Hz, 0.8 H, CHCO), 4.00 (d, J = 5 Hz, 0.8 H, $(C_6H_5)_2CH$), 2.13 (s, 3 H, p-$CH_3C_6H_2(CH_3)_2$), 1.77 (s, 7 H, o-$(CH_3)_2C_6H_2(CH_3)$), 3.53 (s, br, 0.6 H, OH); IR 3450 (br, OH), 1690 cm^{-1} (CO). To a rapidly stirred solution of 8 (64.1 mg, 0.186 mmol) in 1 mL of absolute ethanol at 50 °C was added a mixture of 74.3 mg (0.372 mmol) of $Cu(OCOCH_3)_2 \cdot H_2O$ in 0.5 mL of water. Stirring at 50–60 °C was continued for 2 h, and the mixture was filtered after cooling. The precipitate was washed with ethanol, and the filtrate was saturated with calcium carbonate and then extracted with ether. The ether extract was dried over magnesium sulfate, filtered, and rotevaporated to give 42.7 mg (67% yield) of a bright yellow oil. The oil was chromatographed on silica gel with carbon tetrachloride as the eluent. Attempts to crystallize the oil from 95% ethanol were unsuccessful (lit.[15] mp 76 °C): NMR (90 MHz) δ 7.08 (m, 10 H, $(C_6H_5)_2$), 6.50 (s, 2 H, $C_6H_2(CH_3)_3$), 6.00 (s, 1 H, $(C_6H_5)_2CH$), 2.15 (s, 3 H, p-$CH_3C_6H_2(CH_3)_2$), 1.77 (s, 6 H, o-$(CH_3)_2C_6H_2(CH_3)$); IR 1710, 1730 cm^{-1} (COCO).

Product Studies. Concentrations of carbon tetrachloride solutions of 2 and 3 were determined by NMR relative to a known amount of methylene chloride as an internal standard. With 2, an aliquot of the carbon tetrachloride solution was concentrated in a stream of nitrogen, and then chlorobenzene was added to give a 6.44×10^{-2} M stock solution of 2. Equal volumes of this stock solution and a 0.171 M solution of biphenyl were mixed, and the resulting solution was sealed in capillary tubes. The carbon tetrachloride solution of 3 was sealed in capillary tubes, and the peroxides were heated for 93 h in a thermostated oil bath at 110 °C. The GLC analysis for thermolysis of 2 was carried out on a 5 ft × $^1/_8$ in., 5% methyl vinyl silicone on Chromosorb W column (temperature column 200 °C, injector 275 °C, FID 275 °C; flow rate 19 mL of N_2/min): t_R 1.53 ($C_6H_5N(CH_3)CHO$), 2.08 (C_6H_5–C_6H_5), 4.14 min ($(C_6H_5)_2CO$). Analysis for thermolysis of 3 was carried out on the same column [temperature column 200 °C (temperature 1), 275 °C (temperature 2), time = 8.0 min, rate = 25 °C/min, injector 300 °C, FID 300 °C; flow rate 19 mL/min]: t_R 1.71 ($C_6H_5N(CH_3)CHO$), 17.6 min (6). The retention times were confirmed with authentic samples. Yields were calculated with reference to solutions of known amounts of authentic samples. With 2 the yield was determined with reference to the internal standard biphenyl, while constant (1 μL) injection volumes were used with 3.

Luminescence Studies. Luminescence measurements were made with an instrument that was previously calibrated with luminol.[17] With this calibration, the light intensity produced from the phosphors plus a β emitter (sealed in glass ampules, which were contained in frosted Lucite cylinders) was determined.[16] These "β lights" were then used to calibrate the luminescence from 2 and 3. Xylene or a xylene solution of an acceptor (DBA or DPA) was thermally equilibrated at 110 °C in a cell contained in a heated aluminum block. To the thermally equilibrated solution was added 100 μL of a stock solution of peroxide 2 or 3. The amplified output from the photomultiplier tube was recorded and integrated by the disk integrator of the recorder. With these integrated light intensities (In), Φ_{CL} values were calculated as described above.

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Registry No. 2, 72101-01-0; 3, 72101-02-1; 4, 93-61-8; 5, 119-61-9; 6, 72101-03-2; 7, 25056-05-7; 8, 72101-04-3; *N*-methylaniline, 100-61-8; formalin, 50-00-0; benzylhydryl hydroperoxide, 20614-54-4.

(14) GLC analyses were performed with a Hewlett-Packard 5830A-FID chromatograph. NMR spectra were obtained with Varian T-60, EM-360, and EM-390 spectrometers. Infrared spectra were measured with a Perkin-Elmer 337 spectrometer. Spectra were measured in 5–10% (w/v) carbon tetrachloride, and external Me_4Si was employed to calibrate the NMR spectra.

(15) G. H. Anderson and J. G. Smith, *Can. J. Chem.*, **46**, 1553 (1968).

(16) (a) E. P. Kohler and R. B. Thompson, *J. Am. Chem. Soc.*, **59**, 887 (1937); (b) R. C. Fuson and H. L. Jackson, *ibid.*, **72**, 1637 (1950).

(17) F. McCapra and R. Hart, University of Sussex, Falmer/Brighton, England.