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Synthesis and Verification of 9,10-Diphenylanthracene and Its Utility as a Fluorescer in a Peroxyoxalate Chemiluminescence System. An Organic Laboratory Project Integrating Synthesis with Fluorescence and Chemiluminescence

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Abstract: A project for the organic laboratory integrating the organic synthesis of 9,10-diphenylanthracene with fluorescence and chemiluminescence is described. The fluorescent compound is synthesized from anthraquinone by reaction with phenyllithium and subsequent hydrolysis and reduction with KI and NaH_2PO_2 in acetic acid. The structure of the product is verified by its melting point and by IR, ^1H NMR, and fluorescence spectroscopy. A peroxyoxalate chemiluminescent reaction using bis(2-butoxycarbonyl-3,4,6-trichlorophenyl) oxalate and hydrogen peroxide as the energy source is tested. The chemiluminescence emittance spectrum of the prepared diphenylanthracene is found to be essentially identical to that of the fluorescence spectrum of the same compound. Finally, the kinetics of the chemiluminescent reactions using different intensity-modifiers are monitored by measuring intensity-versus-time decay curves.

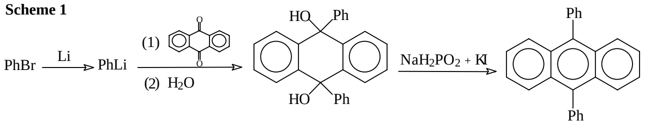
Chemiluminescence is a fascinating phenomenon that can be used as an effective pedagogical tool for the illustration of several fundamental chemical principles. The most efficient chemiluminescent reaction yet discovered results from the oxidation of a diaryloxalate ester by a peroxide in the presence of a fluorescer. This reaction is commonly known as peroxyoxalate chemiluminescence [1, 2]. Over the years, a number of educational papers describing chemiluminescence have been published [3–5]. Virtually all of these papers present procedures designed for lecture demonstration purposes, and there are very few educational articles presenting chemiluminescence laboratory experiments. As a means of explaining this phenomenon and stimulating interest in this field, we designed a project involving the synthesis, identification, and investigation of the fluorescent and chemiluminescent features of a fluorescent compound, 9,10-diphenylanthracene. This substance was selected because it is a very stable and efficient fluorescer, and it has been widely adopted as the fluorescent additive to use in peroxyoxalate chemiluminescence systems to achieve a purple emission. Moreover, the relatively simple and rapid three-step synthesis procedure for the compound, the easily accessible (concentrated hydrogen peroxide can be prepared in any laboratory from the commercial product) and nontoxic chemicals required, and a sufficiently stable product and intermediate, allowing for thier isolation and analysis, make this a useful laboratory experiment for organic chemistry.

This experiment provides students the opportunity to: (a) synthesize a compound using an organolithium reagent, (b) work with an inert atmosphere, anhydrous solvents, and dry glassware, (c) isolate using recrystallization; (d) identify products by a variety of characterization techniques, (e) obtain and analyze fluorescence and chemiluminescence emittance spectra as well as investigate the kinetics of the chemiluminescent reaction by measuring intensity decay curves; and (f) experience one method of obtaining chemiluminescence from the peroxyoxalate reaction.

The whole experiment can be completed by students (working in pairs) in three 3-h sessions, one for the preparative work with part of the isolation to be finished in the second session, one for melting point determination and measurement and analysis of spectral data (NMR experiments were performed by the assistance of a TA during the second session), and the third session for the evaluation of the fluorescent and chemiluminescent results obtained with the product. The intense purple fluorescence and chemiluminescence light emissions produced from the compound that the students' prepared on their own stimulate their motivation and interest, considerably.

The overall synthetic route, which is based on a reported procedure [1], is outlined in Scheme 1.

Scheme 1



The synthesis is operationally easy. Phenyllithum forms smoothly from the reaction of lithium and bromobenzene in refluxing diethyl ether under N_2. Addition of anthraquinone and brief reflux, followed by addition of H_2O gives 9,10-diphenylanthracene-9,10-diol as a white solid.

In order to ensure a complete transformation of the two carbonyl groups of anthraquinone to hydroxyl groups, an excess of phenyllithium must be present. Because the yield of the reaction of bromobenzene with lithium is normally quantitative (not less than 95%), our experience shows that a 20% excess of the stoichiometric amount of bromobenzene is enough for a complete conversion.

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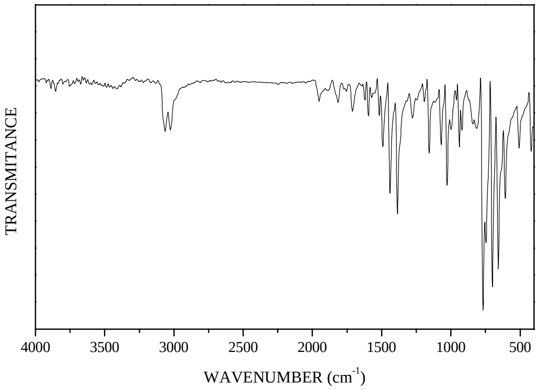

Figure 1. FTIR spectrum of 9,10-diphenylanthracene.

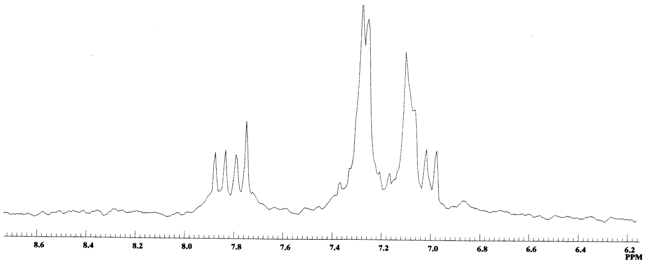

Figure 2. ^{1}H-NMR spectrum (ppm) of 9,10-diphenylanthracene.

Reduction of the resulting diol with KI and NaH_2PO_2 in acetic acid produces the final product. This conversion can bereadily confirmed via IR spectroscopy because the peaks at 3400–3600 cm^{-1}, which correspond to the two hydroxyl groups of the diol, disappeared upon reduction.

Recrystallizing the crude product twice yields the pure product as verified by a constant melting point. The expected structure of the product can be verified from IR and ^{1}H-NMR spectral data by comparison with that of an authentic sample. Further, the expected fluorescence spectrum of the sample can be obtained reliably by exciting a solution containing 10^{-4} M diphenylanthracene at 350 nm and scanning the emission between 380 and 550 nm.

For testing the chemiluminscence, the reaction of bis(2-butoxycarbonyl-3,4,6-trichlorophenyl) oxalate (BBTPO) and hydrogen peroxide in dimethylphthalate was adopted. An excellent explanation of the peroxyoxalate chemiluminescence system may be found in the references [3, 5]. As background information, students are told that the light emitted is not an inherent property of the reaction of the oxalate ester with H_2O_2, but requires a controllable addition of a fluorescent material to capture the chemical energy and convert it to visible light; the emission wavelength and efficiency of the process can be altered by changing the fluorescent material. Upon initiation of the reaction with the prepared product as the fluorescer, an immediate and bright purple chemiluminescence is observed with a duration of at least 1 h. Students are asked to record the chemiluminescent emitting spectrum using a spectrofluorometer without the external excitation. By comparing the spectra obtained from fluorescence and chemiluminescence, students readily find that the emission occurs at almost the same wavelength in both processes for the same emitter and similar concentration range. This can be explained by the fact that the light-emission steps for both fluorescence and chemiluminescence are essentially analogous, and the primary difference between the processes is the method of excitation.

A light-intensity- (in arbitrary units) versus-time decay curve can be measured by operating the spectrofluorometer at the emission wavelength of 437 nm with the exciting light turned off. Students can add a small amount of catalyst (sodium salicylate) or inhibitor (oxalic acid) to demonstrate an increase or decrease of the reaction kinetics. Students find that in the absence of intensity-modifying additives the oxalate ester produces an initial burst of light followed by a relatively constant but lower intensity output and, subsequently, a gradual decline to a nonobservable level. The addition of sodium salicylate increases intensity at expense of emission lifetime; however, the addition of oxalic acid retards the chemiluminescent reaction rate and this results in a lower emission intensity and an extended lifetime.

Experimental Section

Chemicals and Equipment. CAUTION: Lithium and phenyllithium are extremely reactive, particularly with water; therefore, care must be taken while dispensing or disposing of them. Concentrated H_2O_2 or an organic solvent diluted H_2O_2 solution may cause skin irritation upon contact with skin or body!

Bis(2-butoxycarbonyl-3,4,6-trichlorophenyl) oxalate was prepared in advance with an established procedure [2]; alternatively, it is also available from Fluka. Concentrated hydrogen peroxide (> 90%) (handle with care!) was prepared by a teaching assistant in the laboratory according to a procedure described elsewhere [6]. Diethyl ether was dried over anhydrous magnesium sulfate. Other reagents for this experiment were used as received from the supplier. All spent materials must be disposed of according to local regulations.

IR spectra were recorded as KBr pellets using a Bruker Vector 22 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian FT-80 spectrometer; the chemical shifts are reported in ppm on δ scale. Fluorescent and chemiluminescent spectra were measured with a Hitachi 204-A spectrophotofluorometer. Melting points were determined in capillaries.

Procedure. Lithium (0.8 g) is flattened with a hammer to 1.5-mm thickness and subsequently cut into 50 mL of anhydrous diethyl ether contained in a 250-mL dried three-necked flask fitted with a reflux condenser and flushed slowly with N_2. From a dropping funnel, bromobenzene (6 g) and anhydrous diethyl ether (50 mL) are added dropwise. The reaction mixture is stirred using a magnetic stirrer. After brief heating, a white turbidity appears and a distinct rise in temperature is observed. The heater is then removed and the reaction is maintained at a gentle reflux for 1 hr and then cooled with ice water. Anthraquinone (5 g) is added slowly under N_2 and the mixture is refluxed for 15 min. The mixture is then cooled with ice water and added to water (100 mL) slowly. The resulting precipitate is collected by filtration to give the crude diol (ca. 10 g, wet weight). The IR spectrum shows strong peaks at 3400–3600 cm^{-1}, corresponding to the two hydroxyl groups of the diol.

The crude diol obtained need not be dried and can be transferred at once for reduction to the flask (which does not need to be cleaned) in which it was prepared. Potassium iodide (15 g), sodium hypophosphite (15 g) and acetic acid (100 mL) are added, and the mixture is heated under reflux for 15 min. The cooled mixture is collected by filtration and dried under an IR lamp. Recrystallization of the product twice from toluene gives a yellow solid (60–70% yield), mp 243–5 °C (lit. 245–8 °C). The IR and ^{1}H-NMR spectra of the product are shown in Figures 1 and 2, respectively. Major spectral data are as follows: IR (KBr) $\tilde{V}$ (cm^{-1}): 3054, 3025, 1595, 1489, 1435, 1397; ^{1}H NMR (80 MHz, $CDCl_3$, δ) 6.98–7.4 (m, 14 H); 7.66–7.92 (m, 4 H).

Fluorescence Spectrum. First, a diphenylanthracene stock solution (10^{-3} M) is prepared by dissolving 3.3 mg of diphenylanthracene in enough dimethyl phthalate to make 10 mL of solution. The working solution (10^{-4} M) is prepared by diluting a 1-mL aliquot of stock solution to 10 mL. A 3-mL portion of this solution is transferred into a fluorometric cuvette and the fluorescence spectrum is recorded by excitation of the solution at 350 nm and scanning the emission between 380–550 nm; the maximum of the emission is at 427 nm.

Chemiluminescence Spectrum. A two-component system was adopted for the chemiluminescence testing. Component A is prepared by adding 20 mL of dimethyl phthalate and 20 mg of diphenylanthracene to 2.0 g BBTPO and heating the mixture in a water bath to provide complete dissolution of the solids. Component B is prepared by adding enough dimethylphthate/tertiary butanol (4/1, v/v) to bring the volume to 10 mL to 0.5 mL of concentrated H_2O_2. This solution can be prepared in advance as a stock solution by a teaching assistant. Aliquots of this solution are then distributed to each student group.

The chemiluminescence is initiated by pipetting a 1-mL aliquot of component B to 2 mL of the solution of Component A in a test tube and shaking the tube to provide thorough mixing. A bright purple chemiluminescence emission is observed for at least 1 h. The emission spectrum is obtained by scanning the emission between 380 and 550 nm after transferring this solution to a cuvette and placing it in the holder of the spectrophotofluorometer.

Chemiluminescence Intensity Decay Curves. Three samples are prepared in test tubes. Into one is weighed 2 mg of sodium salicylate, into another is weighed 2 mg oxalic acid, and the last is left as the blank. Into each tube, 2 mL of component A and 1 mL of component B are combined via pipette. After complete mixing, the solutions are transferred rapidly to three cuvettes. The time-dependent emission intensities of the samples at λ_{em} = 427 nm are measured every 5 min during 1 h. Plots of intensity versus time (the intensity decay curve) are then obtained.

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