Anodic Oxidation of Anthracenes and Related Compounds

Part VI. Reactions of 9-Phenylanthracene

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The anodic oxidation of 9-phenylanthracene in acetonitrile pro-
duces the dimer, 10,10'-diphenyl-9,9'-bianthranyl, when the reaction
is conducted in the absence of added nucleophiles. In the presence of
water, hydroxylation competes with dimerization and 9-hydroxy-9-
phenylanthrone-10 is a major product. The oxidation in the presence
of either sodium acetate or methanol is accompanied by the con-
sumption of 4 Faradays per mole of substrate and the formation of
9-acetoxy-9-phenylanthrone-10 or 9-methoxy-9-phenylanthrone-10,
respectively.

The anodic oxidation of anthracene in acetonitrile under voltammetric conditions is characterized by rapid chemical reactions following electron transfer.[1-3] The nature of the products have been determined under widely varying conditions and have been found to depend upon the nature and the concentration of nucleophiles present.[4-9] Blocking one of the reactive 9,10-positions of anthracene with phenyl has been shown to greatly stabilize the product of the first electron transfer, the cation radical.[3] In nitrobenzene solution [3] the cyclic voltammogram of 9-phenylanthracene has a peak current ratio (i_{pc}/i_{pa}) [10] equal to about 0.5 at the relatively slow scan rate of 5V/min indicating appreciable stability of the cation-radical.

Although the voltammetry for the anodic oxidation of 9-phenylanthracene is well established,[3,11] little is known about the reactions that take place after electron transfer. The cation-radical from 9-phenylanthracene has been shown to react with lutidines by two different pathways depending on the degree of hindrance toward nucleophilic reactions of the nitrogen.[11]

The reactions of anodically generated cation-radicals are of considerable interest to electro-organic chemists.[12] Cation-radicals have unequivocally been implicated in several anodic substitution processes.[13] It is the purpose of this work to present evidence for the nature of reactions following electron transfer

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during the anodic oxidation of 9-phenylanthracene in acetonitrile and to show the effect of purposely adding nucleophiles such as water, methanol, and acetate ion. The influence of the 9-phenyl group is not only to stabilize the intermediate cation-radical but also to restrict the number of possible reactions. Thus, this somewhat simplified case should provide understanding which can be related to the more complex reactions of anthracene and other polynuclear aromatic hydrocarbons.

RESULTS

Voltammetry. The cyclic voltammogram for the anodic oxidation of 9-phenylanthracene in acetonitrile * countaining tetraethylammonium perchlorate (0.1 M) is shown in Fig. 1a. An oxidation peak, 0, is observed at +1.13 V (*vs.* SCE), and on reversing the direction of the voltage scan a cathodic peak, R, is observed at +1.08 V. In the presence of water (40 mM) the oxida-
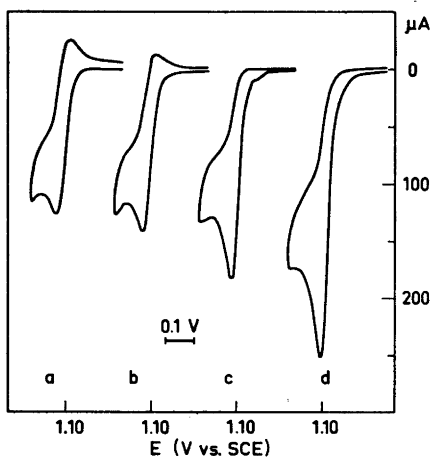
Fig. 1. Cyclic voltammograms for the oxidation of 9-phenylanthracene. Added water: a, 0; b, 40 mM; c, 400 mM; d, 2000 mM.

tion peak current is greater, and the reduction peak smaller (Fig. 1b). Addition of still more water (400 mM) results in a further increase in the anodic current and the complete elimination of the cathodic current (Fig. 1 c). At very high water concentration (2 M) the anodic current is twice as great as in dry solution (Fig. 1d). Further increases in the water concentration brings about only small changes in the peak current. The same general behavior is observed when other nucleophiles, methanol or acetate ion, are incrementally added to solutions of 9-phenylanthracene in acetonitrile.

Coulometry. Runs conducted either in dry acetonitrile or acetonitrile containing water did not give integral n values. During constant-current coulometry,[14] the anode potential continuously drifted to more positive values, and it was not possible to observe a clearly defined end-point. Results from the

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* The water content of the solvent-electrolyte system was estimated to be less than 10m M by Karl Fischer analysis.

coulometric oxidation of 9-phenylanthracene in acetonitrile containing methanol (1.5 M) or in acetonitrile-acetic acid (3:1) containing sodium acetate (0.25 M) are summarized in Table 1. At a substrate concentration of 1.25 mM, coulometric n values slightly lower than 4.0 are observed when the oxidations were carried out either in the presence of sodium acetate (runs 1 − 3) or methanol (runs 5 − 7). The preparative runs were accompanied by the consumption of 3.98 (sodium acetate) and 3.90 (methanol) Faradays per mole of substrate.

Products. When a saturated solution of 9-phenylanthracene is oxidized in the presence of excess solid substrate in dry acetonitrile a solid product, 10,10′-diphenyl-9,9′-bianthranyl (I) separates from solution. If the electrolysis is continued until the 9-phenylanthracene is depleted, I redissolves and is further oxidized.
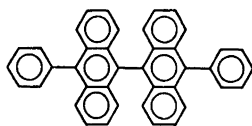
I

The structure I was assigned on the basis of elemental analysis and the mass spectrum. A parent ion ($m/e = 506$) and a fragment ($m/e = 253$) arising from cleavage of the bond between the two anthracene rings were the strongest peaks in the spectrum. The NMR spectrum showed only aromatic protons and the IR spectrum showed the absence of functional groups.

When the oxidation of 9-phenylanthracene was carried out in acetonitrile containing water (3 M), a small amount of I is formed along with the major product 9-hydroxy-9-phenylanthrone-10 (II). The IR spectrum of II showed the presence of hydroxyl ($\nu_{max} = 3400$ cm^{-1}) and anthronyl carbonyl ($\nu_{max} = 1645$) groups. The product was obtained as an impure oil and was not characterized as such, but was converted to the acetate (III) by heating in acetic anhydride-pyridine (1:1).

|	R
II	H
III	Ac
IV	Me
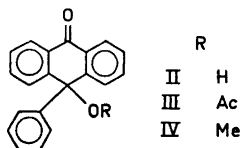
The acetate, III, was obtained in high yield when 9-phenylanthracene was exhaustively oxidized in acetonitrile-acetic acid (3:1) containing sodium acetate (0.25 M). The IR, mass, and NMR spectra were all consistent with structure III which was further substantiated by elemental analysis and comparison of the melting point with the known value.[15]

9-Methoxy-9-phenylanthrone-10 (IV) was isolated in high yield from the anodic oxidation of 9-phenylanthracene in acetonitrile containing methanol (1.5 M). The structure was verified by IR, mass, and NMR spectra as well as by elemental analysis and melting point data.[16]

DISCUSSION

In the absence of added nucleophiles, the fate of the anodically generated cation-radical of 9-phenylanthracene is dimerization to I. It is possible to isolate I from the electrolytic oxidation due to low solubility in acetonitrile. Under comparable conditions, anthracene produces anthraquinone and unidentified polymer-like products.[7] It appears that increasing the stability of the cation-radical (relative to that of anthracene) not only decreases the rate of reaction with residual water in acetonitrile, but causes it to behave as a radical. That is, electrophilic reaction with water is completely overcome by the dimerization pathway. This provides evidence that the polymerlike products from anthracene probably form by radical coupling reactions. In the case of 9-phenylanthracene, this dimerization produces the insoluble compound I which is also stabilized by virtue of the "blocking" groups in the 10,10'-positions. The dimer from anthracene with no such blocking groups can undergo further oxidation with the ultimate result being polymer formation.
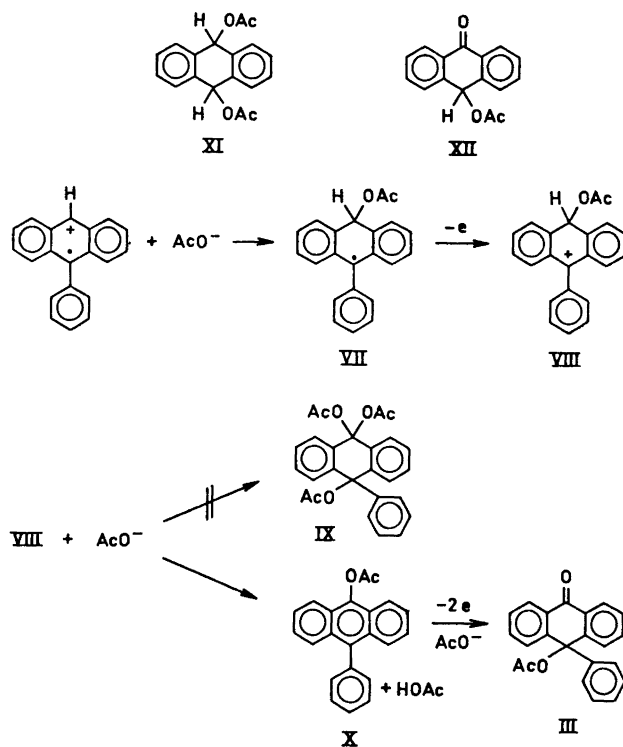
The dimerization of 9-phenylanthracene cation-radical can be overcome by reaction with water if the water concentration in acetonitrile is sufficiently increased. However, even at water concentrations as high as 3 M some dimer is produced. However, the major product under these conditions is 9-hydroxy-9-phenylanthrone-10 (II), the result of a four electron oxidation. The first step in the formation of II is no doubt generation of the cation-radical and nucleophilic attack by water to produce V. Two electron oxidation of V results in the formation of VI, which on reaction with water would yield the product II. The two electron oxidation of V to VI is most likely a stepwise ECE process
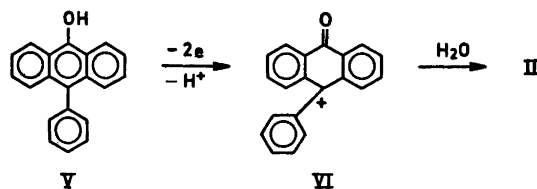
with the chemical step between electron transfers simply involving loss of the phenolic proton. Some indication of the water concentration necessary for nucleophilic reaction to occur can be obtained from the experiments represented by Fig. 1. In the absence of added water (Fig. 1a) the peak current for oxidation of 9-phenylanthracene (1.0 mM) in acetonitrile was 125 μA. Making the concentration of added water 40 mM (Fig. 1b) increased the oxidation peak current to 140 μA, and a cathodic peak for reduction of the cation-radical could still be observed. Adding enough water to make the concentration 400 mM increased the oxidation peak current to 178 μA and eliminated the cathodic peak. Increasing the water concentration to 2.0 M further increased the oxidation peak current to 250 μA. The peak current for the oxidation of 9,10-diphenylanthracene in dry acetonitrile to give the stable cation-radical[1] under these conditions was found to be 92 μA. Thus, at a water concentration of 2 M, considerably more than 2e are transferred during the cyclic voltam-
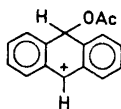
metric oxidation of 9-phenylanthracene. These experiments indicate that a wa-
ter concentration of about 400 mM is necessary for nucleophilic reaction to
effectively compete with the 1e dimerization. The preparative runs and
attempted coulometric runs indicate that even at a water concentration of 3
M the fate of an appreciable portion of the cation-radical is dimerization.

Anodic acetoxylation of anthracene involves addition of acetate ions to
the 9,10-positions.[8] However, the only product observed for the acetoxylation
of 9-phenylanthracene is 9-acetoxy-9-phenyl-anthrone-10 (III). The most
likely mode of formation of III is depicted by Scheme 1. Reaction of the
cation-radical with acetate ion gives VII which on oxidation generates the
cation VIII. The next step is crucial in determining whether addition or
substitution will prevail. Attack by acetate ion at the 9-position produces
the addition product, IX. However, if instead acetate ion acts as a base attack-
ing the proton at the 10-position, 9-acetoxy-10-phenylanthracene, X, would
result. The addition product, IX, would be expected to be stable to the reac-
tion conditions, and, if formed, would be isolated as such. However, X, still
being completely aromatic would undergo further oxidation to produce the
observed product III. Under identical conditions, 9,10-diacetoxy-9,10-di-
hydroanthracene (XI) is the product of the anodic acetoxylation of anthracene,
while 10-acetoxyanthrone (XII) results from oxidation of 9-acetoxyanthra-
cene.[8]

Scheme 1

Both mechanisms, addition and substitution, occur during lutidination of 9-phenylanthracene.[11] The unhindered nucleophile, 3,5-lutidine, gave a high degree of addition, while the more hindered compounds, 2,5- and 2,6-lutidine gave predominant substitution. This behavior was ascribed to the differences in steric hindrance of nitrogen to attack at the 9-position of an intermediate similar to VIII. On this basis we can speculate that the steric requirements for nucleophilic attack by acetate are more similar to that of the hindered lutidines than that of 3,5-lutidine. The postulate, that the reason that substitution rather than addition occurs is of steric origin, is supported by the fact that the unhindered intermediate, XIII, gives predominantly addition product upon attack by acetate ion.[8]

XIII

Both coulometry and product studies for the anodic methoxylation of 9-phenylanthracene indicate that a four electron anodic oxidation takes place accompanied by the generation of 9-methoxy-9-phenylanthrone-10, IV, in high yield. The probably mechanism for the formation of IV is the same as that observed for acetoxylation, and the discussion of that mechanism need not be repeated.

EXPERIMENTAL

The apparatus used for voltammetry, coulometry, and preparative scale electrolysis has been described.[14] Tetraethylammonium, lithium, or sodium perchlorate were used as supporting electrolytes and dried for 24 h at 150° in a vacuum oven before use. Carefully purified acetonitrile [17] was used for all electrolyses, and Karl Fischer analysis showed less than 4 mM in water.

Infrared absorption spectra were measured on a Beckman IR5A spectrometer. Either a Varian T 60 or A 60 spectrometer was used for obtaining NMR spectra in deuterochloroform. Chemical shifts are expressed in ppm relative to tetramethylsilane. Mass spectra were measured with an Atlas Mass Spectrometer CH4.

10,10'-Diphenyl-9,9'-bianthranyl (I). 9-Phenylanthracene (2.54 g, 10 mmoles was electrolyzed at a constant current of 200 mA until 1.5 Faradays per mole of substrate has been consumed. During this time the anode potential remained lower than +1.0 V (*vs.* SCE). During electrolysis a fine solid (0.95 g) separated and was filtered and washed with acetonitrile. The solid, which crystallized from benzene and did not melt below 300°C [18] was identified as I. (Found: C 94.5; H 5.2. Calc. for $C_{40}H_{26}$: C 94.8; H 5.2.) The NMR spectrum (in $CDCl_3$) showed only one peak, a broad multiplet at 7.52 ppm (ArH). The mass spectrum contained peaks at m/e 506 (100 %) and 253 (39 %). The filtrate was evaporated and found to contain 9-phenylanthracene, I, and polymer-like material.

9-Hydroxy-9-phenylanthrone-10 (II). 9-Phenylanthracene (127 mg, 0.5 mmole) was oxidized at a constant current of 200 mA in acetonitrile (40 ml) containing water (3 M) and sodium perchlorate (0.5 M). During electrolysis the anode potential increased from an initial value of +1.01 V (*vs.* SCE) to +1.30 V at 9.0 min, at which time the electrolysis was terminated. A small amount of solid (I) separated and was filtered off. Water (200 ml) was added to the electrolysis mixture, and the organic material was extracted with methylene chloride. After drying over anhydrous magnesium sulfate, the solvent was evaporated leaving a dark oil. Ether was added to the oil and a solid separated, which after filtering and washing with ether was light brown. ν_{max} (Nujol) 3400 cm^{-1} (OH)

and 1645 cm^{-1} (anthronyl). II was not further characterized as such, but was converted to III by heating in Ac$_2$O (5 ml) and pyridine (5 ml) at 100°C for 3 h.

9-Acetoxy-9-phenylanthrone-10 (III). 9-Phenylanthracene (508 mg, 2 mmoles) was electrolyzed in acetonitrile (30 ml), acetic acid (10 ml) containing sodium acetate (0.25 M) at a constant current of 200 mA. The initial anode potential was +0.94 V (*vs.* SCE) and remained less than 1.0 V until 60 min had passed, and began to rise slowly with a sharp increase occurring at 64.25 min ($n=3.98$). Methylene chloride (100 ml) was added, and the solution was extracted first with water and then with saturated sodium bicarbonate, followed by one more water extraction. After drying over anhydrous magnesium sulfate, the solvent was evaporated leaving a crude product (520 mg). III crystallized from n-PrOH, m.p. 194—196° (lit. 196—198).[15] (Found: C 80.2; H 5.1. Calc. for C$_{22}$H$_{16}$O$_3$: C 80.5; H 4.9.) The mass spectrum had peaks at *m/e* 328 (59 %), 286 (100 %), 270 (67 %), and 269 (67 %). The NMR spectrum (in CDCl$_3$) showed a singlet at 2.18 ppm (3 H, acetate); multiplets at 7.35 (11 H, aryl) and at 8.40 (2 H, aryl). ν_{max} (Nujol) 1738 cm^{-1} (acetate), 1655 cm^{-1} (anthronyl), and 1593 cm^{-1} (aryl).

9-Methoxy-9-phenylanthrone-10. 9-Phenylanthracene (254 mg, 1.0 mmole) was electrolyzed in acetonitrile (40 ml) containing methanol (1.5 M) and lithium perchlorate (0.1 M) at a constant current of 200 mA. The initial anode potential was +0.93 V (*vs.* SCE) and remained below +1.0 V for the first 30 min. A sharp increase in the anode potential occurred at 31.4 min ($n=3.90$). The work-up was the same as for II, and after evaporation of the methylene chloride a light brown solid (238 mg) remained. The solid was first washed with ether and then crystallized from n-PrOH—H$_2$O, m.p. 172—174° (lit. 173—174°).[16] The largest peaks in the mass spectrum were at *m/e* 300 (27 %), 269 (100 %), 239 (18 %), and 223 (29 %). The NMR spectrum showed a singlet at 2.96 (3 H, methoxyl); broad peaks at 7.18 (6 H, aryl) and 7.50 (5 H, aryl); and a multiplet at 8.05 (2 H, aryl). ν_{max} (Nujol) 1665 cm^{-1} (anthronyl), 1595 cm^{-1} (aryl), and 1072 cm^{-1} (methoxyl).

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