

Anodic Oxidation of Anthracenes and Related Compounds

Part IV. Acetoxylation of Anthracene and 9-Acetoxyanthracene

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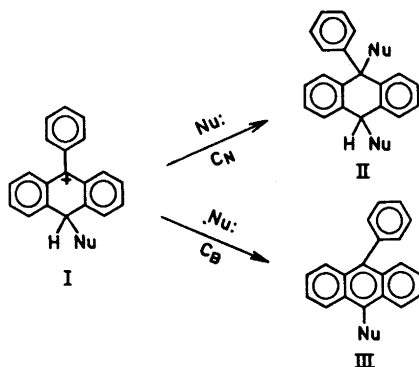
The anodic oxidation of anthracene in acetonitrile containing acetic acid produces bianthrone as the major product. 9-Acetoxyanthracene was found to undergo quantitative one electron oxidation to form bianthrone and thus was implicated as a possible intermediate in the oxidation of anthracene. Acetoxylation occurs in the presence of acetate ion, and a 3:1 ratio of *trans* and *cis*-9,10-diacetoxy-9,10-dihydroanthracene was formed from anthracene. Lead tetraacetate oxidation of anthracene gave equal quantities of *cis* and *trans* isomers. 10-Acetoxyanthrone is the acetoxylation product of 9-acetoxyanthracene.

In a previous paper in this series,¹ we demonstrated that the course of the anodic oxidation of anthracene in acetonitrile is profoundly influenced by the concentration of water. This study is concerned with the anodic oxidation of anthracene in acetonitrile containing acetic acid and acetate ion and was initiated in order to gain more information about reactions following electron transfer during oxidation of anthracene and related compounds.

Anodic acetoxylation of aromatic hydrocarbons has been a subject of much interest to organic electrochemists.²⁻⁷ The suggestion by Ebersson² that the aromatic compound is oxidized at the anode during acetoxylation has been verified. Voltammetry in acetic acid-sodium acetate^{3,4,6,7} clearly showed that such aromatic hydrocarbons as anthracene, naphthalene and anisole are oxidized more readily than acetate ion, and the mechanism of acetoxylation involves the anodic generation of an electrophilic species from the aromatic substrate. The overall mechanism involves loss of two electrons and reaction with acetate ion accompanied by loss of a proton.^{6,7} The sequence of steps occurring to give the substitution product has been shown to be electron transfer (E) followed by reaction of the cation-radical with nucleophile (C) and finally loss of the second electron (E) and proton transfer.⁸ In the case

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of the anthracenes such as 9-phenylanthracene, the ECE process produces a cation (I) which can either undergo addition of a second nucleophilic moiety (C_N) or lose a proton to the nucleophile acting as a base (C_B).⁹



Previous work on the anodic oxidation of anthracene in acetic acid has been limited to determination of the polarographic half-wave potential.^{3,6} This work was undertaken to establish the products formed and the mechanisms followed during the anodic oxidation of anthracene in the presence of acetate ion and (or) acetic acid.

RESULTS

Voltammetric curves observed for oxidation of anthracene and 9-acetoxyanthracene in acetonitrile-acetic acid (3:1) * in the presence and absence of

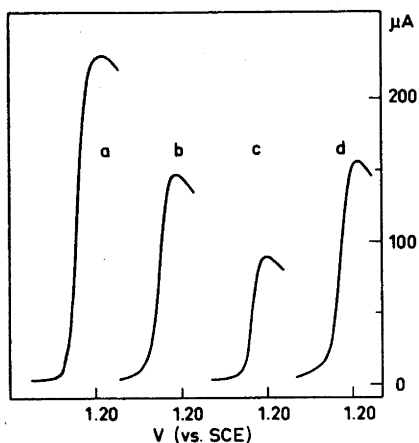


Fig. 1. Peak voltammograms for the oxidation of anthracene in the absence (a) and presence (b) of sodium acetate. 9-Acetoxyanthracene in the absence (c) and presence (d) of sodium acetate. Solvent: acetonitrile-acetic acid (3:1), $[LiClO_4] = 0.1$ M.

* The supporting electrolyte was lithium perchlorate (0.1 M).

sodium acetate are illustrated in Fig. 1. In the absence of acetate ion, a 1.0 mM solution of anthracene exhibits a voltammetric peak current of 230 μA at a sweep rate of 10 V/min. In the presence of sodium acetate (0.25 M) the peak current is reduced to 146 μA . An opposite effect is observed with 9-acetoxyanthracene, a 1.0 mM solution shows a peak current of 90 μA in the absence of sodium acetate, and 156 μA in its presence. These results, along with peak potentials and n values * are summarized in Table 1.

Table 1. Voltammetry in acetonitrile-acetic acid.^a

Substrate	(NaOAc) M	E_p^b	i_p^b	n
Anthracene	0	1.24	230	2.65
Anthracene	0.25	1.17	146	1.6
9-Acetoxyanthracene	0	1.20	90	1.00
9-Acetoxyanthracene	0.25	1.22	156	1.7

^a MeCN-HOAc (3:1) containing LiClO_4 (0.1 M) as supporting electrolyte.

^b Measured at a voltage sweep rate of 10 V/min vs. aqueous saturated calomel electrode.

Table 2. Coulometric oxidation of anthracene and 6-acetoxyanthracene.

Run	Substrate ^a	(NaOAc)	E_{initial}^b	n^c
1	Anthracene	0.0	1.03	2.72
2		0.0	1.02	2.73
3		0.0	1.03	2.96
4		0.25	0.99	1.55
5		0.25	1.01	1.60
6	9-Acetoxyanthracene	0.25	0.98	1.58
7		0.0	1.02	1.08
8		0.0	1.02	1.01
9		0.0	1.03	1.05
10		0.25	1.03	1.96
11		0.25	1.02	1.98
12		0.25	1.04	2.03

^a 1.0 mmole of substrate in 40 ml of MeCN-HOAc (3:1), $[\text{LiClO}_4] = 0.1 \text{ M}$.

^b Constant current of 50.0 mA.

^c Expressed as Faradays per mole of substrate.

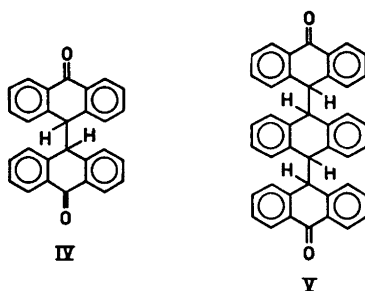
A coulometric study, using the constant current methods previously described¹⁰ resulted in n values consistent with the voltammetric data. Results from representative runs are summarized in Table 2.

* The n value for 9-acetoxyanthracene in the absence of sodium acetate was assigned the value 1.0 on the basis of coulometry and product analysis; other n values are relative to this value.

The oxidation of anthracene in acetonitrile-acetic acid (3:1) was accompanied by the consumption of 2.8 Faradays per mole of substrate. When the same experiment was carried out in the presence of sodium acetate (0.25 M), an n value of 1.6 was observed. Once again, the effect of acetate ion on the number of electrons involved in the oxidation of 9-acetoxyanthracene is opposite to that observed for anthracene. In the absence of sodium acetate 1.05 Faradays per mole were consumed, while in the presence of sodium acetate (0.25 M) an n value of 2.0 was determined. Many runs conducted in acetic acid as the solvent gave comparable results. The solvent mixture, MeCN – HOAc (3:1), was used because it gives less background current and hence is a better voltammetric solvent.

PRODUCTS

Exhaustive electrolysis of anthracene in MeCN – HOAc (3:1) resulted in the formation of a mixture of compounds, IV and V. Bianthrone (IV) is the

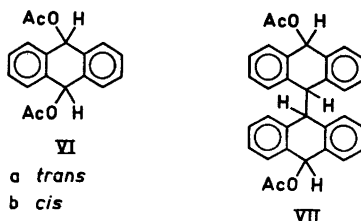


usual product of anthracene oxidation in acetonitrile,^{11,12} and the trimer (V) has recently been shown to be a major product of oxidation of anthracene in aqueous acetonitrile.¹ The product mixture was found to consist of IV (73 %) and V (27 %) by IR analysis.¹ Both products were also obtained when the reaction was carried out in acetic acid in the absence of acetonitrile.

Analysis of the crude product mixture from oxidation of anthracene in MeCN – HOAc (3:1) containing sodium acetate (0.25 M) showed the presence of a small amount of IV (5 %) and a major component, VIa (~60 %) along with the *cis* isomer, VIb (~20 %).^{*} Another compound was isolated in very small quantity from the crude mixture and was tentatively assigned structure VII on the basis of the mass, NMR, and IR spectra.

The structures of VI were determined by comparison with the known compounds produced by the lead tetraacetate oxidation of anthracene.¹³ Previous workers found that a mixture of *cis* and *trans* 9,10-diacetoxy-9,10-dihydroanthracenes was formed during the reaction of anthracene with lead-tetraacetate in benzene.¹³ The higher melting isomer (m.p. 172–173°) was

^{*} VIa was isolated from the mixture, and the presence of VIb was verified by comparison of the NMR spectrum of the crude mixture with that of authentic *cis* isomer.



found to have the *cis* configuration by preparing it from the diol obtained by reduction of anthracene photo-oxide.¹⁴

The NMR spectra of VIa and VIb are summarized in Table 3. Literature data¹⁵ for the epimeric 9,10-dihydro-9,10-dimethylantracenes are included

Table 3. Nuclear magnetic resonance data (δ -values) for 9,10-dihydroanthracene, measured in CDCl_3 , expressed in ppm from internal TMS.

	CH_3 (acetate or methyl)	9,10-protons	Aryl protons
<i>trans</i> -9,10-Diacetoxy ^a	2.20	7.10	7.45
<i>cis</i> -9,10-Diacetoxy ^b	2.10	6.95	7.45
<i>trans</i> -9,10-Dimethyl ^c	1.50	3.94	7.10
<i>cis</i> -9,10-Dimethyl ^c	1.48	3.87	7.10

^a Obtained from the anodic oxidation of anthracene.

^b Obtained from the lead tetraacetate oxidation of anthracene.

^c Ref. 15.

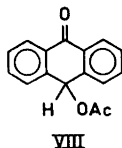
for comparison. In the spectra of the latter compounds, the signals for the 9,10-protons are separated by 0.07 ppm, and that of the methyl groups are separated by only 0.02 ppm. In both cases the signals for the *trans* isomer are further downfield. The corresponding signals for *trans* and *cis*-9,10-diacetoxy-9,10-dihydroanthracenes are separated by 0.15 and 0.10 ppm, respectively. The relative shift in going from *trans* to *cis* is in the same direction, but is more pronounced with the acetates.

Heating the crude reaction mixture from the anodic oxidation of anthracene in acetic acid, conditions known¹³ to convert both isomers to 9-acetoxyanthracene, eliminated the NMR signals at 7.10 and 6.95 ppm, and NMR and IR analysis of the crude product indicated that it contained 9-acetoxyanthracene (~80 %) as the predominant product. Analysis by GLC showed the presence of a small amount of a compound having a retention time identical to that of 9,9'-bianthranyl. 9,9'-Bianthranyl would be expected to form by thermal decomposition of VII.

The oxidation of 9-acetoxyanthracene in $\text{MeCN} - \text{HOAc}$ (3:1) produced bianthrone (IV) in a quantitative reaction. The crude product was pure IV.

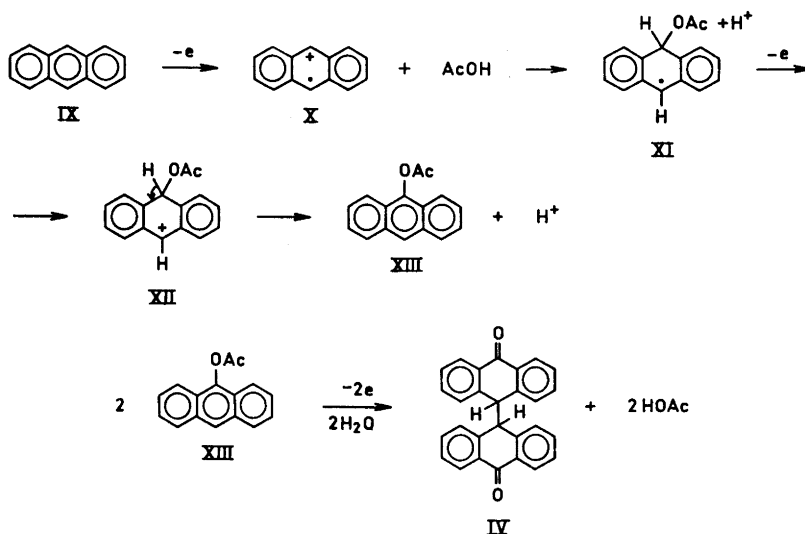
In the presence of sodium acetate (0.25 M) the oxidation of 9-acetoxyanthracene resulted in the formation of a compound, the IR spectrum of which

showed the presence of carbonyl adsorptions at 1722 cm^{-1} (acetate) and 1660 cm^{-1} (anthronyl). The NMR spectrum showed singlets at 2.15 ppm (3H, acetate) and 7.23 (1, H) and multiplets centered at 7.60 (6H) and 8.35 ppm (2H). The mass spectrum indicated a parent ion at m/e of 252. Accordingly, the product was assigned structure VIII.



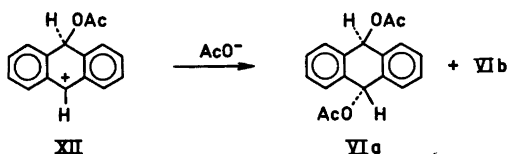
DISCUSSION

In a medium consisting of acetonitrile-acetic acid (3:1) and lithium perchlorate (0.1 M), bianthrone is the major product from the anodic oxidation of anthracene. The possibility that 9-acetoxyanthracene is an intermediate in this reaction is indicated by the observation that bianthrone is obtained in a quantitative reaction when 9-acetoxyanthracene is subjected to the electrolysis conditions. The oxidation peak potential for anthracene in this system was found to be +1.24 V, and that for 9-acetoxyanthracene +1.18 V (*vs.* SCE). Therefore, any 9-acetoxyanthracene formed at an anode potential great enough to oxidize anthracene would likewise undergo oxidation. A mechanism consistent with these observations is shown in Scheme 1. The generation of bianthrone from 9-acetoxyanthracene involves acyl transfer to either water to form acetic acid or acetic acid to form acetic anhydride. Acyl transfer has been observed in other systems¹⁶ and the mechanism of this reaction is now



being investigated.¹⁷ Although the intermediate formation of 9-acetoxyanthracene is an attractive hypothesis, it is not necessary to account for the formation of bianthrone. Water could interact with the cation-radical of anthracene to form 9-anthranol which could undergo one electron oxidation to bianthrone. However, the absence of anthraquinone, which is a major product of the oxidation of anthracene in acetonitrile at low water concentration,¹ is indicative that acetic acid is acting as a nucleophile to generate XIII.

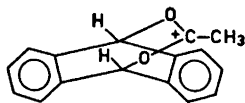
A more complex situation arises when the oxidation of anthracene is carried out in the presence of sodium acetate. The major product of the reaction is *trans*-9,10-diacetoxy-9,10-dihydroanthracene (VIa), which is estimated to form in about 60 % yield. The formation of VIa and the isomer, *cis*-9,10-diacetoxy-9,10-dihydroanthracene, VIb, is best explained by the interaction of XII with acetate ion.



The ratio of the *trans* to *cis* isomers was found to be very close to 3. This observation is contrary to prediction based on the fact that aromatic compounds are known to be adsorbed to platinum electrodes,¹⁸ at least in aqueous solution, and it is believed that the mode of adsorption is such that the plane of the aromatic system is parallel to the electrode surface.^{18,19} Thus, if the first step in the oxidation is adsorption of anthracene, which is then followed by electron transfer to form the cation radical, attack by acetate ion would have to take place from the back side (away from the electrode). Subsequent transfer of the second electron to produce XII would occur instantaneously. If XII were produced in this manner it would still be shielded on one side by the electrode, and attack by the second acetate moiety would have to take place from the same side as the first, giving rise to the formation of the *cis* isomer VIb.

The lead tetraacetate oxidation of anthracene in homogeneous solution was found to produce equal quantities of VIa and VIb. The non-stereospecific nature of this reaction would indicate that steric factors do not contribute to the isomer distribution. This observation would argue against the possibility that the conversion of XII to VI during anodic oxidation takes place away from the influence of the electrode and that the *trans*-isomer is favored due to hindrance by the 9-acetoxy group to attack by acetate ion from the *cis* side. Thus, it would appear that either (1) the electrode plays a role in determining the stereochemistry of the product or (2) the anodic oxidation is accompanied by the formation of an intermediate which reacts with acetate ion stereospecifically to give predominantly *trans* addition.

Such an intermediate has been postulated to form during anodic oxidation of *trans*-stilbene. Mango and Bonner proposed that the oxidative *trans* addition of acetate to *trans*-stilbene proceeds through intermediate formation of a cyclic acetoxonium ion.²⁰ A similar intermediate can be drawn for anthracene. The

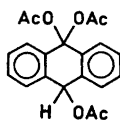


XIV

cation (XII) could undergo cyclization to XIV before reaction with acetate ion takes place. Nucleophilic attack by acetate ion on XIV should give the *trans* diacetate in accordance with the results obtained on *trans*-stilbene.²⁰ Even more compelling evidence for the cyclic acetoxyonium intermediate was obtained in the latter case.²⁰ The major product of the reaction was the *threo*-monoacetate which was the predicted product of reaction of the acetoxyonium ion with water in analogy with the findings of Winstein.^{21,22} Although the existing evidence is consistent with intermediate formation of XIV, other factors such as specific adsorption could play a part in dictation of the stereochemistry of the addition product.

It is significant that coulometry shows that considerably less than two electrons per molecule of substrate are transferred during oxidation of anthracene in the presence of acetate ion. Only a small portion of this discrepancy can be accounted for by the formation of the dimer, VII. Analysis of the crude reaction mixtures by NMR shows that the acetate methyl and 9,10-dihydro protons of VIa and VIb are the only significant proton signals other than those from aromatic protons; yet the signal from the aromatic protons is about 20 % greater than expected. This indicates that other aromatic compounds are formed, probably by one electron oxidation and end up as polymer or tars.

The anodic oxidation of 9-acetoxyanthracene in the presence of sodium acetate is accompanied by the consumption of 2.0 Faradays per mole of substrate and the ultimate formation of 10-acetoxyanthrone (VIII). Comparison of the NMR and IR spectra of the crude product with those of pure VIII showed it to be the major product; however, the presence of another product in lesser amounts was revealed. The oxidation of 9-acetoxyanthracene

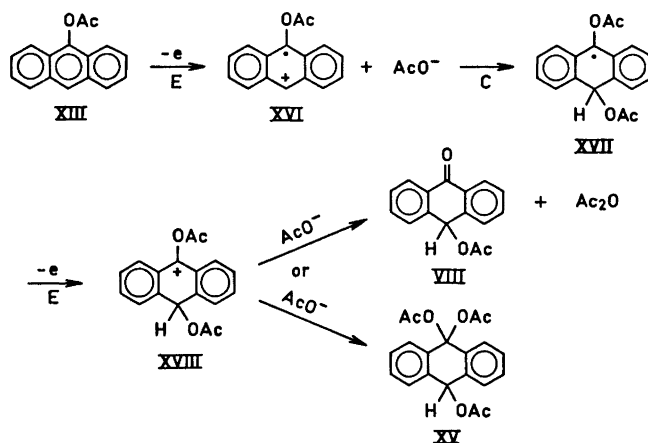


XV

by lead tetraacetate in benzene has been shown to produce triacetoxydihydroanthracene XV.¹³ When the lead tetraacetate oxidation was carried out in acetic acid, VIII was the only product. It is conceivable that XV is the product of anodic oxidation and is converted to VIII in a chemical step. However, the electrolytic conditions of this study are considerably milder than those used for the lead tetraacetate oxidation in acetic acid and XV would probably survive if formed.* Although XV was not isolated, the NMR and IR spectra

* The epimeric 9,10-diacetoxy-9,10-dihydroanthracenes do not survive when formed by lead tetraacetate oxidation in acetic acid. However, they are stable to the electrolytic conditions.

of the crude product indicated that the acetate content was greater than expected for VIII (ratio of acetate to aromatic protons and acetate carbonyl to anthronyl carbonyl adsorption). Furthermore, a definite odor of acetic anhydride was observed during the work-up procedure. (XV was found to undergo decomposition to VIII and acetic anhydride.¹³) A mechanism consistent with these observations is illustrated by Scheme 2. The intermediate involved in the product forming step, XVIII, is formed by the now familiar



ECE mechanism. In the final step, acetate ion can either attack at the acetoxy carbonyl to give VIII or at the positive 9-position to give XV. Since these reactions occur after electron transfer, the electrochemical techniques do not give any indication of the importance of the two steps. However, the product studies are indicative that direct formation of VIII is the predominant reaction pathway.

EXPERIMENTAL

The apparatus used for voltammetry, coulometry, and preparative scale electrolysis has been described.¹⁰ Lithium perchlorate and sodium acetate were anhydrous reagent grade and further dried for 24 h at 150° under vacuum before use. Acetonitrile was purified by a published procedure,²³ and Karl Fischer analysis showed it to contain less than 4 mM water. Reagent grade glacial acetic acid was used without further purification. Anthracene was K & K Laboratories Scintillator grade. 9-Acetoxyanthracene was prepared according to a published procedure.²⁴

Oxidation of anthracene in MeCN-HOAc (3:1). Anthracene (534 mg, 3 mmoles) was exhaustively electrolyzed at 200 mA in the mixed solvent (40 ml) containing lithium perchlorate (0.1 M). The anode potential remained nearly constant at about +1.03 V (*vs.* SCE) until very near the end of the run. A sharp increase in the anode potential occurred after 66.1 min ($n \pm 2.73$). During the electrolysis a white solid separated, which was filtered and washed with water and dried at 150°. The solid (108 mg) was shown to be identical to V by comparison of the IR and mass spectra with that of the authentic material.¹ Methylene chloride (50 ml) was added to the electrolysis mixture, and the solution was extracted with water (200 ml), then with sat. sodium bicarbonate (200 ml),

and finally with one more portion of water. The methylene chloride solution was dried over anhydrous magnesium sulfate and then evaporated under vacuum. The residue (415 mg) was estimated to contain bianthrone (93 %) and V (7 %) by IR analysis.

Oxidation of anthracene in MeCN-HOAc (3:1) containing sodium acetate (0.25 M). Anthracene (1.78 g, 10 mmoles) was exhaustively electrolyzed at a constant current of 1.00 A in the electrolysis medium (200 ml) containing lithium perchlorate (0.1 M). The electrolysis was complete in 27.9 min ($n=1.73$). The product mixture was worked up as before, yielding a light brown oil (1.92 g). Ether (10 ml) was added to the residue, dissolving the oil and leaving a fine white solid (92 mg) which was shown to be bianthrone (IV) by comparison of the IR and NMR spectra with those of the authentic compound. The ether was evaporated from the oil which was then dissolved in a small amount of methanol. After standing for several days, large transparent platelets were formed. The crystals were shown to account for the major amount of the crude material by comparison of the NMR and IR spectra with that of the crude mixture. Recrystallization from petroleum ether gave white needles (VIa), m.p. 120–123° (lit. 124–127).¹³ (Found: C 73.15; H 5.5. Calc. for C₁₈H₁₄O₂: C 73.0; H 5.44.) The mass spectrum had peaks at m/e 237 (7 %), 236 (14 %), 195 (35 %), 194 (100 %) and 178 (19 %). The NMR spectrum is summarized in Table 3. ν_{\max} (Nujol) 1745 cm⁻¹ (acetate).

After standing, the methanolic mother liquor deposited a small amount of white needles (VII). A weak NMR spectrum was obtained with singlets at 2.15 ppm (~6H, acetate), 4.40 (~2H, 9,9'-protons) and 6.50 ppm (~2H, 10,10'-protons) as well as a multiplet centered at 7.40 ppm (~16H, aryl). The highest peak in the mass spectrum was at m/e 237 (47 %) which could be due to cleavage of the central bond of VII, giving a fragment equal to one half the molecular weight. Other peaks appeared at m/e 236 (21 %), 195 (82 %), 195 (66 %), 178 (100 %), and 149 (29 %). ν_{\max} (Nujol) 1725 cm⁻¹ (acetate).

Oxidation of 9-acetoxyanthracene in MeCN-HOAc (3:1). 9-Acetoxyanthracene (236 mg, 1.0 mmole) was exhaustively oxidized at a constant current of 100 mA in the mixed solvent (40 ml) containing lithium perchlorate (0.1 M). The anode potential remained at about +0.98 V (vs. SCE) for almost the entire run with a sharp increase occurring at 16.2 min ($n=1.01$). Work-up in the normal way produced a white residue (242 mg) which was found to be pure bianthrone by NMR and IR analysis.

Oxidation of 9-acetoxyanthracene in MeCN-HOAc (3:1) containing sodium acetate (0.25 M). 9-Acetoxyanthracene (236 mg, 1 mmole) was oxidized at a constant current of 100 mA in the electrolysis medium containing lithium perchlorate (0.1 M). The anode potential changed sharply from +1.05 V at 31.9 min ($m=1.98$). The isolation procedure produced a low melting solid (250 mg) which crystallized from petroleum ether as colorless needles of 10-acetoxyanthrone, m.p. 107–109° (lit. 108–110).¹³ (Found: C 76.4; H 4.6. Calc. for C₁₈H₁₄O₃: C 76.2; H 4.76.) The mass spectrum had peaks at m/e 252 (41 %), 210 (100 %), 194 (45 %), 193 (59 %), and 165 (53 %). The NMR spectrum (in CDCl₃) showed singlets at 2.15 ppm (3H, acetate) and 7.23 (1H, 9-proton) and multiplets centered at 7.60 ppm (6H, aryl) and 8.35 (2H, aryl). ν_{\max} (Nujol) 1722 cm⁻¹ (acetate), 1660 cm⁻¹ (anthronyl carbonyl).

Lead tetraacetate oxidation of anthracene. A mixture of 2.0 g of anthracene and 5.0 g of lead tetraacetate in 300 ml of benzene was allowed to reflux for 2 days. The solution was filtered from lead diacetate and washed with saturated sodium bicarbonate solution. A portion of the benzene solution was evaporated to dryness, and the NMR spectrum in CDCl₃ was recorded. Singlets at 2.10 ppm (3H, acetate), 2.20 (3H, acetate), 6.95 (1H), and 7.10 (1H) indicate that the mixture contained equal amounts of *trans* and *cis* 9,10-diacetoxy-9,10-dihydro-anthracene (VIa and b). The remainder of the benzene solution was evaporated to a small volume. On cooling the solution deposited white crystals which were a mixture of anthracene and VIb. After filtering and allowing to stand another crop of crystals (0.45 g) separated, and two recrystallizations from alcohol gave VIb, m.p. 170–172°. The NMR data for VIb are given in Table 3.

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