cussions with W. S. Johnson. This work was supported in part by NSF Grant MPS-75-17816.

Registry No.—**1a**, 1665-79-8; **1b**, 4850-55-9; **1c**, 1566-72-9; **1d**, 52938-47-3; 2,3-butanedione, 431-03-8; diphenylethanedione, 134-81-6; 1-phenyl-1,2-propanedione, 579-07-7; 2,3-pentanedione, 600-14-6; trimethyl phosphite, 121-45-9; 2-butanone, 78-93-3; 1,2-diphenylethanone, 451-40-1; 1-phenyl-2-propanone, 103-79-7; 2-pentanone, 107-87-9; 3-pentanone, 96-22-0.

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(9) Camille and Henry Dreyfus Teacher-Scholar, Alfred P. Sloan Foundation Fellow. Case Western Reserve University.

Chemiluminescent Oxidations of 4- and 7-Aminophthalide

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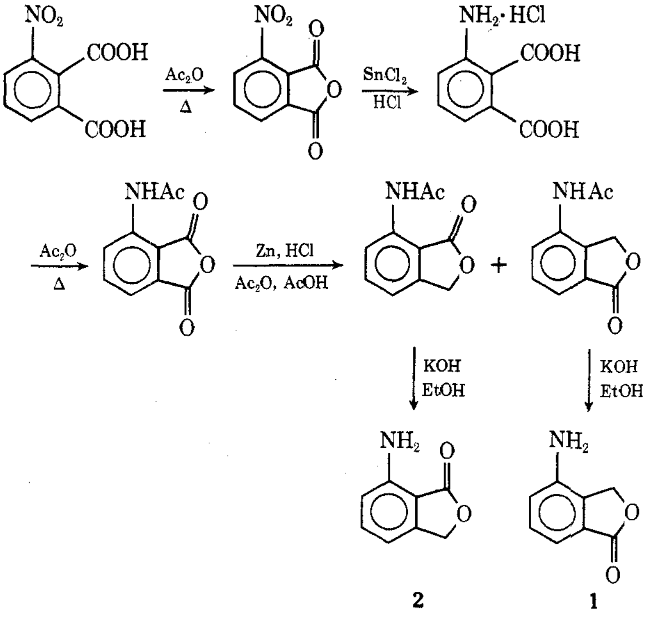
Received August 26, 1975

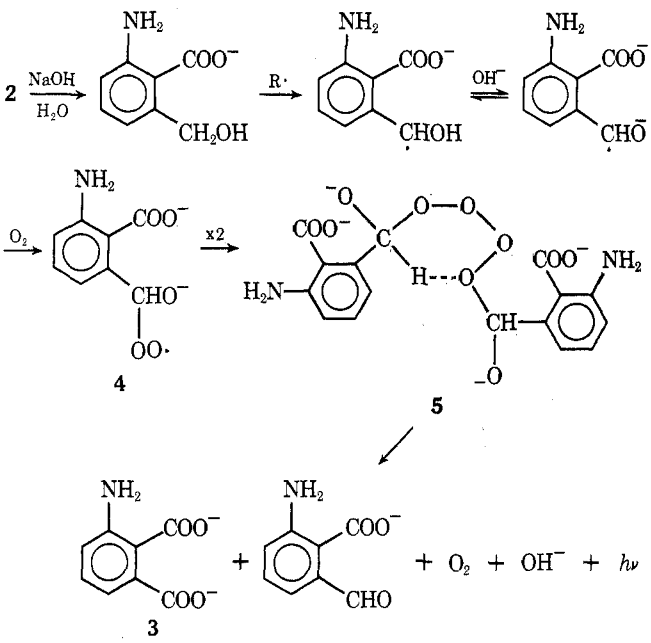
A large variety of organic compounds undergo oxidation with chemiluminescence. Acyl hydrazides are one important class of chemiluminescent substrates, with luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) probably the most notable example.[2] Radical autoxidation of hydrocarbons can also lead to chemiluminescence, by disproportionation of peroxy radicals via a tetroxide intermediate.[3,4] Recently, it has been proposed that a tetroxide intermediate could play a significant role in the chemiluminescent oxidation of luminol.[5]

We have synthesized 4- and 7-aminophthalide (**1** and **2**, respectively; see Scheme I) and subjected them to free-radical autoxidation and other oxidation conditions. The aminophthalides would be expected to be oxidized to 3-aminophthalate (**3**), which has been demonstrated to be the oxidation product and the emitting species in luminol chemiluminescence.[6] The expected oxidation mechanism for the aminophthalides would be that of radical autoxidation, consistent with the mechanism established for hydrocarbon oxidations[3,4] (Scheme II). Thus, we expected to generate an independent route to the intermediates (**4** and **5**) which were suggested for the mechanism of luminol chemiluminescence.[5]

Scheme I. Synthesis of the Aminophthalides



Scheme II. Oxidation of the Aminophthalides



The 4- and 7-aminophthalides were dissolved in basic aqueous solution, which opens the lactone ring, and they were subjected to a variety of oxidants: (a) oxygen with peroxydisulfate as radical initiator; (b) hydrogen peroxide with a catalytic amount of hemin; (c) calcium hypochlorite; (d) sodium hypochlorite. In all cases, the red-brown product solution was shown by paper chromatography to be equivalent to the product mixture obtained by subjecting luminol or authentic 3-aminophthalic acid to the same conditions. We were unable to specifically isolate 3-aminophthalic acid from the reaction mixtures, however, or conclusively prove its presence. The very mild oxidation conditions necessary to isolate 3-aminophthalic acid from luminol oxidations in aqueous solution[2] were ineffective toward the aminophthalides; furthermore, the aminophthalides were unreactive in Me$_2$SO toward simply O_2 and base (n-Bu$_4$N$^+$OH$^-$), which is an effective procedure for isolation of aminophthalic acid in nonaqueous luminol oxidations.[2]

When either of the aminophthalides was oxidized by peroxydisulfate or H_2O_2–hemin (radical oxidants), weak chemiluninescence was observed, detected by photon counting. Treatment of either of the aminophthalides with sodium or calcium hypochlorite (ionic oxidants) led to oxidation but did not lead to any detectable chemiluminescence. Figure 1 shows the chemiluminescence yields from the aminophthalides as a function of their concentration. Steady-state analysis indicates that the chemiluminescence intensity should be proportional to concentration.[7] Maximum chemiluminescence efficiencies, which are proportional to concentration, are observed at low concentrations; these are indicated by the lines on the figure, the slopes of which are the quantum yields. Pronounced curvature was observed at higher concentrations, probably owing to absorption of some chemiluminescence by

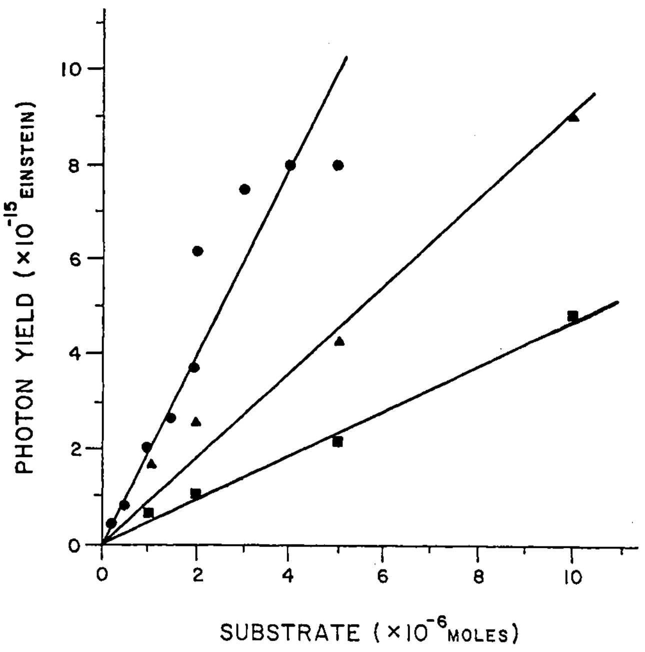


Figure 1. Chemiluminescence yields (H_2O_2–hemin oxidant): ●, 4-aminophthalide (1), $\Phi = 2 \times 10^{-9}$; ■, 7-aminophthalide (2), $\Phi = 5 \times 10^{-10}$; ▲, dimedone, $\Phi = 9 \times 10^{-10}$ (based upon luminol standard,[8] $\Phi = 1.1 \times 10^{-2}$).

the dark-colored oxidation products. The corresponding data for the chemiluminescence of dimedone (5,5-dimethyl-1,3-cyclohexanedione)[7] are also shown in Figure 1.

The quantum yields shown in Figure 1 were based upon the chemiluminescence yield from luminol under standardized conditions which permit calibration of our apparatus with respect to absolute photon yields (quantum yield = 1.1×10^{-2} einstein/mol).[8] That this calibration is still valid at these low intensities is indicated by our measured quantum yield for dimedone chemiluminescence of 9×10^{-10} einstein/mol, compared to the reported value of 2.5×10^{-10} einstein/mol (under somewhat different conditions).[7] Quantum yields for chemiluminescence from 1 and 2 were measured to be 2×10^{-9} and 5×10^{-10} einstein/mol, respectively. The fourfold greater efficiency of chemiluminescence from 1 compared to 2 indicates the significance of the neighboring amino group in determining chemiluminescence efficiency, an effect which has been noted in the chemiluminescence of luminol and its derivatives.[9] In this case, proximity of the amino group to the center undergoing oxidation enhances the efficiency of chemiluminescence.

The substantial difference in the chemiluminescence efficiency of luminol as compared to 1 or 2 suggests that the intermediates in the oxidation of 1 and 2 (i.e., peroxy radical 4 and tetroxide 5) are not the key intermediates which lead to the efficient chemiluminescence of luminol, as has been suggested.[5] The conditions of our experiments were designed to be those conditions which lead to efficient chemiluminescence of luminol.[8] Thus if peroxy radical 4 and tetroxide 5 were intermediates in the normal chemiluminescent oxidation of luminol, they should lead to chemiluminescence as effectively when produced from 2 as from luminol itself. Furthermore, dimedone was subjected to these oxidation conditions and was observed to chemiluminesce with approximately the yield reported.[7] Since dimedone reportedly undergoes chemiluminescent oxidation via the peroxy radical–tetroxide mechanism, this indicates that an authentic peroxy radical reaction works very well under these conditions, both in terms of formation of the peroxy radical and its ultimate chemiluminescence. We therefore conclude that peroxy radical intermediates are not involved in the major light-producing pathway of luminol oxidation. Since it has been reported that luminol can undergo oxidation through several different pathways,[10] the peroxy radical pathway could be one oxidation pathway for luminol; however, our data indicate that it could not be the pathway which leads to the majority of the chemiluminescence.

Experimental Section

Materials. Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) was obtained from Aldrich Chemical Co. 3-Aminophthalic acid was obtained from Alfred Bader Rare Chemicals (Aldrich). Dimedone (5,5-dimethyl-1,3-cyclohexanedione) was obtained from Matheson Coleman and Bell.

Aminophthalides. The isomeric 4- and 7-aminophthalides (1 and 2, respectively) were prepared from 3-nitrophthalic acid via 3-acetaminophthalic anhydride[11] according to the procedure of Tirouflet[12] (Scheme I). Recrystallized 4-aminophthalide had mp 150–153 °C (lit. 158 °C)[12] and gave ir and NMR spectra identical with those shown in the Sadtler Catalog (ir 19325K, NMR 10075M). Recrystallized 7-aminophthalide had mp 113–117 °C (lit. 121–123 °C)[12] and gave ir and NMR spectra identical with those shown in the Sadtler Catalog (ir 19326K, NMR 10076M).

Oxidation Procedures. Luminol, dimedone, and each of the aminophthalides were oxidized under each of the following conditions: (a) substrate dissolved in 10% aqueous NaOH maintained at 55–75 °C, saturated with O_2 by bubbling, with addition of potassium peroxydisulfate as radical initiator; (b) substrate dissolved in 10% aqueous NaOH with addition of a solution of 1×10^{-4} M hemin followed by addition of 1×10^{-1} M H_2O_2; (c) substrate dissolved in 10% aqueous NaOH with addition of an aqueous solution of 5×10^{-2} M $Ca(OCl)_2$; (d) substrate dissolved in 10% aqueous NaOH with addition of a 5% aqueous solution of NaOCl.

Oxidation product analyses were performed by paper chromatography. Luminol, both aminophthalides, and authentic 3-aminophthalic acid, when subjected to any of the oxidation conditions above, all gave comparable red-brown solutions which analyzed similarly (main component had R_f 0.9 in ether–acetone, with characteristic blue fluorescence under uv light).[2]

Chemiluminescence Measurements. Typical oxidation reactions were carried out on 2 ml of the substrate solution contained in a 1-cm Pyrex square cell in a light-tight compartment.[13] The entire compartment could be controlled in temperature, monitored by thermocouple and a Lewis Engineering Co. pyrometer-potentiometer, calibrated at 0 and 100 °C. Oxidants were added by syringe through a rubber septum without introduction of light. The chemiluminescent emission was detected by a Princeton Applied Research Model 1140A,B photon counter, with an RCA 1P28 phototube. Typical background counts were always less than 300 photons/s. Appropriate blank reactions, with all components but substrate present, always showed negligible emission. After the completion of the chemiluminescence, subsequent addition of oxidant gave no further chemiluminescence. The emission output was recorded on a Heath Model EU-200 recorder, such that either peak emission or total (integrated) emission could be determined. Total photon yields shown in Figure 1 were obtained in the following standardized manner: all photon counter and recorder settings were held constant (photon counter range 10 000 photons/s at 1.3% root mean square deviation; recorder range 1.0 V, chart speed 25 s/cm); the emission vs. time curves thus obtained were cut out and weighed for relative emission yields.

Quantum Yield Determinations. Relative integrated emission yields were converted to absolute photon yields by the method of Lee and Seliger.[8] The quantum yield of luminol chemiluminescence upon oxidation by H_2O_2 and hemin in basic aqueous solution was taken to be 1.1×10^{-2} einstein/mol.[8] The luminol chemiluminescence intensity was proportional to the luminol concentration for the intensity ranges studied; this effectively calibrated our apparatus for conversion of relative intensity to absolute photon yields.

Acknowledgments. We are pleased to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for generous financial support of this work.

Registry No.—1, 59434-19-4; 2, 3883-64-5; luminol, 521-31-3; dimedone, 126-81-8.

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An Unusual Oxidation–Reduction Reaction of Benzylbis(α-hydroxybenzyl)phosphine Oxide[1a]

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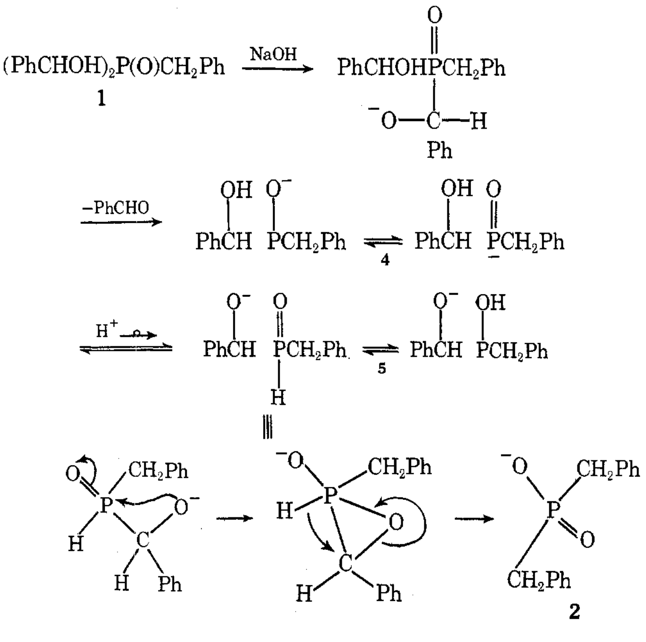
Received February 24, 1976

In previous publications[2–4] we have discussed the tendency of benzylbis(α-hydroxybenzyl)phosphine oxide (1) to undergo decomposition through the loss of benzaldehyde. Similar decompositions have been reported by other researchers.[5–7] In this work we wish to report an unusual oxidation–reduction reaction which was found to occur when 1 was treated with an equimolar amount of sodium hydroxide in refluxing benzene.

The product of this reaction (93% yield) was identified as the sodium salt of dibenzylphosphinic acid, 2, from the NMR spectrum and elemental analysis.

$$\underset{\textbf{1}}{(PhCHOH)_2P(O)CH_2Ph} \xrightarrow[\text{benzene}]{\text{NaOH}} \underset{\textbf{2}}{(PhCH_2)_2P(O)O^-Na^+} + PhCHO$$



Acidification of 2 with HCl caused precipitation of a white solid which was identified as dibenzylphosphinic acid (3) by the melting point, ir, and NMR spectra.

Our previous work[2–4] showed that 1 would react with base to eliminate benzaldehyde and form the anion of the secondary phosphine oxide 4. A proton shift yields 5, which can rearrange by hydride transfer from phosphorus to carbon by an intramolecular process (as shown, or a similar rearrangement, involving two molecules, which has a six-membered ring intermediate) to yield the dibenzyl phosphinate anion, 2.

This apparent hydride transfer from phosphorus to carbon is, to our knowledge, the first of its kind in α-hydroxyalkylphosphorus compounds. Hydride transfers from phosphorus to carbon are known, however, to occur during the alkaline hydrolysis of chloromethyl phosphinates.[8] Reductions of hydroxy groups in α-hydroxyalkylphosphorus compounds have been shown to occur but these involve reducing conditions,[9] disproportionations,[10,11] or transfer of hydrogen from oxygen to carbon.[12]

Experimental Section

Reagent grade chemicals and solvents were used without further purification. The ir spectra were taken on a Perkin-Elmer 137[1d] with NaCl optics. Solid samples were run as KBr pellets, using about 1% of the sample. The NMR spectra were taken on a Varian A-60A.[1d] Elemental analyses were performed by Enviro Analytical Laboratory, Knoxville, Tenn. All melting points are uncorrected.

Benzylbis(α-hydroxybenzyl)phosphine oxide (1) was prepared as described in an earlier publication.[2]

Reaction of 1 with Sodium Hydroxide. A mixture of 5 mmol of 1, 5 mmol of sodium hydroxide, and 300 ml of benzene was refluxed for 48 h. On cooling to room temperature, the solid which formed was collected (1.25 g) and washed with ether to remove benzaldehyde, the odor of which was quite noticeable above the reaction mixture. The solid was identified as the sodium salt of dibenzylphosphinic acid (2, 93% conversion) from the NMR spectrum and elemental analysis: NMR (D_2O) δ 2.97 (d, $J = 16$ Hz, 4 H, PCH_2Ph), 7.33 (m, 10 H, aromatics).

Anal. Calcd for $C_{14}H_{14}NaO_2P$: C, 62.69; H, 5.26; P, 11.55. Found: C, 62.45; H, 5.51; P, 11.36.

Acidification of an aqueous solution of 2 with HCl caused precipitation of a white solid which had mp 185–188 °C. Recrystallization from an ethanol (20 ml)–water (5 ml) mixture gave white platelets, 3, with mp 190–191 °C (lit.[13] 191°C); ir (KBr) 2.88 (OH), 3.28 (aromatic C–H), 3.65–4.8 (broad strong P–OH), 8.5 μ (P=O): NMR (Me_2SO-d_6) δ 3.0 (d, $J = 16$ Hz, 4 H, PCH_2Ph), 7.22 (m, 10 H, aromatics).

Registry No.—1, 36871-68-8; 2, 13422-04-3; 3, 7369-51-9; NaOH, 1310-73-2.

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(1) (a) Decomposition Reactions of Hydroxyalkylphosphorus Compounds. 4. For parts 1, 2, and 3 see ref 2, 3, and 4. (b) One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture. (c) Formerly Louisiana State University in New Orleans. (d) Mention of companies or commercial products does not imply recommendations or endorsement by the U.S. Department of Agriculture over others not mentioned.
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