

## Anodic Oxidation of Anthracenes and Related Compounds

### Part V. Oxidation of Anthracene and 9-Methoxyanthracene in the Presence of Alcohols in Acetonitrile

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The anodic oxidation of anthracene in acetonitrile containing alcohol is accompanied by the consumption of 3.0 Faradays per mole of substrate. Anthrone was definitely ruled out as an intermediate by showing it to be stable to the isolation procedure or to air-oxidation in acetonitrile. 9-Alkoxyanthracene was shown to be a likely intermediate in formation of bianthrone. 9-Methoxyanthracene was observed to undergo 1.0 electron oxidation accompanied by the quantitative generation of bianthrone.

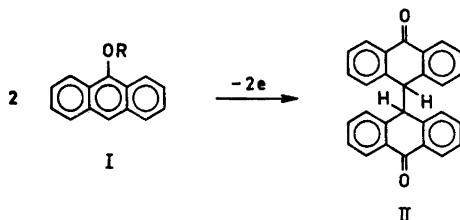
Several years ago it was discovered that the anodic oxidation of anthracene in acetonitrile containing ethanol produced bianthrone.<sup>1</sup> A coulometric investigation of this reaction led to the conclusion that the mechanism involves 2 electron oxidation to 9-anthrone which is converted to bianthrone by air oxidation during isolation.<sup>2</sup> In a preliminary account of this work, it was found that bianthrone results from a three electron anodic oxidation, and that 9-anthrone is stable to the reaction conditions and, if formed, would be isolated as such.<sup>3</sup>

Since these results<sup>3</sup> are so radically different from those of other authors<sup>2</sup> it is necessary to critically evaluate the results in terms of product purity, possible intermediates, and the effect of water on the coulometry and yield of products. Previous work did not involve the determination of the yield of bianthrone, and it seemed desirable to do so at this time.

Furthermore, the role of alcohol in the oxidation had not been adequately investigated. Majeski *et al.*<sup>2</sup> did not consider intermediates which are the result of alcohol acting as a nucleophile toward anodically generated species. One possible intermediate, 9-alkoxyanthracene (I), a two electron oxidation product, could undergo one electron oxidation accompanied by alkyl transfer

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to give the dimeric product. An oxidative alkyl transfer of this type has been observed to occur during the anodic oxidation of the dimethylether of durohydroquinone in acetonitrile.<sup>4</sup> 9-Acetoxyanthracene has been observed to undergo one electron oxidation and produce bianthrone when oxidized in acetonitrile-acetic acid,<sup>5</sup> implicating it as a possible intermediate of the



oxidation of anthracene to bianthrone in that solvent system. We have shown that anthraquinone, not bianthrone, is the major product obtained during the anodic oxidation of anthracene in acetonitrile containing low concentrations of water.<sup>6</sup> Since the presence of alcohol, even at low water concentration, brings about the formation of bianthrone as the major product it appeared likely that 9-alkoxyanthracene is indeed an intermediate.

## RESULTS

Peak voltammograms for the anodic oxidation of anthracene and 9-methoxyanthracene in "dry" acetonitrile in the presence and absence of ethanol are illustrated in Fig. 1. The peak current for the anodic oxidation of anthracene at a voltage sweep rate of 10 V/min was 382  $\mu$ A in the absence of ethanol, and 336  $\mu$ A with ethanol (100 mM) present. The same concentration (1.5 mM) of 9-methoxyanthracene produced a peak current of 94  $\mu$ A and 100  $\mu$ A in the presence and absence of ethanol (100 mM), respectively.

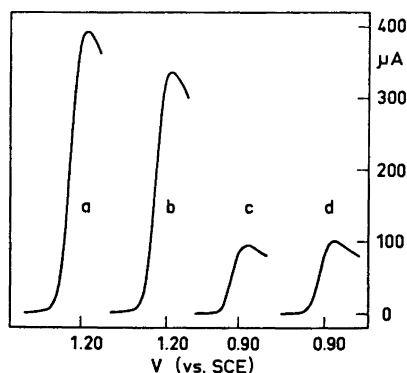


Fig. 1. Peak voltammograms for the oxidation of anthracene in the absence (a) and presence (b) of ethanol; 9-methoxyanthracene in the absence (c) and presence (d) of ethanol.

Controlled potential<sup>3</sup> and constant current coulometry<sup>7</sup> data have previously been presented for the anodic oxidation of anthracene in the presence of ethanol. Several runs were conducted on the oxidation of anthracene in the presence of methanol and on 9-methoxyanthracene, both in the presence and

Table 1. Constant current coulometry<sup>7</sup> of the anodic oxidation of anthracene and 9-methoxyanthracene.

Run	Substrate <sup>a</sup>	Nucleophile <sup>b</sup>	<i>n</i> <sup>c</sup>
1	Anthracene	MeOH	3.06
2	Anthracene	MeOH	3.08
3	Anthracene	MeOH	3.03
4	9-MA	—	0.96
5	9-MA	—	0.97
6	9-MA	MeOH	0.97
7	9-MA	MeOH	0.98
8	9-MA	EtOH	0.95
9	9-MA	EtOH	0.97

<sup>a</sup> Substrate (0.1 mmole) in acetonitrile (40 ml) containing LiClO<sub>4</sub> (0.1 M).

<sup>b</sup> Concentration equal to 100 mM.

<sup>c</sup> Obtained at a constant current of 50.0 mA and expressed in Faradays per mole of substrate.

absence of methanol or ethanol. These runs are summarized in Table 1. The coulometric *n* value for the oxidation of anthracene in the presence of methanol was found to be equal to 3.06 Faradays per mole of anthracene. The *n* value for the anodic oxidation of 9-methoxyanthracene was found to be equal to 0.97 either in the presence or absence of the alcohols. These runs were conducted using anhydrous (4 mM) acetonitrile under an atmosphere of dry argon without any other special precautions to keep out water.

Several runs were carried out to determine the effect of water concentration on the coulometric *n* value for the anodic oxidation of anthracene in acetonitrile containing ethanol. In order to rigorously exclude water, a specially constructed cell was used. The reference electrode was a silver wire inserted through the gas inlet which entered the bottom of the cell. The only other opening to the anode compartment was a small hole near the top which served both as gas outlet and lead-in for the anode. Before use, the apparatus was thoroughly flamed while passing dry argon through the cell. With argon still flowing through the cell, anhydrous lithium perchlorate and silver perchlorate along with anthracene were added by momentarily removing the upper part of the cell (which also served as the auxiliary compartment), separated from the anode chamber by a glass frit. Acetonitrile ((H<sub>2</sub>O) ≥ 2 mM) was added to the cell with a syringe. The electrolysis was started after most of the anthracene dissolved. Stirring was accomplished by bubbling argon through the electrolyte. Three runs conducted in this manner, along with several others in which water was intentionally added, are summarized in Table 2. The results of the three "anhydrous runs" show an average of 2.87 Faradays per mole of substrate. Run 13,

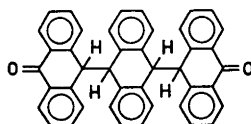
Table 2. Effect of water on the anodic oxidation of anthracene in acetonitrile containing ethanol.

Run	(H <sub>2</sub> O added)	<i>n</i> <sup>a</sup>
11	0	2.90
12	0	2.84
13 <sup>b</sup>	0	2.88
14	14	3.18
15	42	3.08
16	140	2.94
17	1400	2.87
18	3000	2.81

<sup>a</sup> From constant current coulometry,<sup>7</sup> expressed as Faradays per mole of substrate.

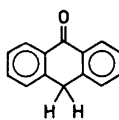
<sup>b</sup> 0.5 mmoles of substrate oxidized at 100 mA, all other runs on 0.1 mmoles at 50 mA.

in which enough substrate (89 mg) was oxidized to allow product isolation, was carried out by adding more anthracene to the solution from run 12 immediately after finishing that run. The effect of adding water on the coulometric *n* value was to cause first an increase (run 14), and then a gradual decrease to the lowest value (run 18) at a water concentration of 3 M. During two runs (17 and 18), a small amount of a white solid separated, which was recovered and identified as the trimer, III, by comparison of the IR spectrum with that of authentic material.<sup>6</sup>



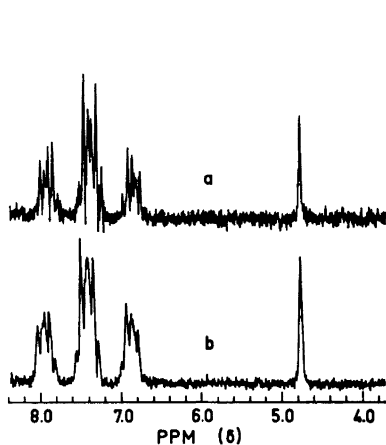
III

The product isolated from coulometric run 13 appeared to be pure bianthrone (II) by IR analysis. The NMR spectrum of the product (Fig. 2a) integrated correctly for pure bianthrone and was identical to the spectrum of three times recrystallized bianthrone (Fig 2b). The crude product was slightly green in color, while the pure compound is white.

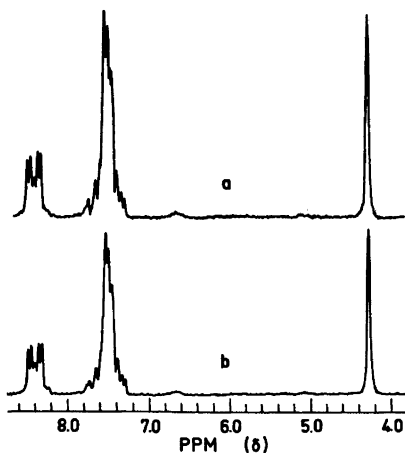


IV

In order to investigate the report<sup>2</sup> that 9-anthrone (IV) is readily air-oxidized to bianthrone, air was vigorously bubbled through a solution of 9-anthrone (100 mg) in acetonitrile containing lithium perchlorate (0.1 M) at 45°C. The IR spectrum of the compound isolated from this experiment was



*Fig. 2.* NMR spectrum of bianthrone in chloroform-*d*. a) Crude product from anthracene oxidation in anhydrous acetonitrile containing ethanol. b) Authentic sample recrystallized from chloroform three times.



*Fig. 3.* NMR spectrum of 9-anthrone in chloroform-*d*. a) Before attempted air-oxidation. b) After attempted air-oxidation.

identical to that of 9-anthrone before the attempted oxidation. Furthermore, the NMR spectrum (Fig. 3a) was identical to that of authentic 9-anthrone (Fig. 3b).

Preparative runs on the oxidation of 9-methoxyanthracene either in the presence or absence of alcohol (methanol or ethanol) yielded only bianthrone. The product obtained from this substrate was white, and the IR and NMR spectra were identical to that of recrystallized material. Preparative runs on the oxidation of anthracene in the presence of methanol likewise only produced bianthrone.

To investigate the electrolytic oxidation of anthracene in acetonitrile containing ethanol as a preparative route to bianthrone, a run was conducted on 5.0 g of material. Anhydrous reagents were used; however, no precaution was taken to keep out atmospheric moisture. Constant current electrolysis at 1.00 A was carried out, until 3.0 Faradays per mole of anthracene had been consumed. The crude product was isolated by diluting the electrolytic solution with water and filtering. After drying under vacuum, IR and NMR spectra showed the crude material to be essentially pure bianthrone. The isolated yield was 91 %. The material obtained in this manner is much more pure than a commercial sample which was found to be less than 90 % pure by NMR analysis.

#### DISCUSSION

The voltammetric data for the anodic oxidation of anthracene in anhydrous acetonitrile containing ethanol (Fig. 1b) clearly shows that the effect of ethanol is to reduce the peak current as compared to that in the absence of alcohol

(Fig. 1a). This observation supports our report<sup>6</sup> that the product isolated from oxidation of anthracene in dry acetonitrile is not bianthrone as previously reported.<sup>2</sup> Multielectron voltammetric oxidation of anthracene in dry acetonitrile<sup>8</sup> and in nitrobenzene<sup>9</sup> has been observed in other investigations. Since the coulometry and product isolation experiments on 9-methoxyanthracene indicate that the oxidation of this compound is a 1.0 electron oxidation producing bianthrone in a quantitative reaction, we can consider this reaction a standard by which to compare the oxidation of anthracene. Thus, voltammetry on solutions of 9-methoxyanthracene (Fig. 1c,d) show peak currents less than one third of that observed for a solution of anthracene in the presence of ethanol. Since coulometric and voltammetric  $n$  values should be the same in the absence of such complicating factors as slow chemical reactions which produce electro-active compounds from the initial product,\* we feel that the combination of voltammetric data with our previous coulometric data<sup>3,6</sup> is overwhelming evidence that the anodic oxidation of anthracene in the presence of ethanol involves a three electron oxidation of anthracene accompanied by the formation of bianthrone, and not a two-electron oxidation as proposed from other coulometric work.<sup>2</sup>

Majeski *et al.* concluded that a 2.0 electron oxidation occurs at water concentration less than 30 mM, and that between 3 and 4 electrons are transferred at higher water concentrations.<sup>2</sup> However, that paper<sup>2</sup> contains conflicting data, *i.e.*, at an initial water concentration of 40 mM, one run produced an  $n$  value of 2.14 (run 20), while another resulted in an  $n$  value of 3.31 (run 19). Since these data are rather inconsistent, it was necessary to determine the effect of water on the coulometric  $n$  value for the anodic oxidation of anthracene in acetonitrile containing ethanol. The water concentration in our most carefully conducted experiments (Table 2, runs 11 – 13) was less than 10 mM, which is as low as any reported previously.<sup>2</sup> These experiments resulted in an average coulometric  $n$  value of 2.87, very close to the values obtained in our preliminary report.<sup>3</sup> Increasing the amount of water present (14 mM) indeed did give an increase in the  $n$  value (to 3.18); however, further increases in water concentration were accompanied by a lowering in the coulometric  $n$  value, reaching a low of 2.81 in solutions with high water concentration (3 M). These data conclusively show that the effect of water on the coulometric  $n$  value is not to increase  $n$  by a factor of almost 2,<sup>2</sup> but rather to cause only small, however, significant \*\* changes.

Another point on which our work<sup>3</sup> differs from that of others<sup>2</sup> is on the ease of air-oxidation of 9-anthrone in acetonitrile. Our experiments which involved bubbling air through a heated (45°) solution of 9-anthrone in acetonitrile for 30 min are considerably more drastic than the mild work-up conditions used for product isolation.<sup>2</sup> The NMR spectra of 9-anthrone and bianthrone are sufficiently different \*\*\* for this to be a very sensitive tool for

\* This situation generally gives rise to coulometric  $n$  values greater than predicted by voltammetry.

\*\* At high water concentration the formation of another product, III, in addition to bianthrone is observed.

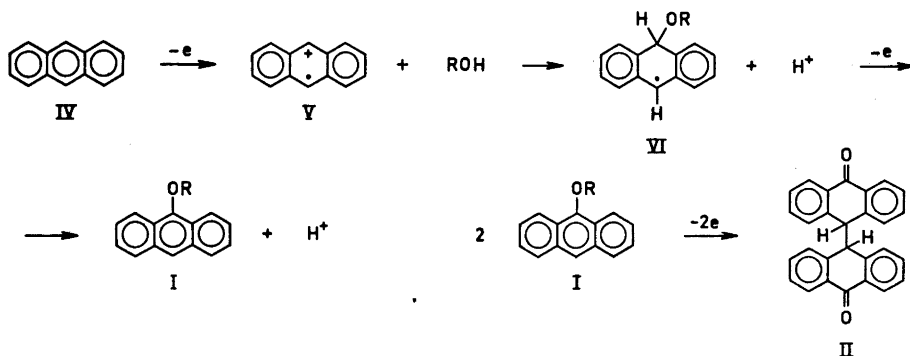
\*\*\* Singlets at 4.27 ppm for 9-anthrone and 4.78 ppm for bianthrone are in regions uncomplicated by other signals.

analyzing mixtures of the compounds. No bianthrone was detected by NMR analysis of the recovered material from attempted air oxidation of 9-anthrone. The spectrum of recovered material was identical to that of the starting 9-anthrone. The work of Bradshaw and Chapman<sup>10</sup> was cited<sup>2</sup> as an indication of the ease of oxidation of 9-anthrone. However, the latter study<sup>10</sup> did not involve the air oxidation of 9-anthrone, although the ease of oxidation of anthranol anion was discussed. This is not surprising, even 9-anthranol, which should be considerably more difficult to oxidize than its conjugate base, is oxidized at low anode potentials.<sup>11,12</sup> Although the keto-enol equilibrium for anthrone-anthranol greatly favors the keto form,<sup>13</sup> it is not certain that the rate of enolization of 9-anthranol would be sufficiently great to allow isomerization to occur at the anode, the potential of which being considerably more positive than necessary to oxidize 9-anthranol. On the contrary, it seems more likely that electron transfer would at least compete with enolization and most probably occur to such an extent that 9-anthrone would not form at all. It seems highly probable that 9-anthranol is not an intermediate in the formation of bianthrone from anthracene oxidation in solutions of high alcohol (100 mM) and low water (20 mM) concentration. It is more likely that any electrophilic species generated at the anode would react with alcohol rather than with water when the concentration of the former is at least five times that of the latter.

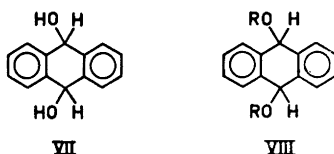
It is now well established that the first step in the anodic oxidation of anthracene and other polynuclear aromatic hydrocarbons is the loss of a single electron to form the cation-radical.<sup>9,14,15</sup> Anodic substitution reactions of substituted anthracenes, such as pyridination,<sup>16</sup> hydroxylation,<sup>17</sup> and methoxylation,<sup>18</sup> have recently been shown to involve interaction of the anodically generated cation-radical with the nucleophile. The first step of the oxidation of anthracene in this system must be the formation of the cation-radical<sup>14</sup> (Scheme 1), which is then followed by rapid reaction with alcohol to form VI, which is converted to 9-alkoxyanthracene (I) by oxidation and loss of a proton. The mechanism to this point can be implied from previous works.<sup>9,14-17</sup> Evidence for the final step, conversion of 9-alkoxyanthracene to bianthrone, emerged from this work. 9-Methoxyanthracene was found to undergo 1.0 electron oxidation to form bianthrone. Under the conditions of this work, anthracene was oxidized at +1.25 V, while 9-methoxyanthracene underwent oxidation at +0.96 V (Fig. 1b,d). Surely, any 9-methoxyanthracene generated during oxidation of anthracene in the presence of methanol would undergo further oxidation to bianthrone. There is no reason to believe that ethoxy or other alkoxy anthracenes would behave differently.

Although not conclusive, the evidence is strong that 9-alkoxyanthracenes are intermediates leading to the formation of bianthrone during anodic oxidation of anthracene in the presence of alcohols. Voltammetric and coulometric data very strongly indicate that bianthrone is formed at the anode and not by some subsequent air-oxidation during isolation. The evidence is conclusive that 9-anthrone is not an intermediate in the formation of bianthrone.

Two other products, which we were not able to detect, could give rise to two electron coulometry. Both result from anodic addition reactions, of water (VII) and alcohol (VIII), to anthracene. Such products were considered



likely in view of our finding that *trans*-9,10-diacetoxy-9,10-dihydroanthracene is the major product of anodic acetoxylation of anthracene.<sup>5</sup> However, since neither VII or VIII were found, we can conclude that these



compounds are not formed during anodic oxidation of anthracene in acetonitrile containing alcohol. VII is a known, stable compound,<sup>18</sup> and VIII (R = Me) is the major product of anodic methoxylation of anthracene in methanol containing sodium methoxide<sup>19</sup> and survives the isolation procedure.

In conclusion, the results of the preparative anodic oxidation of anthracene in acetonitrile containing alcohol show that this reaction is suitable for the synthesis of bianthrone. A product of higher purity is obtained when 9-methoxyanthracene is the starting material and thus the latter is the substrate of choice.

### EXPERIMENTAL

The techniques used for constant current coulometry and macro-scale electrolysis have been described previously.<sup>7</sup> Anthracene was K & K Laboratories Scintillator grade and used as obtained. 9-Methoxyanthracene was prepared by a literature procedure.<sup>20</sup> Purification of solvents and electrolytes was as usual.<sup>1</sup> Anhydrous grade ethanol and methanol were used without further purification. The cell used for the "anhydrous" runs is described under Results.

*Preparative electrolysis.* Anthracene (5.0 g) in acetonitrile (950 ml) containing lithium perchlorate (0.1 M) and ethanol (100 mM) was electrolyzed at a constant current of 1.0 A, until 3.0 Faradays per mole of substrate had been consumed. The product was isolated by diluting the electrolysis mixture with water (3 l) and filtering. The crude product was dried under vacuum at 110° for 24 h. Yield of bianthrone was 4.9 g (91 %).



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