Photooxidative Transformations of Anthrone, Bianthronyl, and Bianthrone in Acid Solution

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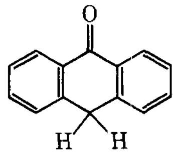
Time-lapse spectrometry and preparative-scale analytical data have shown that the hydroxylcarbocation of anthrone, when irradiated with visible or near-ultraviolet light, undergoes a three-step photooxidative transformation. The first is a photodehydrodimerization to protonated bianthronyl which in the next less efficient step is converted to the hydroxycarbocation of anthraquinone. As the irradiation time is extended, the protonated anthraquinone is further photooxidized to the sulfuric ester of 2-hydroxyanthraquinone. There is no evidence for the formation of bianthrone or naphthobianthrone, the "natural" photooxidative products of anthrone and bianthronyl in neutral solvents. In separate experiments, bianthrone was smoothly converted to *meso*-naphthobianthrone by photolysis is sulfuric acid.

The photochemistry of anthrone (1), $\Delta^{10,10'}$-bianthrone (2), dibenzo[*a,o*]perylene-7,16-dione ("helianthrone") (3), and their derivatives in neutral organic solvents has been investigated[2-7] not only because of their own synthetic and mechanistic significance but also because these molecular systems offer a suitable structural model for photodehydrocyclization, a general reaction of considerable theoretical and bichemical importance.[8]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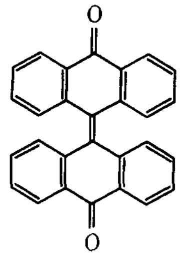
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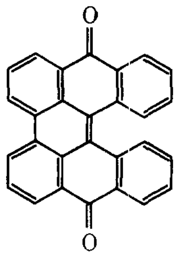
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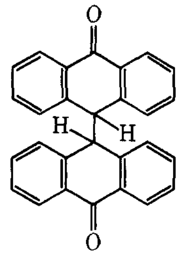
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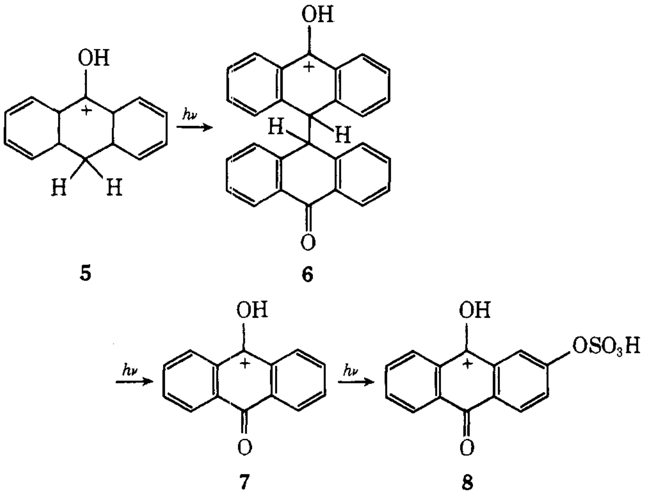
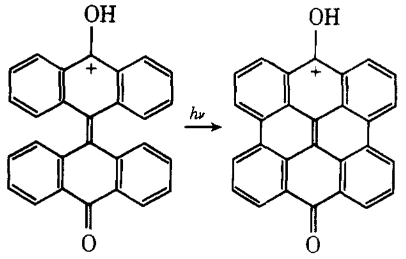
As a natural extension of our own interest in photocyclization[9] and in the photochemistry and molecular spectroscopy of representative carbonyl compounds in strongly acidic media.[10-12] we have investigated the light-induced reactions of anthrone 1, bianthrone 2, and bianthronyl 4 in concentrated sulfuric acid. In this paper, we present spectroscopic and preparative-analytical evidence for a sequential three-step photooxidative transformation of anthrone. In the first step protonated anthrone 5 undergoes photodehydrodimerization to the hydroxycarbocation derived from bianthronyl 6. In the second slower step, bianthronyl 6 is converted to protonated anthraquinone 7, which, in turn, is changed photochemically in the last step to anthraquinone 2-sulfate 8.



5 6 7 8

We also show that bianthrone 9, when irradiated in concentrated sulfuric acid, undergoes double photodehydrocyclization to protonated phenanthro[1,10,9,8-*opqra*]perylene-7,14-dione (*meso*-naphthiobianthrone, 10).



9 10

Results

Anthrone dissolved readily in concentrated sulfuric acid to form stable yellow solutions with ultraviolet absorption maxima at 352, 282, 273 (sh), 247, 240 (sh), and 210 nm, as shown in Figure 1, curve 1. Since the electronic absorption spectrum is completely different from that of anthrone in neutral organic solvents, it is reasonable to assume[10] that, in sulfuric acid, 1 is completely protonated to 5.

Solutions of 5 (10^{-4}–10^{-5} M) displayed no significant spectral changes over extended periods of time (weeks) while stored in the dark at ambient temperature under nitrogen. That no irreversible chemical transformations take place either on dissolving or on storage in the dark for weeks in closed containers was also shown by recovery experiments in which more concentrated (10^{-1} M) solutions of anthrone in acid were hydrolyzed weeks after preparation, and extracted with methylene chloride: virtually quantitative amounts of unchanged anthrone were recuperated.

Dark Reactions of Anthrone. In the presence of dissolved oxygen, protonated anthrone undergoes a slow dark reaction to anthraquinone. This transformation was conveniently followed by time-lapse UV–visible spectrometry.[13] The absorption spectra of dilute acid solutions of 1 in closed and open cells with initial oxygen saturation or with continuous O_2

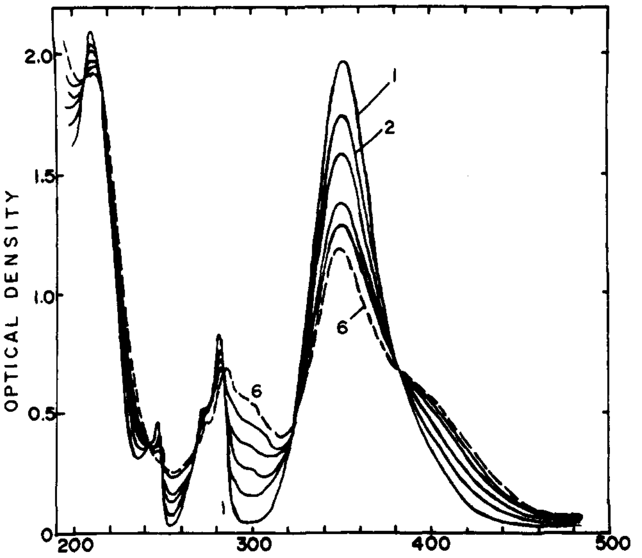


Figure 1. Changes in the UV-visible absorption spectrum of a 7 × 10^{-5} M solution of anthrone in sulfuric acid on irradiation with a 9-W long-wave UV hand lamp. 1: before irradiation. 2–6: after 0.5, 1, 2, 3, and 4 h total irradiation, respectively.

passage were intermittently monitored over periods of weeks.

The progressive changes in the spectra of these solutions stored in the absence of light at room temperature clearly showed that **5** reacts slowly with available oxygen to form only one product, protonated anthraquinone. The corresponding intermediate spectra could be reproduced with equivalent solutions prepared from anthrone and anthraquinone. If no additional oxygen was provided, the reaction mixture remained stable indefinitely after consumption of dissolved oxygen. Under continuous oxygen bubbling, however, the transformation continued to completion. Ultimately, a typical protonated anthraquinone spectrum[12] with λ_{max} at 270, 310, and 410 nm was obtained.

It should be pointed out that the reaction of protonated anthrone **5** with residual oxygen in sealed cells, with or without prior deoxygenation, is too slow to interfere significantly with the photochemical reactions described below.

The other aromatic ketones in this study were found to be stable indefinitely in concentrated sulfuric acid. The UV-visible absorption spectra of dilute acid solutions of bianthrone, bianthronyl, anthraquinone, and naphthobianthrone remained unchanged after many weeks of storage in the dark in capped cells.

Time-Lapse Spectrometry. A. Anthrone and Bianthronyl. Figure 1 shows the successive changes taking place in the UV-visible absorption spectrum of a 7 × 10^{-5} M solution of anthrone **1** in sulfuric acid over an initial period of 5 h on continuous irradiation in a 1-cm cell with 9-W long-wave hand lamp. The consecutive spectral recordings formed seven clearly defined isosbestic points at 381, 321, 285, 270, 249, 241, 216, and 205 nm. The presence of these points of equivalent absorbance indicate that the photoreaction taking place throughout this irradiation period is quite free of significant side reactions.

The spectral changes observed in the same solution on further continuous irradiation beyond the initial 5 h are shown in Figure 2. Since the total photolysis time represented in this second diagram extends from 5 to more than 350 h, it is quite evident that the monitored photoreaction is much slower. Close inspection of Figure 2 reveals the presence of three "nearly isosbestic" points around 225, 305, and 415 nm. The slight departure from "isosbesticity" around 305 nm is easily understood in terms of the still-present tail end of the original phototransformation depicted in Figure 1 and of two other slow consecutive photochemical reactions which became evident in the preparative-scale irradiations described below.

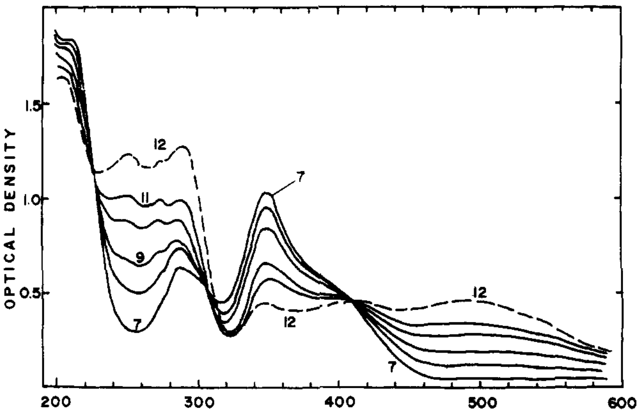


Figure 2. Photolysis of anthrone in acid, continuation. 7–12: after 19, 65, 134, 206, 254, and 376 h total irradiation, respectively.

During the continuous-irradiation experiments, the initial yellow anthrone solution changed to a deep brown-purple color consistent with the attendant increase in absorbance in the visible region.

The time-lapse spectrometry of *bianthronyl* in sulfuric acid will not be shown in a separate diagram because it would represent a duplication. The UV-visible absorption of bianthronyl in acid was virtually identical with that shown in Figure 2, scan 7, with maxima at 286 and 347 nm. The changes in this absorption on irradiation with near-ultraviolet light closely paralleled those shown in Figure 2 for the photolysis of anthrone in excess of the first 5 h.

The virtual identity of bianthronyl absorption in acid and curve 7 in Figure 2 and their subsequent changes under irradiation strongly suggested that bianthronyl is the first photoproduct formed during photolysis of anthrone in acid. This was confirmed by the preparative-scale photoreactions described below. The identity of the final photoproduct from either **1** or **4**, anthraquinone 2-sulfate **8**, however, cannot be easily inferred from the TLS experiments.

The progress of the photochemical reaction of anthrone or bianthronyl in acid was also followed conveniently by monitoring the fluorescence spectrum of dilute (~10^{-5} M) solutions undergoing photolysis. Protonated anthrone **4** exhibited broad-band blue-green fluorescence centered at 472 nm in good mirror-image relationship with its excitation maximum at 352 nm. As the phototransformation proceeded, the fluorescence of protonated bianthronyl centered at 508 nm became detectable and increased in intensity with extent of irradiation. The excitation spectrum of this emission was concordant with the absorption spectrum of bianthronyl in sulfuric acid. Finally, after prolonged irradition (~2 weeks, 9-W lamp) the orange fluorescence of anthraquinone 2-sulfate **8** with λ_{max} at 583 nm became readily detectable.

Comparison of these emission spectra with those of authentic samples of bianthronyl and 2-hydroxyanthraquinone[14,15] in acid confirmed their origin. Both the emission and excitation spectra of **5**, **6**, and **8** are sufficiently different to allow sensible interpretation of the emission from mixed solutions. Besides, since the photodehydrodimerization of **5** takes place much more rapidly than the subsequent photooxidation of **6** to **8**, one essentially determines only emission from binary mixtures of either **5** and **6** or **6** and **8**. In separate experiments with both anthrone and bianthronyl, it was found that the electronic absorption spectra of solutions undergoing

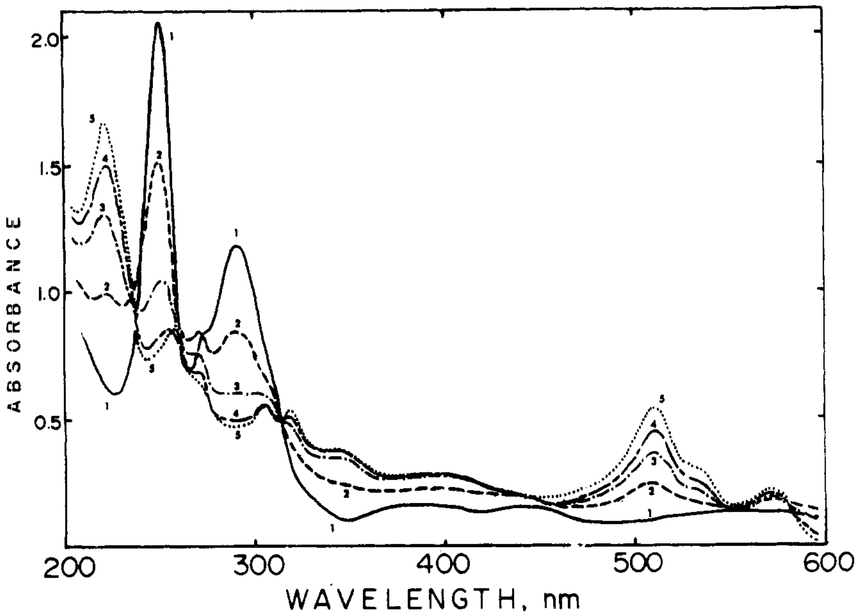


Figure 3. Photolysis of bianthrone in acid. 1: 4 × 10^{-4} M bianthrone in sulfuric acid, before irradiation. 2–5: after 15, 30, and 45, and 70 min total photolysis, respectively.

photolysis did not change at all when the irradiation was interrupted and the cells stored in the dark. This was true at any stage throughout the photolysis. The lack of spectral change testifies that the reactions illustrated in Figures 1 and 2 are indeed photochemically initiated with no significant contribution from slow parallel dark transformations.

B. Bianthrone. The absorption spectrum of dilute **2** in concentrated acid is shown in Figure 3, scan 1. Consecutive irradiations in the UV or visible range caused progressive decrease in bianthrone maxima and appearence and increase in new peaks characteristic of *meso*-naphthobianthrone in acid.

The naphthobianthrone was separately prepared from bianthrone by photolysis if *p*-xylene.[14] Its UV-visible absorption spectrum in pure sulfuric acid resembled closely that of an acid solution of bianthrone after prolonged near-UV or visible irradiation. Although the scans in Figure 3 pass through an isosbestic point at 315 nm, the isosbestic behavior is not preserved in the visible and in the short-ultraviolet regions of the spectrum. The significance of these observations will be discussed below.

Preparative-Scale Photoreactions. A. Anthrone. Relatively concentrated sulfuric acid solutions of anthrone (10^{-2}–10^{-1} M) were irradiated in the Hanovia immersion well with a 450-W medium-pressure Hg arc lamp under inert atmosphere for 25–35 h. At the end of this interval, the acid solution was poured over ice and extracted with methylene chloride. From the extract, bianthronyl was isolated in amounts equivalent to 50–65% of initial anthrone used. The identity of the bianthronyl photoproduct was established not only by elemental analysis, molecular weight, and melting point but also by comparison of IR, NMR, and UV spectra with those of an authentic sample. Unreacted anthrone (25–40%) was also recovered from the hydrolyzed photolysate.

B. Bianthronyl. Acid solutions of bianthronyl (10^{-2}–10^{-1} M) were exposed in separated reaction tubes under nitrogen to near-ultraviolet and/or visible light for periods extending from a few days to several weeks. The UV–visible spectra of acid-diluted aliquots were examined periodically. The reaction tubes were removed from exposure at various intervals during photolysis and their content quenched in sodium bicarbonate aqueous solutions or on ice and extracted with ether, benzene, or methylene chloride. The products were separated using silica gel thin layer and column chromatography and analyzed by UV–visible and IR spectrometry and comparison with authentic samples. Four components were identified: unreacted bianthronyl, anthraquinone, 2-hydroxyanthraquinone, and anthrone. The last two were found only in trace amounts even after lengthy irradiation. It is important to point out that at no time throughout several weeks of photolysis of bianthronyl in acid were we able to detect the presence of any other intermediates or products. This was true for both the diluted aliquots and the quenched preparative samples. The bianthronyl concentration decreased slowly with extent of irradiation while anthraquinone content increased proportionally. The 2-hydroxyanthraquinone accumulated only to a minor extent toward the end of the exposure while anthrone was present only in minute amounts. The UV–visible spectrum of a diluted acid aliquot did not differ significantly from that of a quenched sample, extracted, evaporated, and redissolved in acid. Such an absorption spectrum could be reproduced closely with fresh bianthronyl, anthraquinone, and 2-hydroxyanthraquinone dissolved in sulfuric acid in appropriate concentrations.

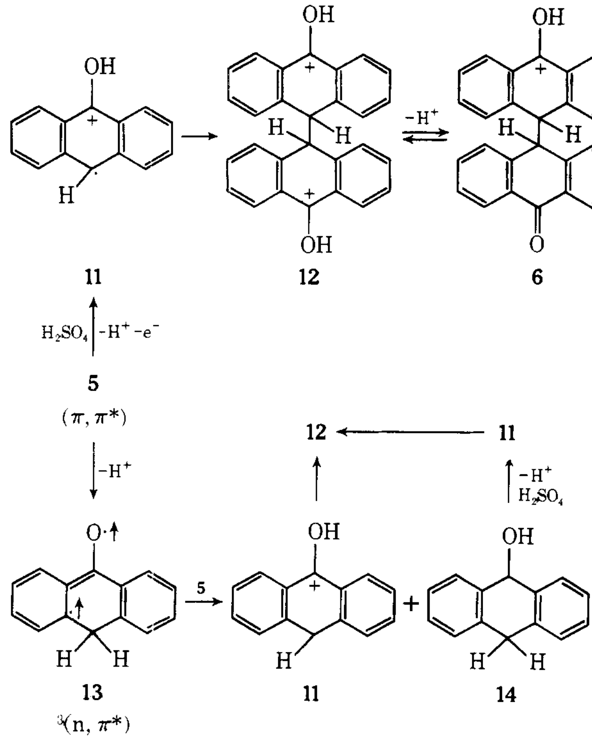
C. Bianthrone. Irradiation of 10^{-2} M solutions of bianthrone in sulfuric acid for 1 to 2 weeks with a 275-W sun lamp followed by quenching on ice, extraction with benzene, evaporation, and analysis showed variable conversion to *meso*-naphthobianthrone. Attempts to isolate helianthrone in significant amounts were unsuccessful. The identity of naphthobianthrone product was readily established by comparison of its IR spectrum with that of an authentic sample.

Discussion

The initial clean photochemical reaction of dilute anthrone in acid during the first 5 h of irradiation corresponds to a nearly quantitative conversion to protonated bianthronyl **6.** The identity of **6** was established not only by the ability to reproduce the spectral changes illustrated in Figure 1 with equivalent nonirradiated acid solutions of anthrone and bianthronyl, but also by isolation of bianthronyl in better than 50% yield from preparative-scale reactions in which the irradiation was interrupted before the next slower photoconversion became significant.

Close examination of the last curve in Figure 1 reveals that there was very little residual anthrone at the end of 5 h of photolysis. This is shown by comparing the absorbance at 420 nm, where only photoproduct **6** exhibits absorption, with that around 348 nm, where both **5** and **6** have significant absorption. For instance, a pure solution of bianthronyl in sulfuric acid with an absorbance of 0.25 OD units at 420 nm has a corresponding 1.1 units absorbance at 340 nm. If significant amounts of residual anthrone were present in the solution irradiated for 4 h (curve 6, Figure 1), the absorbance at 348 nm would certainly exceed the observed 1.1 OD units.

Scheme I



The formation of the first photoproduct, protonated bianthronyl **6**, seems to require bimolecular coupling of radical ion **11** (see Scheme I). This assumption is not based only on analogy with the photodimerizations of acridines,[16-19] acridinium salts,[16,20,21] and 9-bromoanthrones[22] but also on the lack of other reasonable alternatives. For example, radical addition to the 9 position, a path which had to be ruled out in the case of acridine photooxidative dimerization,[17-19] is not available for the Dneaction of protonated anthrone **4**.

Although the coupling of two cationic radicals postulated above seems to be an electrostatically unfKvorable event, such reactions are well documented both in ground-state[23] and in photochemical[24] reactions.

The generation of **11** can be visualized to occur in two ways as depicted in Scheme I. The first would involve interaction of the π,π^* excited state of **5** with the solvent and direct formation of **11** presumably by hydrogen-atom transfer. The other alternative would require deprotonation of the π,π^* state followed by radiationless transition to a lower lying n,π^* triplet **13** which in turn would abstract a hydrogen atom from a ground-state **5** molecule with formation of a radical cation **11** and a neutral radical **14**. This latter species would then react with the solvent to generate another molecule of **11**. However, the second process seems much less probable in view of estimated rate constants for the individual steps and the need for a bimolecular reaction between excited **13** and **5** at low solute concentrations (10^{-5}).

Both redox reactions involving the solvent and either the π,π^* excited **5** or radical **14** are possible. For example, Deno et al.[25] have shown that concentrated sulfuric acid readily converted xanthene to xanthyl cation. If the acid concentration was 85% or higher, this hydride transfer reaction to the solvent was instantaneous.[25]

Since no intermediates in the **5** → **6** reaction were detected spectroscopically and no products other than bianthronyl could be identified, it is difficult to differentiate between the two mechanistic possibilities outlined in Scheme I. The fact that protonated anthrone **5** emits strong $\pi^* \rightarrow \pi$ fluorescence shows that the radiative deactivation of its π,π^* singlet successfully competes with both reaction with oxidizing solvent and deprotonation.

The subsequent steps in the photochemical reactions of anthrone in acid, namely the conversion of bianthronyl to anthrquininone and then to 2-hydroxyanthraquinone sulfate, are much less efficient than the initial **5** → **6** step. It has been shown that in neutral solvents the photooxidative transformations of bianthronyl lead first to bianthrone **2** and then to *meso*-naphthobianthrone.[2] In sulfuric acid, however, there is no evidence of formation of either one of these two dehydrocyclization products. This behavior in strong acid seems to be a natural consequence of the ground state protonation of bianthronyl. The **12** ⇄ **6** equilibrium is probably displaced greatly toward the double protonated species **12**. This seems reasonable in view of the lack of conjugation between the two "anthrone" halves of bianthronyl and their nearly perpendicular relative orientation.[26] Furthermore, this hypothesis is even more acceptable in view of the demonstrated diprotonation of both carbonyl groups of conjugated aromatic diketones and quinones in concentrated sulfuric acid.[27]

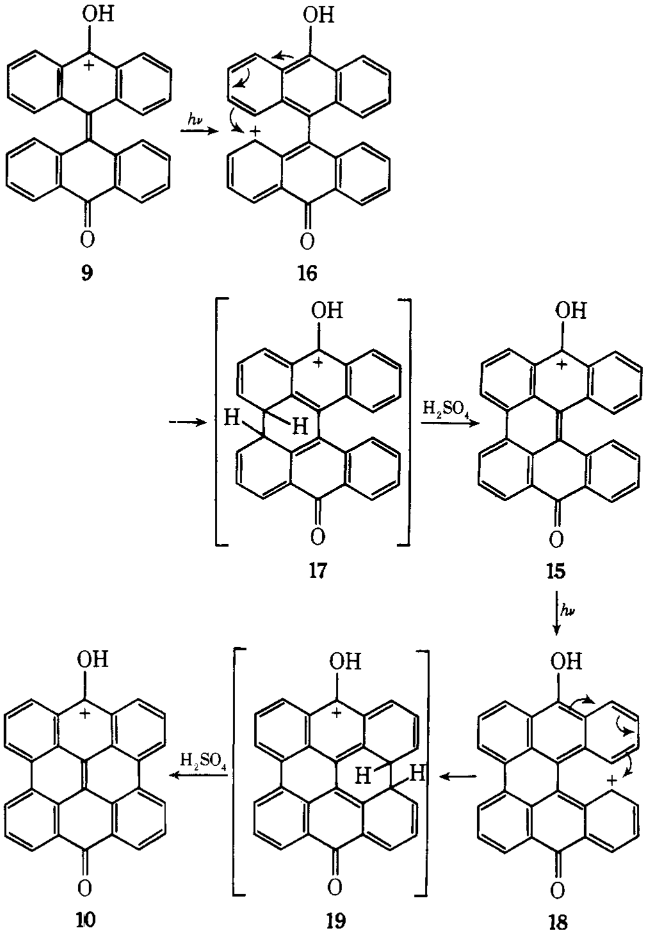
Protonation at both carbonyl groups in **12** eliminates the n,π^* set of levels on direct excitation. Consequently, the π,π^* excited singlet formed on photon absorption has more favorable deactivation paths available than deprotonation and intersystem crossing to an n,π^* triplet which is suspected to be responsible for H abstraction from another bianthronyl molecule in neutral solvents.[2] Furthermore, such a hydrogen abstraction in the case of **12** would involve a collision between a divalent and a monovalent cation, an electrostatically unfavorable event. It is probable that the other options accessible to π,π^* excited **12**, namely, fluorescence, dissociation to two radical cations **11**, and radiationless deactivation, are able to completely suppress photooxidation to bianthrone. The formation of anthraquinone on very long exposure to light in acid is most probably a consequence of the side reaction of cation radicals **11** with the oxidizing solvent. The last step in this sequence of photoreactions, the formation of 2-hydroxyanthraquinone from anthraquinone, has been studied separately and reported elsewhere.[12]

There is little doubt that the irradiation of protonated bianthrone **9** leads eventually to nearly complete conversion to naphthobianthrone **10**. However, the transformation is not a direct **9** → **10** reaction. This is demonstrated by the family of scans in the time-lapse spectrometry diagram shown in Figure 3. In spite of the apparent isosbestic point at 315 nm, there are clear departures from "isosbesticity" in the 230–280-nm and 500–700-nm regions. In addition, there are small peaks detectable in the intermediate scans at 272, 346, and 402 nm which cannot be accounted for by the absorption of either **9** or **10**. In fact these peaks are at the same wavelengths as the maxima reported for the absorption of helianthrone in sulfuric acid.[15] Furthermore, the isosbestic point at 315 nm in Figure 3 coincides with the wavelength of equiabsorptivity of **9**, **10**, and **15**. This not only reinforces the suggested **9** → **15** → **10** photoxidative mechanism but also explains the fortuitous occurrence of an isosbestic point at 315 nm. The existence of this point also testifies to the absence of side reactions, since any intermediate or product other than **9**, **15**, or **10** would either add its own absorbance at 315 nm or depress the total optical density at this wavelength of its absorbs less than its precursor.

The photodehydrocyclizations of bianthrone 2 and helianthrone 3 in nonacidic solvents have been studied by Brockmann and Muhlmann.[4] They clearly established the fate of the hydrogen atoms lost by the reacting molecules. There is no formation of gaseous hydrogen. In the presence of dissolved oxygen in nonoxidizing solvents hydrogen peroxide was detected.[4] On the other hand, in the absence of oxygen and in solvents unable to accept the hydrogen atoms, an exact disproportionation was noted with the molecules undergoing dehydrocyclization being equal to those being converted from diketones to diphenols.

There is little doubt that the hydrogen atoms lost by bianthrone and helianthrone during photolysis in sulfuric acid are readily accepted by the oxidizing solvent. The probable overall mechanism is shown in Scheme II.

Scheme II



The photooxidative cyclization of bianthrone in sulfuric acid is a very efficient reaction. The quantum yield determined from disappearance of reactant at less than 20% conversion was over 0.9. This efficiency may be explained by the high probability of cyclization in protonated excited ketones **18** and **21** and the ability of the solvent to accept hydrogen atoms of intermediates **19** and **22**. The excited states of **9** and **15** were arbitrarily represented by the valence-bond structures **16** and **18**, respectively, which exhibit the difference in electronic density in the carbon atoms involved in cyclization.

The sum of the free valence numbers in the first excited electronic state ΣF_r^* of the atoms involved in the cyclization step was estimated by an MO–SCF–CI calculation with appropriate corrections for the oxygen atoms.[28–31] The π delocalization included both oxygen atoms in bianthrone but extended[10] only over the carbonyl oxygen in its respective hydroxycarbocation **9**. The ΣF_r^* values for bianthrone were 0.879 in the ground state and 0.898 in the first excited singlet or triplet state. For its cation **9**, the ΣF_r^* values in the S_1, T_1, and T_2 states were 0.925, 0.912, and 1.003, respectively. These results are only moderately consistent with the observed more facile photocyclization in the protonated species.[28]

Experimental Section

Fluorometric grade pure sulfuric acid (Matheson) was used for all time-lapse spectrometry determinations. Reagent-grade acid (Fisher, 96%) was adequate for preparative-scale reactions, after verifying that TLS in this acid was the same as in the 100% fluorometric grade. UV–visible absorption spectra were recorded on a Cary Model 15 spectrophotometer in double-beam mode. Infrared spectra were taken on a Perkin-Elmer 221 spectrometer. Emission spectra were recorded on a Hitachi Perkin-Elmer SPF spectrophotometer. Ultraviolet Products 9-W UV hand lamps were used for most TLS experiments. A GE 275-W sun lamp or the Hanovia 450-W Hg lamp were used for preparative-scale photolysis.

Recovery of Anthrone from Acid. Anthrone (1.013 g, 5.2 mmol) was dissolved in 50 ml of 96% sulfuric acid. The yellow solution was kept in a closed flask for 1 week. A diluted aliquot showed an unchanged UV–visible spectrum. The acid solution was added dropwise to 350 g of ice when a white precipitate formed. Extraction with CH_2Cl_2, washing of the organic phase with 5% aqueous $NaHCO_3$, drying over anhydrous $MgSO_4$, and vacuum evaporation of solvent yielded 0.94 g (93%) of an off-white crystalline material, mp 152–156 °C. The IR spectrum and melting point of an ether–benzene recrystallized sample (155 °C) showed it to be unchanged anthrone.

Photolysis of Anthrone. Anthrone (1.17 g, 5 mmol) in 350 ml of 96% sulfuric acid was photolyzed with a 450-W medium-pressure Hg arc lamp in the Hanovia immersion well for 30 h while N_2 was bubbled continuously and cooling water was circulated through the well mantle. The progress of the reaction was followed by recording UV–visible spectra of diluted aliquots. The final solution was added dropwise to crushed ice, extracted with CH_2Cl_2, and worked up as above, obtaining 0.9 g (86%) of a crystalline product. Thin layer and column chromatography on silica gel afforded separations into two components, identified by IR, UV, NMR spectra, and melting point to be unreacted anthrone and bianthronyl in 42 and 58% yield, respectively.

Photolysis of Bianthronyl. Bianthronyl (0.2 g) was dissolved in 5 ml of 96% sulfuric acid under constant magnetic stirring. The deep yellow solution was placed in three different 0.5-cm quartz tubes and irradiated with a GE 275-W sun lamp while bubbling O_2-free nitrogen through capillary tubes immersed in the acid solutions and having the outside of the tubes cooled with running water. The tubes were photolyzed for 200, 500, and 800 h, respectively. Aliquots were taken at different intervals, volumetrically diluted, and the UV–visible spectra recorded. At the end of the photolysis the green content of the tube was poured dropwise with constant stirrings into saturated aqueous $NaHCO_3$ (or ice), extracted repeatedly with ether (or methylene chloride), washed with distilled water, dried over anhydrous $MgSO_4$, filtered, and rotary evaporated. The greenish impure crystals were dissolved in a small amount of $CHCl_3$ and chromatographed on a silica gel column by eluting with petroleum ether, chloroform, and ethyl acetate. Evaporation of fractions and (1) comparison with the thin layer pattern, (2) IR, UV–visible, and emission spectrometry, and (3) comparison with authentic samples confirmed the presence of unreacted bianthronyl, anthraquinone, 2-hydroxyanthraquinone, and anthrone. The last two were found only in trace amounts in all three tubes. The amount of anthraquinone increased at the expense of bianthronyl as the time of photolysis was extended.

Photolysis of Bianthrone. Bianthrone (0.2 g) was dissolved in 10 ml of 96% sulfuric acid and irradiated under N_2 with water cooling for 2 weeks with the GE 275-W sunlamp. Hydrolysis on ice, extraction with benzene, and evaporation yielded 0.11 g of crude *meso*-naphthobianthrone, identified by comparison of IR, UV–visible, and NMR spectra with those of an authentic sample prepared from bianthrone by photolysis in xylene.[14]

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Catecholborane (1,3,2-Benzodioxaborole). A Versatile Reducing Agent[1]

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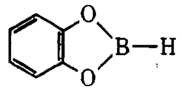
The reaction of 1,3,2-benzodioxaborole [catecholborane (CB)] with representative functional groups was studied to determine the utility of CB as a selective reducing agent. The approximate rates, stoichiometry, and products of the reductions were determined under standard conditions ($CHCl_3$, 25 °C). The results indicate that CB is unique compared to other substituted boranes. The reduction rates appear to be solvent independent with the exception of alkenes. Primary alkenes react very sluggishly, whereas secondary alkenes are unreactive at room temperature; as a result, many selective reductions can be performed in the presence of alkenes.

In the important area of selective reductions, we wish to report on the useful applications of catecholborane (1,3,2-benzodioxaborole, 1). Although borane complexes[2,3] and substituted boranes[4,5,6] have been employed as selective reducing agents, catecholborane (CB) has certain unique properties which merit attention. Recently, a review article on some of the chemistry of CB has appeared.[7]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CB has some practical advantages over other, commonly used reducing agents: (1) It is a liquid at room temperature and may be used without solvent.[8] (2) CB is soluble and stable in all common, aprotic solvents (e.g., benzene, toluene, chloroform, ether, hexane, etc.). (3) CB is stable in dry air and reacts only slowly with moist air. (4) CB may be stored unchanged for over a year at 0 °C, in contrast to certain other substituted boranes.[9,10]

Results and Discussion

Since this study was carried out to determine the relative reactivity of CB toward various functional groups, a standard set of conditions was selected. The reactions were conducted at room temperature, generally in $CHCl_3$, with stoichiometric amounts of hydride and substrate (with the initial concentration of substrate at approximately 0.5 M). Faster reaction can be achieved by using excess hydride, raising the temperature, or increasing the concentration of the substrate. The rates of reduction were usually independent of the solvent utilized, although the hydroboration of alkenes was, in fact, solvent dependent[11] (Table I).

The reactivity exhibited by the various functional groups toward CB in $CHCl_3$ can be classified for convenience into three broad categories:

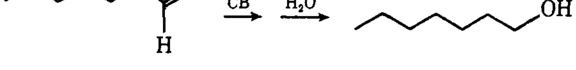
(1) Fast—those functionalities that react in 24 h or less (Table II).

(2) Slow—those functionalities whose reaction times exceed 24 h (Table III).

(3) Inert—those functionalities that exhibit no reactivity toward CB (Table IV).

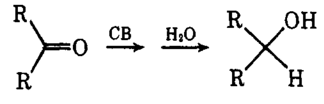
The data in the tables demonstrate that there is a wide range of reactivity within each category.

Aldehydes, Ketones, and Derivatives. Heptanal and benzaldehyde were investigated as representatives of aliphatic and aromatic aldehydes. Heptanal is rapidly and quantitatively reduced to the corresponding alcohol (eq 1).[12] Likewise, benzaldehyde is reduced rapidly to benzyl alcohol.



(1)

Cyclic and acyclic aliphatic ketones were reduced in high yields (eq 2).[12] 2-Octanone was slowly reduced with 1 or 2 equiv of hydride. On the other hand, cyclopentanone and cyclohexanone exhibited varying degrees of reactivity,[13] as shown in the tables.



(2)