Anodic Oxidation of Anthracenes and Related Compounds

Part I. Hydroxylation of Anthracene

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The anodic hydroxylation of anthracene in acetonitrile was
studied at water concentrations from 50 mM to 3 M. At low water
concentration anthraquinone is formed in low yield along with a
major amount of unidentified material. Increasing the water concen-
tration results in the formation of anthraquinone and bianthrone as
the only products with the proportion of bianthrone increasing with
water concentration. High yields of bianthrone with only traces of
anthraquinone are observed at water concentration of 1.8 M. Still
higher water concentration brings about the formation of a new
trimer which consists of a 9,10-dihydroanthracene moiety between
two 9-anthronyl units. Product studies are supported by coulometric
and voltammetric data.

The knowledge of mechanisms of anodic oxidation of aromatic hydrocarbons
has greatly expanded in recent years. The classic investigation of Lund [1]
on the polarographic oxidation of aromatic hydrocarbons paved the way to
revealing studies correlating halfwave potentials with HMO parameters.[2-4]
Elegant investigations from three different groups showed that the initial
anode process in the oxidation of polynuclear aromatic hydrocarbons is loss
of a single electron and formation of the cation-radical.[5-7]

Several aromatic hydrocarbons, examples of which are 9,10-diphenyl-
anthracene [5] and perylene [6] were found to produce relatively stable cation-
radicals. Others, like anthracene, form short-lived cation-radicals which
undergo rapid follow-up reactions to give products of unknown structure.
These follow-up reactions generally lead to electro-active products which are
further oxidized and often produce complex product-mixtures.

Studies of particular importance to organic chemistry are those designed
to show the nature of the products and the reaction pathways accompanying
the anodic generation of intermediates. A successful approach has been to

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carry out the oxidations in the presence of nucleophiles. Lund [1] isolated 9,10-dihydroanthranyldipyridinium diperchlorate from the anodic oxidation of anthracene in acetonitrile containing pyridine. Friend and Ohnesorge found that bianthrone is the final reaction product when ethanol is substituted for pyridine.[8] Eberson and Nyberg conclusively showed that anodic acetoxylation of aromatic compounds involves discharge of the aromatic species as the primary anode process.[9,10] This mechanism was also shown to be operative during anodic cyanation.[11]

Anodic substitution reactions, such as pyridination [1] and acetoxylation [9,10] were assumed to occur by a two electron oxidation of the aromatic species followed by or assisted by the nucleophile. Conclusive evidence that pyridination and other reactions often occur by an ECE process (*i.e.*, oxidation (E) followed by a chemical step (C) and further oxidation (E)) was recently obtained.[12] Thus, limiting one electron behavior, even in the presence of pyridine, was observed at high rotation rates during a rotating disk electrode study of the anodic pyridination of 9,10-diphenylanthracene and other aromatic hydrocarbons.[12]

Recently, the results of a coulometric investigation of the anodic oxidation of anthracene in both "dry" and "wet" acetonitrile was published.[13] The latter investigation led to the conclusion that anthracene undergoes 2.0 electron anodic oxidation in "dry" acetonitrile to form 9-anthrone which undergoes air oxidation during workup to yield bianthrone. When the oxidation was conducted in the presence of small amounts of water, erratic coulometric n values between 3 and 4 were usually observed. Mixtures of bianthrone and anthraquinone were reported as the products in "wet" acetonitrile with increasing amounts of anthraquinone formed with increasing water concentration.

Faulkner and Bard [14] investigated the electrogenerated chemiluminescence of anthracene in N,N-dimethylformamide solution. They concluded that the fluorescent product is anthranol existing in tautomeric equilibrium with anthrone. However, they report that the yield of anthranol plus anthrone is on the order of $1-10\%$ during exhaustive electrolysis of 1 mM solutions of anthracene in N,N-dimethylformamide. We have recently expressed the opinion that the anodic oxidation of anthracene in the presence of ethanol in acetonitrile is accompanied by the passage of 3.0 Faradays per mole of anthracene and the formation of bianthrone as the primary product.[15]

It is obvious from the foregoing discussion that much progress has recently been achieved toward the understanding of mechanisms of anodic oxidation of aromatic hydrocarbons. It is also apparent that results are in many cases fragmentary and a need exists for a systematic study of the products and mechanisms of aromatic hydrocarbon oxidation. It would be an enormous task to study aromatic hydrocarbons in general and we have chosen anthracene and related compounds as model systems to attempt to establish a clear picture of the products produced and mechanisms followed during anodic oxidation in acetonitrile. This, the first paper, is concerned with the anodic hydroxylation of anthracene.

RESULTS

Coulometry. The coulometric n value (the number of Faradays per mole of substrate) is very useful in suggesting structures for the products of an electrolytic reaction. Coulometric n values for organic anode processes are generally obtained by controlled potential coulometry. We have found that precise n values for organic anode processes can be readily obtained by a constant current technique which is described in the following paper.[16] The simplicity and accuracy of the method makes it the method of choice in the author's opinion and it was used extensively in this investigation.

Table 1. Coulometry of the anodic hydroxylation of anthracene in acetonitrile.

$(H_2O)M$ [a]	E Initial V (vs. SCE) [b]	Time (min) [c]	n [d]
0.05	1.07	12.8	3.97
0.05	1.06	12.6	3.91
0.05	1.07	12.7	3.94
1.00	1.03	10.7	3.32
1.00	1.02	10.7	3.32
1.00	1.05	10.6	3.29
2.00	1.06	9.5	2.98
2.00	1.05	9.6	2.98
2.00	1.04	9.5	2.95
3.00	1.02	8.5	2.67
3.00	1.06	8.5	2.64
3.00	1.04	8.4	2.61

[a] Water added to solutions made up from "anhydrous" reagents.
[b] Initial anode potential.
[c] Time required to consume 0.10 mmoles of anthracene at a constant current of 50 mA.
[d] Expressed as Faradays per mole of anthracene.

Results from several representative runs at varying water concentrations for the anodic hydroxylation of anthracene in acetonitrile are tabulated in Table 1. At a water concentration of 50 mM the anodic oxidation of anthracene in acetonitrile is accompanied by the consumption of 4.0 Faradays per mole of substrate. When the water concentration is increased to 1.0 M a decrease in the coulometric n value is observed and 3.3 Faradays per mole of substrate are consumed. At a water concentration of 2.0 M the oxidation consumes 3.0 Faradays per mole of anthracene. A decrease in the coulometric n value to 2.6 is observed on increasing the water concentration to 3.0 M. Runs conducted at still higher water concentration give lower n values but are made difficult due to decreased anthracene solubility.

Voltammetry. In the preceding section an inverse relationship between the water concentration in acetonitrile and the coulometric n value for the anodic oxidation of anthracene was observed. Intuitively, one would expect a similar relationship to exist between water concentration and voltammetric peak currents. This effect is shown in Fig. 1. The peak current (i_p) for the
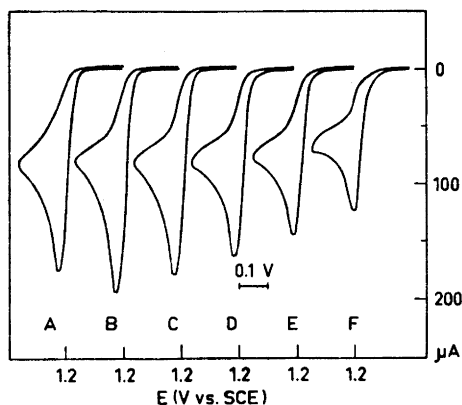
Fig. 1. Cyclic voltammograms for the oxidation of anthracene (1 mM) in acetonitrile. Added water: A, 0; B, 40 mM; C, 100 mM; D, 300 mM; E, 700 mM; F, 2000 mM.

anodic oxidation of anthracene (1 mM) in dry acetonitrile at a voltage sweep rate of 8 V/min was equal to 173 μA (Fig. 1-A). When the water concentration was 40 mM, i_p increased to 187 μA (Fig. 1-B) and at still higher water concentration (100 mM), a value of 176 μA (Fig. 1-C) was observed. This trend continued and at water concentrations of 300 and 700 mM i_p had values of 137 μA (Fig. 1-D) and 122 μA (Fig. 1-E), respectively. At a water concentration of 1.9 M, the value of i_p was 113 μA (Fig. 1-F). Thus, the qualitative effect of water concentration on the voltammetric peak current is similar to that observed on the coulometric n value. Under the same conditions, the peak current for the anodic oxidation of hydroquinone decreased by less than ten per cent in going from dry acetonitrile to a water concentration of 2 M.

Product distribution. Depending on the concentration of water, the anodic hydroxylation of anthracene in acetonitrile results in the formation of one or more of the three compounds, I, II, and III.
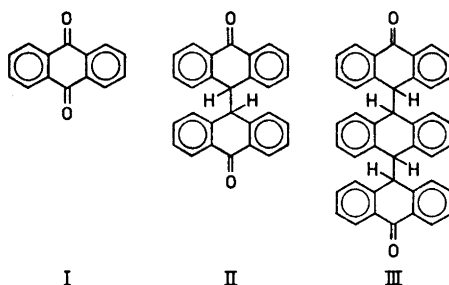
Anthraquinone (I) and bianthrone (II) had previously been observed to form during the anodic oxidation of anthracene in wet acetonitrile.[13] The formation of these compounds was verified by comparison of NMR, IR, and mass spectra with that of authentic compounds.

The structure of III, a new compound, was assigned on the basis of the following considerations. (1) The IR spectrum of III is nearly superimposable on that of II other than in the region between 12.5 and 14.0 μ. The carbonyl band at 6.03 μ is identical for II and III. The close similarity in IR spectra is indicative that the carbonyl environment of II and III must be nearly identical. (2) The trimer, III, is virtually insoluble in organic solvents whereas II shows some solubility in several solvents. For example, II is sufficiently soluble in chloroform to show an NMR spectrum and III is insoluble. In fact, the differences in solubility of II and III in chloroform provides an excellent means of separating the two components. (3) The strongest peaks in the mass spectrum of II occur at m/e 193 (MW/2) and at 165 (loss of CO from MW/2). The mass spectrum of III shows peaks at m/e of 194 (55 %), 193 (97 %), 178 (100 %), and 165 (33 %). The spectrum is consistent with III breaking down to anthracene (178) and the same fragments observed for II (194, 193, 165). (4) More conclusive evidence for structure III was obtained by conversion to a monoacetate. Heating III in acetic anhydride-pyridine (1:1) for 15 min under reflux was accompanied by the formation of IV. The IR spectrum of IV had two different carbonyl bands, 5.68 μ (acetate) and 5.98 μ (anthronyl). The NMR spectrum (in CDCl$_3$) exhibited a singlet at 2.65 * ppm (3H, acetate), signals at 5.00 (2H, at 9,10-positions of central ring) and 4.80 ** (1H, 10-position of the anthronyl ring) and a broad multiplet centered at 7.2 (24H, aromatic protons). At 70 eV the mass spectrum of IV consisted of peaks at m/e 412 (21.8 %), 370 (100 %), 194 (74.5 %) and a small molecular ion at 606. At 12 eV the peaks at 412 and 194 were of equal intensity and were the only significant peaks other than the small 606 peak. This evidence is indicative that thermal fragmentation is the first step producing Va and Vb.
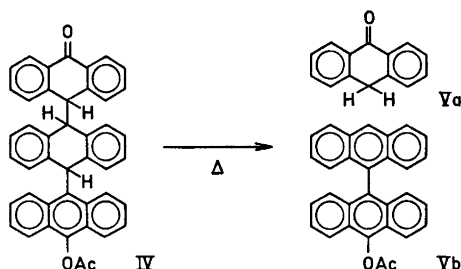
Strong IR bands are observed for I (12.38), II (12.72), and III (12.95) between 12 and 13 μ. The existence of these bands provides a convenient method for accurate determination of the relative amounts of the components in product mixtures. Relative amounts of the compounds present were first estimated from the IR spectra. Known mixtures corresponding to the estimated composition were then prepared from pure components and the actual com-

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* Identical in position to that of 9-acetoxyanthracene.
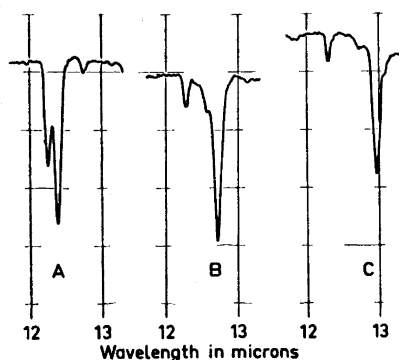** Protons at 10 and 10′ positions of bianthrone show a singlet at 4.78 ppm.

Fig. 2. Infrared spectra of (A) Anthraquinone (I), (B) Bianthrone (II), and (C) Trimer (III).

position of the mixtures then determined by comparison with the known mixtures. The IR spectra $(12-13.5\ \mu)$ of the three components are illustrated in Fig. 2.

The product distributions as a function of water concentration for the anodic oxidation of anthracene (1 mmole) in acetonitrile (40 ml) containing

Table 2. Product distribution from the anodic hydroxylation of anthracene.

(H$_2$O) mM [a]	n [b]	Anthra-quinone [c]	Bianthrone [c]	Trimer [c]
50	5.6	5 [d]	1	0
150	4.2	0.56	1.0	0
600	4.0	0.30	1.0	0
1200	3.5	0.18	1.0	0
1800	3.0	Trace	1.0	Trace
3000	2.6	0	1.0	1

[a] Water added to solution made up from "anhydrous" reagents.
[b] Expressed as Faradays per mole of anthracene.
[c] Relative amounts of products estimated by IR analysis.
[d] The crude product mixture was a brownish-black solid which contained no more than 15 % anthraquinone.

sodium perchlorate (0.5 M) are given in Table 2. The reactions were carried out at a constant current of 100 mA and the n values given in the table were determined by the potentiometric endpoint determination.[16] The run in which enough water was added to make the solution 50 mM resulted in the consumption of 5.6 Faradays per mole of anthracene and about a 5:1 ratio of I/II.*

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* It should be pointed out that anthraquinone (I) accounts for less than 15 % of the total product in this case. At lower water concentrations no bianthrone is observed and still lower amounts of anthraquinone are formed. The product mixture is a brown-black solid, the bulk of which has not been identified. Attempts to separate the mixture into components or to re-crystallize it have been unsuccessful. The behavior of anthracene in anhydrous acetonitrile is being investigated.

Subsequent increases in water concentration increased the amount of II at the expense of I and at a concentration of 1.8 M, bianthrone (II) was the only significant product. Increasing the water concentration to 3.0 M resulted in the formation of nearly equal amounts of II and III.

The n values obtained in acetonitrile with low water content were dependent on the amount of substrate oxidized. Consistent n values of about 4 were obtained using 0.1 mmoles of anthracene and this value increased to greater than 5 when 1 mmole was oxidized. (The same volume of solvent, 40 ml $[H_2O] \simeq 50$ mM) was used in both cases.) If 1 mmole of anthracene were oxidized to anthraquinone in 40 ml of acetonitrile, 2 mmoles of water would be consumed which corresponds to a decrease in water concentration of about 50 mM.* A decrease of only 5 mM would occur for oxidation of 0.1 mmole of substrate. Since n values do depend strongly on water concentration, the difference in amount of water consumed could account for the discrepancy in n values obtained in the coulometric and preparative experiments.

DISCUSSION

The experimental techniques employed in this study, coulometry, voltammetry, and product distribution studies, all indicate that the effect of water concentration on the anodic oxidation of anthracene in acetonitrile is to decrease the number of electrons involved in the overall oxidation process. Since all three techniques lead to the same conclusion and the nature of the products gives the most information regarding mechanism, the discussion will be primarily based on the product distribution, bringing in coulometry and voltammetry as supporting evidence.

The product distribution for the anodic hydroxylation of anthracene in acetonitrile is strongly dependent on the water concentration. At the lowest water concentrations studied, anthraquinone was the only product identified and was found in low yield. Further increases in the water concentration is accompanied by an increase in the amount of bianthrone formed with a corresponding decrease in anthraquinone formation. Bianthrone formation reaches a maximum at about 1.8 M and further increases in water concentration result in the formation of the trimer (III) in increasing amounts.

The effect of water on the hydroxylation of anthracene is unexpected in view of previous investigations. Majeski et al., imply that an increase in water concentration brings about an increase in anthraquinone formation at the expense of bianthrone.[13] Anthraquinone has been observed to be the product of anodic oxidation in aqueous solution.[17] However, the latter may be the result of an indirect oxidation of anthracene since the solubility is extremely low in water.

The suggestion was made that anodic oxidation of anthracene to anthraquinone takes place by intermediate formation of 9,10-dihydroxyanthracene followed by further oxidation.[13] However, the proposal that increasing the water concentration enhances the second hydrolysis step to compete with the

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* Anthraquinone is not the only product, however, water is most likely involved in the formation of other products.

dimerization [13] is unattenable in light of the effect of water concentration observed in this investigation. Therefore, it seems likely that water concentration does not influence the nature of the first oxidation product, but rather dictates the way in which this first product is further oxidized. Furthermore, since anthraquinone only involves one anthracene unit, the first product must be 9-anthranol,* if a common intermediate is responsible for the formation of all products.

Assuming that 9-anthranol is the initial product of anodic hydroxylation of anthracene, the effect of water on the product distribution is not immediately obvious. 9-Anthranol is oxidized considerably more easily than anthracene in acetonitrile [1] or N,N-dimethylformamide [14] solutions. One electron oxidation to the cation-radical (VII), followed by nucleophilic attack by water and further electron transfer would produce 9,10-dihydroxyanthracene. This ECE mechanism of anodic substitution has been unambiguously assigned to other reactions such as pyridination.[12] However, if the only function of water were to act as a nucleophile toward the carbon center at the 10-position of VII, increasing the water concentration would indeed be expected to increase the rate of nucleophilic attack and further oxidation at the expense of dimerization (Scheme I) as previously proposed.[13] Since the latter does not occur we must consider other possible functions of water. In order to accommodate the observed facts, we must find a function of water which either decreases the rate of hydroxylation of 9-anthranol or increases the rate of dimerization.


Scheme 1
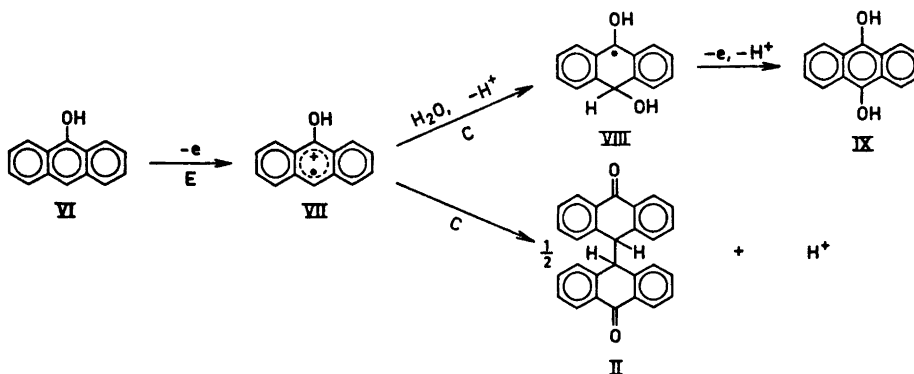
One possibility to be considered is that at low water concentrations the cation-radical (VII) is more basic than the media and deprotonation to XI is slow relative to nucleophilic attack by water (C_N). At higher water concentration the media, $MeCN - H_2O$, becomes more basic and proton transfer forming XI then predominates (Scheme II). This discussion presumes that XI, if formed, is not further oxidized and is consumed by further chemical

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* 9-Anthranol was previously [13] proposed to be the first oxidation product; however, it was believed to undergo rapid enolization to 9-anthrone before further oxidation could occur.

reactions. Two molecules of XI could combine to form bianthrone (II). Duality in function of nucleophiles, i.e., nucleophilicity toward carbon and protons, has previously been observed during anode processes.[19,20]

One other important fact must be taken into account in accessing the function of water. Increasing the water concentration to about 1.8 M appears to optimize the process leading to formation of bianthrone and excludes the formation of anthraquinone. This can be accounted for by the possibility mentioned in the previous paragraph, which would predict that still further increases in water concentration would have no effect on the product distribution since VII would be completely converted to XI which would then form bianthrone.

Scheme 2
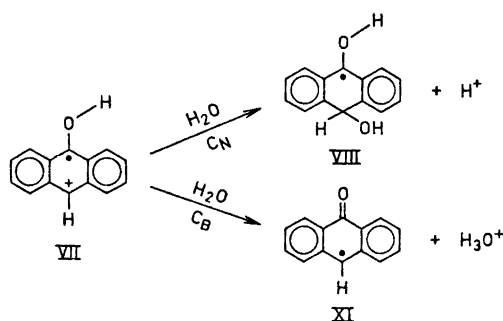
However, a third product, the trimer (III), begins to appear at water concentrations greater than 1.8 M and with increasing water concentration becomes the predominant product. This is more consistent with water exerting a stabilizing effect on some intermediate, perhaps VII, allowing it to become sufficiently stable at high water concentrations so that it is able to diffuse away from the anode (a region of low anthracene concentration) out into the bulk of the solution and react with substrate.

It is just as likely that the increased water concentration causes stronger adsorption of substrate and intermediates, keeping them at the anode surface in close proximity of each other in a favorable position for combination reactions to occur. Aromatic hydrocarbons are known to be adsorbed on platinum electrodes in aqueous solution.[21]

Although it is not possible to definitely account for the effect of water on the anodic oxidation of anthracene in acetonitrile, it is the opinion of the author that adsorption effects, such as those mentioned in the last paragraph, are implicated.

EXPERIMENTAL

The apparatus and experimental procedure used in the constant-current coulometric and macro-scale electrolyses are described in the following paper.[16]

Reagents. Anthracene was K and K Laboratories scintillator grade and used without further purification. Anhydrous sodium perchlorate obtained from K and K Laboratories and anhydrous lithium perchlorate from Alfa Inorganic Chemicals were further dried by heating at 150° in a vacuum oven. Eastman anhydrous acetonitrile (<0.01 %

water) was used without further purification or Eastman practical grade acetonitrile was purified by a published procedure.[22] Identical results were obtained with either solvent for the hydroxylation experiments. Karl Fischer analysis showed the distilled acetonitrile to the <4 mM in water and the commercial anhydrous <2 mM.

Product isolation. A representative experiment is as follows. A suspension of anthracene (1 mmole, 178 mg) in acetonitrile (40 ml) containing water (3.0 M) and sodium perchlorate (0.5 M) was exhaustively oxidized at a constant current of 100 mA in the cell described.[16] The anthracene was consumed in 42.2 min (2.62 Faradays per mole of anthracene). All of the anthracene dissolved during the electrolysis and a fine white solid separated. The solid (68 mg) was collected by filtration, washed thoroughly with water, and dried under vacuum at 100°C for 24 h. The electrolytic solution was poured into a separatory funnel containing chloroform (100 ml). The chloroform solution was extracted with 3 × 200 ml portions of water. After drying over anhydrous magnesium sulfate and filtering, the chloroform was removed under reduced pressure leaving a white solid (105 mg). The solid was separated into two components by heating in a small volume of chloroform. The soluble portion (75 mg) was shown to be nearly pure bianthrone by IR, NMR and mass spectrometry. The insoluble portion was identical to the solid that separated out during electrolysis.

Trimer monoacetate (IV). Anthracene (2.0 g) was dissolved by heating in 800 ml of acetonitrile. Water (40 ml) was added while the solution was still warm and lithium perchlorate (8.0 g) was then added. Electrolysis was carried out at 200 mA in an open beaker until 2.7 Faradays per mole of anthracene had been consumed. During electrolysis a fine white solid separated from the reaction mixture. The white solid was collected by filtration, washed thoroughly with water and dried at 110°. The solid (0.96 g) was stirred in boiling chloroform to remove any bianthrone or anthracene. After filtering the solid was placed in a beaker and acetic anhydride (20 ml) and pyridine (20 ml) were added. When the temperature of the mixture reached about 100°, the solid rapidly went into solution. Heating was continued for 15 min before pouring the reaction mixture into water. The solid which separated was dissolved in chloroform and dried over anhydrous magnesium sulfate. The chloroform was evaporated to about 10 ml and anhydrous ether was added to the solution bringing about the precipitation of IV. After filtering the solid was found to be essentially pure IV by IR, mass, and NMR spectra.

Analysis of product mixtures. Mixtures containing anthraquinone and bianthrone were carefully prepared over a wide range of compositions. The mixtures were thoroughly mixed and ground together. Nujol mulls were prepared of each of the mixtures and the IR spectra were recorded on a Beckman IR-5A spectrometer. The relative intensities of the anthraquinone band at 12.38 μ and the bianthrone band at 12.72 μ were recorded. The same procedure was carried out on mixtures of bianthrone and the trimer (III). The IR spectra of the product mixtures were recorded and the composition of the mixtures was estimated from the spectra of the standard mixture. To verify the determination, a new mixture was made up corresponding to the calculated composition and the IR spectrum of this mixture was compared to the product mixture. The accuracy of this method of analysis is estimated to be of the order of ±5 % of the amount determined.

REFERENCES

1. Lund, H. *Acta Chem. Scand.* **11** (1957) 1323.
2. Hoijtink, T. J. *Rec. Trav. Chim.* **77** (1958) 555.
3. Loveland, J. W. and Dimeler, G. R. *Anal. Chem.* **33** (1961) 1196.
4. Pysch, E. S. and Yang, N. C. *J. Am. Chem. Soc.* **85** (1963) 2124.
5. Peover, M. E. and White, B. S. *J. Electroanal. Chem.* **13** (1967) 93.
6. Phelps, J., Santhanam, K. S. V. and Bard, A. J. *J. Am. Chem. Soc.* **89** (1967) 1752.
7. Marcoux, L. S., Fritsch, J. M. and Adams, R. N. *J. Am. Chem. Soc.* **89** (1967) 5766.
8. Friend, K. E. and Ohnesorge, W. E. *J. Org. Chem.* **28** (1963) 2435.
9. Eberson, L. and Nyberg, K. *Acta Chem. Scand.* **18** (1964) 1568.
10. Eberson, L. and Nyberg, K. *J. Am. Chem. Soc.* **88** (1966) 1686.
11. Parker, V. D. and Burgert, B. E. *Tetrahedron Letters* **1965** 4065.
12. Manning, G., Parker, V. D. and Adams, R. N. *J. Am. Chem. Soc.* **91** (1969) 4584.
13. Majeski, E. J., Stewart, J. D. and Ohnesorge, W. E. *J. Am. Chem. Soc.* **90** (1968) 633.

14. Faulkner, L. R. and Bard, A. J. *J. Am. Chem. Soc.* **90** (1968) 6284.
15. Parker, V. D. *Chem. Comm.* **1969** 1131.
16. Parker, V. D. *Acta Chem. Scand.* **24** (1970) 2768.
17. Krishnan, S., Vyas, V. A., Pathy, M. S. V. and Udupa, H. V. K. *J. Electrochem. Soc. India* **14** (1965) 32; *Chem. Abstr.* **64** (1966) 1618 h.
18. Parkanyi, C. and Zahradnik, R. *Collection Czech. Chem. Commun.* **30** (1965) 4287.
19. Parker, V. D. and Eberson, L. *Tetrahedron Letters* **1969** 2843.
20. Parker, V. D. and Eberson, L. *Tetrahedron Letters* **1969** 2839.
21. Piersma, H. In Gileadi, E. *Electrosorption*, Plenum, New York 1967.
22. O'Donnel, J. F., Ayers, J. T. and Mann, C. K. *Anal. Chem.* **37** (1965) 1161.