For the most part, reaction rates were compared on the basis of half-life, the time required for completion of approximately one-half of the reaction as determined by hydrogen absorption. The total gas absorption was about 5 p.s.i., and the half-life for an uninhibited reduction of *p*-nitrotoluene to *p*-toluidine was about 9 ± 1 min., with the rate roughly zero order with respect to *p*-nitrotoluene. Since there was no attempt to control temperature, the results are semiquantitative. Nevertheless, gross differences in rate were reproducible and meaningful.

Controlled Potential Electrolytic Oxidation of Anthracene in Acetonitrile[1]

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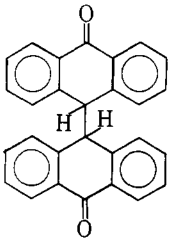
Controlled potential electrolysis has been established as a useful technique in synthetic organic chemistry, especially when the desired product is itself easily oxidized or reduced.[2a,b,3] The efficacy of this approach to synthesis problems is well illustrated by the work of Lingane, Swain, and Fields who successfully reduced 9-(*o*-iodophenyl)acridine to the dihydro derivative.[4] Theory and techniques of controlled potential electrolysis have been adequately discussed by Lingane.[5] Most controlled potential electrolytic syntheses have utilized direct electrolysis of the starting material at the working electrode to produce the desired product, although so-called substitution techniques also have been used.[1,2]

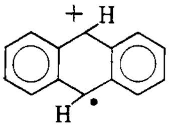
Recent voltammetric studies of aromatic hydrocarbons is acetonitrile solution have suggested that the anodic waves of these compounds are due to the removal of π-electrons. The ion radicals formed are very reactive species and in the case of naphthalene polymerize rapidly to coat the anode and cause a rapid decrease of the electrolysis current.[6] Lund also showed that pyridine in an electrolysis solution of anthracene in acetonitrile reacted with the 9,10-dihydroanthracinum radical ion to form the dipyridinium salt. The present work was undertaken in an attempt to extend the technique to the use of other nucleophiles which might produce useful derivatives of anthracene. Ethanol was selected with the expectation that the 9,10-diethyl ether derivative of anthracene would be obtained. The electrolytic addition of ethoxy groups to furan using the constant current technique has been reported.[7]

Electrolysis of a saturated acetonitrile solution of anthracene which contained supporting electrolyte and was 0.45 *M* in absolute ethanol produced a white compound which was partially soluble (the remainder was recovered by adding water). The electrolysis product was shown to be bianthrone (I) (10,10′-bianthronyl).

Based on the observed formation of the dipyridinium perchlorate salt and on the amount of electricity consumed, Lund stated that the electrolytic oxidation of anthracene resulted in the loss of two π-electrons.[6] The production of bianthrone, however, would indicate that the anode reaction occurring in the present system involved the loss of only one π-electron from each anthracene molecule to form the free radical ion species (II) which then dimerized. The additional oxidation of any 9,9′-bianthryl formed was in fact predicted by Lund.[6]

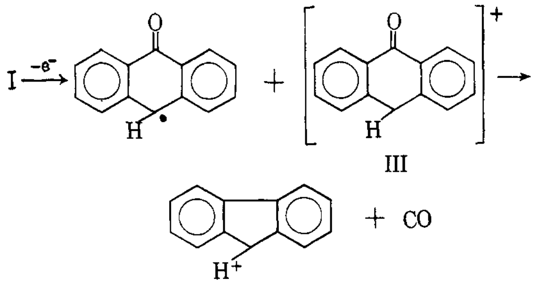


I



II

The following considerations would account for the observed peaks in the mass spectra and for the failure to observe a peak at *m/e* 386. Cleavage of the labile 10–10′ bond in bianthrone would likely occur upon electron impact and could produce the benzylically stabilized 10-anthrone radical and the highly stable aromatic fragment (III) with *m/e* 193. The peak at *m/e* 165 would appear upon loss of CO (twenty-eight mass units) from III in a manner analogous to that reported for anthraquinone.[8]



Experimental

Reagents and Solutions.—Eastman (Practical) acetonitrile was distilled from phosphorus pentoxide and used to prepare all solutions. Chemically pure sodium perchlorate (Amend Drug and Chemical Co.), dried at 150° for 24 hr. and stored over phosphorus pentoxide in a vacuum desiccator, was used to prepare the supporting electrolyte. Anyhydrous silver perchlorate was used on special order from Fisher Scientific Co. Other chemicals were reagent grade quality.

Apparatus.—A Sargent Model XV polarograph was used to record current–voltage curves. A modified[9] Kelley, Jones, and Fisher controlled potential coulometric titrator[10] was used as a potentiostat for all electrolyses and also to determine the exact working electrode potentials for the electrolyses as described later. Ultraviolet absorption spectra were recorded on a Beckman Model DK-2 spectrophotometer, infrared spectra on a Baird-Atomic Model KM-1 spectrophotometer, and mass spectra on a Bendix Time of Flight and on a Consolidated Model 21-103C mass spectrometer.

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(1) Abstracted from the thesis submitted by K. E. Friend for the M.S. degree in chemistry, University of Rhode Island, July, 1962.

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(4) J. J. Lingane, C. G. Swain, and M. Fields, *J. Am. Chem. Soc.*, **65**, 1348 (1943).

(5) J. J. Lingane, "Electroanalytical Chemistry," 2nd Ed., Interscience Publishing Co., New York, N. Y., 1958.

(6) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(7) N. Clauson-Kaas, *ibid.*, **6**, 569 (1952).

(8) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Van Nostrand Publishing Co., Princeton, N. J., 1960, pp. 271, 272.

(9) W. J. Curren, M.S. thesis, University of Rhode Island, 1960.

(10) M. T. Kelley, H. C. Jones, and D. J. Fisher, *Anal. Chem.*, **31**, 488 (1959).

A platinum electrode was the anode; for voltammetric studies a wire with an exposed surface area of about 0.15 cm.^{2} was used and a foil electrode (surface area about 6 cm.^{2}) was used for electrolyses. A silver wire coiled in a helix of *ca.* 1.3-cm. diameter and immersed in a solution of silver perchlorate and sodium perchlorate in acetonitrile served as the reference electrode and as the cathode. It was necessary to isolate the silver electrode from the anthracene solution during electrolysis by means of a cylinder fitted with a fine porosity fritted disk to avoid reduction of the electrolysis products to the starting material. All solutions were deaerated for at least 30 min. by bubbling with nitrogen which had been passed through vanadous chloride solution, concentrated sulfuric acid, and finally acetonitrile. An atmosphere of nitrogen was maintained above the solution during electrolysis.

Current–Voltage Curves.—An approximate current–voltage curve (uncorrected for the *iR*-drop in the cell) was recorded on each electrolysis solution over the voltage range: 0 to +3 v. (*vs.* Ag/Ag$^-$). The exact position of the anodic wave was then determined point by point using the potentiostat by setting the platinum electrode potential manually and observing the current. Electrolyses were performed with the anode potential set to a value about 0.1 v. more positive than the half-wave potential determined from the latter current–voltage curve, which was corrected for the *iR*-drop in the cell. The electrolysis was allowed to proceed until the current decreased to a constant value. Magnetic stirring continued throughout the electrolysis.

An acetonitrile solution 0.5 *N* in sodium perchlorate and 0.1 *N* in silver perchlorate and a solution of ethanol in acetonitrile plus supporting electrolyte showed no appreciable current at potentials less anodic than +1.2 v. (*vs.* Ag/Ag$^+$). Anthracene in this solvent is oxidized at potentials more anodic than about +0.88 v. (*vs.* Ag/Ag$^+$).

Properties of the Electrolysis Product.—The compound was not appreciably soluble in absolute ethanol, ether, water, benzene, or chloroform, but could be recrystallized from acetone. On heating it turned brown slowly near 250° and melted to a dark brown liquid at about 275°. Addition of concentrated sulfuric acid to the product caused the formation of a green color; upon standing for less than 1 min. the color became a ruby red. No color change was observed upon heating a solution of the electrolysis product in benzonitrile, anisole, or xylene.

The results of direct elemental analyses for C, H, and O were 87.24, 4.80, and 8.22%, respectively, and are in excellent agreement with those calculated for bianthrone: C, 87.02; H, 4.70; and O, 8.28%. Duplicate molecular weight determinations (cryoscopy in benzene) of 319 and 329 were reported; the low results are attributed to experimental error.

The ultraviolet absorption spectrum of the electrolysis product in absolute ethanol solution showed a peak at 267 mμ (log ϵ 4.39), a shoulder at 300 mμ (log ϵ 3.9), and a minimum at 242 mμ (log ϵ 4.07). The infrared absorption spectrum (potassium bromide pellet) showed strong peaks at 1320 cm.$^{-1}$, 1660 cm.$^{-1}$ (conjugated carbonyl), and peaks of moderate intensity at 1580 cm.$^{-1}$, 690 cm.$^{-1}$, 930 cm.$^{-1}$, and 790 cm.$^{-1}$.

Mass spectra were obtained by introducing the sample directly into the electron beam of the mass spectrometer[11] and showed peaks at *m/e* 193 and 165; at the sample pressures used no peaks were evident at higher *m/e* values.

Chemical Synthesis of Bianthrone.—Bianthrone was prepared chemically by the action of concentrated nitric acid on a suspension of anthracene in glacial acetic acid.[12] The melting point and infrared and ultraviolet spectra of this preparation were identical to those of the electrolysis product. The reactivities with the reagents previously mentioned were also the same for the two preparations. The mass spectrum of this compound when injected directly into the electron beam was identical with that obtained from the electrolysis product.

Acknowledgment.—The authors are grateful to Mr. A. L. Burlingame and to Mr. James A. McCloskey, Department of Chemistry, Massachusetts Institute of Technology, for their interest and for their assistance in obtaining and interpreting the mass spectral data.

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[11] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc. New York, N. Y., 1962, pp. 33, 34.

[12] E. Josephy and F. Radt, "Elsevier's Encyclopedia of Organic Chemistry," Vol. 13, Elsevier Publishing Co., New York, N. Y., 1946, p. 766.

Beckmann Rearrangement of Arylglyoxylonitrile Oxime *p*-Toluenesulfonates[1]

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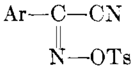
Oxime esters readily undergo the Beckmann rearrangement,[2,3] and references to literature on this subject are available in recent papers.[4,5]

A brief study of the rearrangement of the *p*-toluenesulfonates (I) of five phenylglyoxylonitrile oximes is reported here. Characterization of these oxime tosylates, prepared from the sodium salt of the corresponding phenylglyoxylonitrile oxime[6] and tosyl chloride, is summarized in Table I.[7]

TABLE I

OXIME TOSYLATES (I)



$$\mathrm{Ar{-}C({=}N{-}OTs){-}CN}$$

I, Ar	M.p., °C.	Yield, %	Anal. Calcd. C	Anal. Calcd. H	Anal. Calcd. N	Anal. Found C	Anal. Found H	Anal. Found N
Phenyl	135	64	59.98	4.03	9.33	60.12	4.09	9.01
p-Chlorophenyl	154	66	53.81	3.31	8.37	53.74	3.40	8.18
p-Nitrophenyl	146	34	52.17	3.21	12.27	52.11	3.11	11.98
p-Methoxyphenyl	141	55	58.18	4.27	8.48	58.07	4.43	8.32
Mesityl	152	86	63.14	5.30	8.18	62.99	5.47	8.14

The α-cyano tosyl esters (I) appeared to be much more stable than ordinary oxime tosylates.[2,4] They did not undergo solvolysis in refluxing ethanol, and could be recovered unchanged either after a three-hour period of refluxing in benzene containing an equivalent of aniline or after a pyridine solution was warmed on the steam bath for two hours.[8]

When treated with excess sodium ethoxide in ethanol or with ethanolic potassium hydroxide, the first four tosylates listed in Table I were converted to diethyl

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[1] This research was supported by the Advanced Research Projects gency under Army Ordnance contract no. DA-01-021-ORD-11909.

[2] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948); W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5880, 5972 (1958).

[3] J. C. Craig and A. R. Naik, *ibid.*, **84**, 3410 (1962).

[4] W. Z. Heldt, *J. Org. Chem.*, **26**, 1695 (1961).

[5] J. P. Freeman, *ibid.*, **26**, 3507 (1961).

[6] M. R. Zimmermann, *J. prakt. Chem.*, (2) **66**, 353 (1902).

[7] Although both *syn* and *anti* forms of all the oximes apparently exist,[6] isomeric tosylates were isolated only in the mesityl case (see Experimental). The *anti* configuration of the oxime tosylates indicated in Table I and in the discussion following cannot be considered to have been established; a *syn* configuration also could explain the results obtained here. Since the type of migration observed here corresponds to that usually associated with an *anti* configuration, these oximes tosylates are written in the *anti* configuration.

[8] With I, Ar = *p*-chlorophenyl, some rearrangement probably occurred during chromatography on an alumina column[3] for only 75% recovery of tosylate was possible. Characterization of any rearrangement product was not attempted. Rearrangement of phenylglyoxylonitrile oxime to N-phenyloxamide by phosphorus pentachloride in ether, followed by hydrolysis, has been reported,[6] but the *p*-nitro-, *p*-chloro-, and *o*-chlorophenylglyoxylonitrile oximes were reported to be unaffected by this treatment. We have observed that both the phenyl and *p*-chlorophenyl oximes and phosphorus pentachloride in ether or methylene chloride yield not only some oxamide, but also significant amounts (15–30%) of the α-chloroiminoarylacetonitrile. The results of this study will be reported later.