with water. The ether layer was separated, dried, and concentrated *in vacuo* yielding a crystalline solid which after recrystallization from benzene gave 0.04 g of pure material, mp 171–173°, whose spectral and physical properties were indistinguishable from those of tetramethylphthalyldiol prepared by another route (*vide supra*).

Registry No.—**2,** 20145-50-0; **3,** 29002-53-7; **4,** 29002-54-8; **5,** 29002-55-9; **6,** 3205-92-3; **7,** 484-65-1; **8,** 484-66-2; **9,** 17432-38-1; **15,** 28195-45-1; hexamethylbenzene, 87-85-4.

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The Pschorr Reaction by Electrochemical Generation of Free Radicals. I. Phenanthrene Synthesis

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Diazonium tetrafluoroborates of 2-amino-α-(R-phenyl)cinnamic acids have been reduced electrolytically at 0 V *vs.* sce and nonelectrolytically in aprotic solvents to produce substituted and nonsubstituted phenanthrene-10-carboxylic acids in near-quantitative yields. These cyclized products were produced by other methods in lower yields. The efficacy of a homolytic pathway through generation of phenyl σ radicals by a number of schemes is discussed.

Pschorr and Pschorr-like reactions have been the subject of numerous investigations since they were discovered by Graebe and Ullman[1] in 1894 and Pschorr[2] in 1896. These reactions are of importance not only as synthetic tools but from a mechanistic viewpoint as well. De Tar[3] and others[4–6] have pointed out that some of these reactions appear to proceed by a heterolytic and others by a homolytic pathway. We have recently developed a new route to intermolecular arylation by the electrochemical reduction of diazonium salts in aprotic solvents.[7] Since this method, as carried out in our laboratories, occurs under mild conditions, 0°, and goes by exclusively homolytic pathway, we decided to investigate two intramolecular reactions (*i.e.*, phenanthrene and fluorenone synthesis) to obtain improved yields and/or new information on mechanisms. How far we have succeeded with these objectives in cyclization to phenanthrene is the subject of this paper.

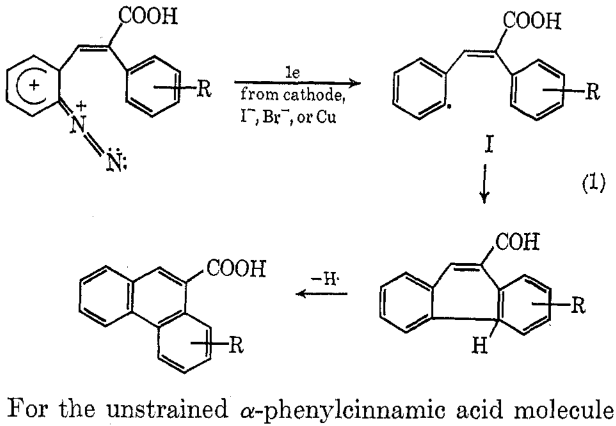
Results

The results of electrochemical reduction of diazonium salts of 2-amino-α-arylcinnamic acids are presented in Table I. For comparison, results of cyclizations of the same diazonium salts in aqueous fluoroboric acid (with and without copper) are included, as are results of one reduction of diazotized unsubstituted acid using iodide ion as the reducing agent, and, finally, results from other laboratories.

Yields from the electrochemical method were consistently high. Examination of products by melting points and infrared and mass spectral analysis gave no indication of by-products from such usual side reactions as replacement of the diazonium with hydrogen or fluoride ions. Substitution by hydroxyl group, not anticipated in an aprotic medium, was absent. Substituent effects on yields were insignificant within limits of experimental error incurred during isolation of products. The iodide ion cyclization also gave an excellent yield but about 10% of the by-product, 2-iodo-α-phenylcinnamic acid, was recovered. Replacing iodide with bromide gave high yields of cyclization comparable to the iodide reaction. The low (62%) yield obtained from cyclization by heating with aqueous fluoroboric acid was increased to 93% by the addition of copper powder.

Discussion

Intermolecular arylations by electrochemical reduction of benzenediazonium tetrafluoroborate in acetonitrile and monosubstituted benzenes produced considerable amounts of benzene (50–60%) due to abstraction of hydrogen atoms from the solvent.[7] No detectable hydrogen abstraction or dimerization occurred during intramolecular arylation of cinnamic acid derivatives, suggesting that conditions strongly favored cyclization (eq 1).



(1)

For the unstrained α-phenylcinnamic acid molecule, Hey and Mulley[8] have calculated the distance between positions to be linked by intramolecular bond formation to be 1.5 Å, and, hence, very favorable to cyclization. Since 1.5 Å applies only to the molecular configuration in which the rings are coplanar, the lifetimes of the

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(1) C. Graebe and F. Ullmann, *Ber.*, **27**, 3483 (1894).

(2) R. Pschorr, *ibid.*, **29**, 496 (1896).

(3) D. F. De Tar, *Org. React.*, **9**, 409 (1957).

(4) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.

(5) R. Huisgen and R. E. Zahler, *Ber.*, **96**, 736 (1963).

(6) R. A. Abramovitch, *Advan. Free-Radical Chem.*, **2**, 87 (1966).

(7) F. F. Gadallah and R. M. Elofson, *J. Org. Chem.*, **34**, 3335 (1969).

(8) D. H. Hey and R. D. Mulley, *J. Chem. Soc.*, 2276 (1952).

TABLE I

PSCHORR CYCLIZATION OF DIAZONIUM SALTS OF 2-AMINO-α-ARYLCINNAMIC ACIDS UNDER DIFFERENT CONDITIONS

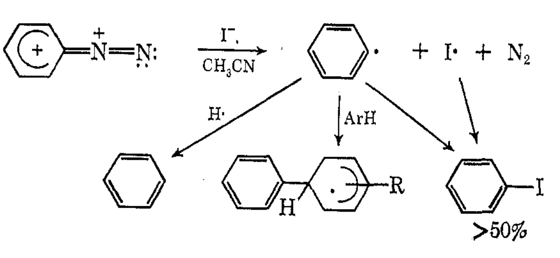
		Reaction conditions and yields, %						
R	Registry no.	Electrochemical reduction	H^+	H^+, Cu	$(CH_3)_2CO$, Cu	I^-	Br^-	Br^-, Hg
H	28987-33-9	95	62[a] 60[d,e]	93[a] 93[d,f,g]	 81, 94[g,h]	85[b] 70[i,j]	78[c]	82[c]
4-CH_3	28987-34-0	90	20[d,e]	70[e,k]				
2-OCH_3	28987-35-1	80	55[d,l]					
3-OCH_3	28987-36-2	94[m]						
4-OCH_3	29038-90-2	93	50[d,l]					
2-Br	28987-37-3	94	60[n]					
4-Br	28987-32-8	96						

[a] Aqueous HBF_4 (10%). [b] CH_3CN, Pr_4NI. [c] CH_3CN, Pr_4NBr. [d] Aqueous H_2SO_4. [e] See ref 15. [f] See ref 2. [g] D. H. Hey and M. Osbond, *J. Chem. Soc.*, 3164 (1949). [h] See ref 8. [i] Aqueous H_2SO_4, $(CH_3)_2CO$, NaI. [j] B. Chauncy and E. Giullert, *Aust. J. Chem.*, **22**, 993 (1969). [k] Aqueous HCl, EtOH. [l] See ref 17. [m] A mixture of 2- and 4-methoxyphenanthrenecarboxylic acids. [n] See ref 20.

free radical must be long relative to the time of oscillation or rotation of the rings.

In the normal course of a Pschorr phenanthrene synthesis, 60% yields can be obtained by simply heating the appropriate diazonium chloride or sulfate in dilute mineral acid. Addition of copper powder increases both the rate of reaction and the yield. Other workers have therefore concluded that these reactions probably proceed by some combination of heterolytic and homolytic mechanisms.[3-6]

In an attempt to assess the effect of the heterolytic pathway, the diazonium salt of 2-amino-α-phenylcinnamic acid was heated in 10% fluoroboric acid; 62% of cyclized product was obtained. When copper was added, a redox system capable of reducing the diazonium salt to a σ radical I resulted, giving a yield of 93%. A similar redox system could be produced with iodide ion in aprotic medium, which also gave high yields, but which was accompanied by the formation of about 10% of iodo-substituted acid. In intermolecular arylations, iodo substitution can be the major reaction, accounting for more than 50% of the products[9] (eq 2).



(2)

Some relevant redox potentials are listed in Table II. This tabulation shows why copper and copper salts facilitate replacement of diazonium groups by chlorine or bromine, though not by iodine, atoms not only in Pschorr reactions but in Sandmeyer and Meerwein reactions as well.

TABLE II

REDOX POTENTIALS *vs.* N HYDROGEN ELECTRODE[a,b]

$ArN_2 = ArN_2^+ + e$	$E_0 = -0.541$ V[c]
$I^- = {}^1/_2I_2 + e$	$= -0.536$ V
$CNS^- = {}^1/_2(CNS)_2 + e$	$= -0.77$ V
$Br^- = {}^1/_2Br_2 + e$	$= -1.066$ V
$Cl^- = {}^1/_2Cl_2 + e$	$= -1.360$ V
$F^- = {}^1/_2F_2 + e$	$= -2.85$ V
$Cu = Cu^+ + e$	$= -0.521$ V
$CuCl + Cl^- = Cu^+Cl_2 + e$	$= -0.538$ V
$CuBr + Br^- = Cu^+Br_2 + e$	$= -0.640$ V

[a] R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, **34**, 854 (1969). [b] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice Hall, New York, N. Y., 1952. [c] From reversible $E_{1/2} = +0.295$ V *vs.* sce (ref 9).

There is some error inherent in comparing potentials in acetonitrile with those determined in aqueous systems. For instance, benzenediazonium salts, $E_0 = -0.541$, are readily reduced by iodide in aprotic solvents, but the *N,N*-dimethylaminobenzenediazonium ion, $E_0 = -0.151$, is not reduced at all.

Bromide ion is apparently on the borderline of ions capable of reducing diazonium salts. In aprotic media diazonium salts of 2-amino-α-phenylcinnamic acid were reduced by bromide, giving high yields (*ca.* 82%) of cyclized products, but the reaction is very slow. Free bromine was produced. Bromine could be produced from bromide *via* one route only, *i.e.*

$$Br^- \xrightarrow{-e} Br\cdot \xrightarrow{Br\cdot} Br_2$$

Recently, Lewis and his coworkers[10] suggested that aqueous bromide participated in the decomposition of diazonium salts by a one-step mechanism (SN2). We now believe that the bromide ion with diazonium salts, in aprotic media at least, constitutes a redox system. The reaction proceeds some ten times faster in the presence of Hg^0 because mercury facilitates the one-electron transfer.[10a] The situation in aqueous and acidic systems is questioned in our laboratory, and investigations are in progress to be reported in subsequent publications.

Experimental Section

Reagents.—All reagents and solvents were purified by published methods.[7] Solid reagents and reference compounds were recrystallized and melting points agreed with literature values. Diazonium tetrafluoroborate salts were recrystallized from cold acetonitrile and ether and kept under high vacuum in the refrigerator. Gattermann copper powder[11] was prepared by adding zinc dust to a saturated aqueous solution of copper sulfate until the deep blue color started to change. The copper powder was filtered, washed with dilute HCl (four times), distilled water until test for chloride was negative, dry methanol, and dry ether, and then put under vacuum. Fluoroboric acid purified (48.5%)[12] and tetrabutylammonium perchlorate[13] were obtained commercially.

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[9] R. M. Elofson and F. F. Gadallah, unpublished results.

[10] E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Amer. Chem. Soc.*, **91**, 419 (1969).

[10a] NOTE ADDED IN PROOF.—Pyridine reduced the diazonium salt of 2-amino-α-phenylcinnamic acid (1:1 molar ratio in acetonitrile) and produced the cyclized compound in 84% yield: R. M. Elofson, F. F. Gadallah, and K. F. Schultz, *J. Org. Chem.*, **36**, 1526 (1971).

[11] C. Gattermann, *Ber.*, **2B**, 1219 (1890).

[12] J. T. Baker Chemical Co., Phillipsburg, N. J.

[13] Southwestern Analytical Chemicals, Inc., Austin, Texas.

General Procedure for the Preparation of 2-Amino-α-arylcinnamic Acids.—*o*-Nitrobenzaldehyde, arylacetic acid, acetic anhydride, and triethylamine were refluxed and cooled, and water was added.[14] The nitro compounds were reduced with H_2S and ammonia. Melting points and mass spectra verified the crystallized compounds.

General Procedure for the Electrolytic Reduction.—The apparatus has been described previously.[7] Tetrabutylammonium perchlorate, the electrolytic support,[7] was dissolved in acetonitrile to make a 0.1 *M* solution. This solution was used for both cathode and anode compartments. The diazonium salt was dissolved in the degassed and cooled solution in the cathode compartment to make 0.01 *M*. The reaction was run at 0 V *vs.* sce under purified nitrogen. A run was considered complete when the current dropped to less than 1 mA and the test for diazonium salt was negative. After completion, each reaction mixture was taken to dryness under vacuum at room temperature. The solid was extracted with ether (four times). The ether solution was dried and evaporated, the residue was dissolved in ammonium hydroxide solution (10%), precipitated with dilute hydrochloric acid, and filtered, and the precipitate was washed with water several times and dried by suction. Dissolving, precipitating, washing, and drying were repeated three times to remove tetrabutylammonium perchlorate. The vacuum-dried products were identified by melting points and infrared. Mass spectral analysis, in each case, gave the proper parent peak and fragmentations for the cyclized products only. The phenanthrene-10-carboxylic acid and its derivatives (R's) were crystallized from glacial acetic acid with a loss of *ca.* 5%; the melting points reported are uncorrected: phenanthrene-10-carboxylic acid, mp 256–257° (lit.[15] 250–252°); R, 3-CH_3, mp 238–240° (lit.[16] 238–239°), R, 1-OCH_3, mp 218–220° (lit.[17] 215°); R, 2-OCH_3, mp 238° (lit.[18] 236.7°); R, 3-OCH_3, mp 240–241° (lit.[17] 239°); R, 3-Br, mp 285° (lit.[19] 290–291°); R, 1-Br, mp 296–297° (lit.[20] 295°).

Using Tetrapropylammonium Iodide for Reduction.—The diazonium salt was dissolved in dry, degassed acetonitrile at 0°. The solid iodide salt was added gradually with vigorous stirring under nitrogen. After 10 min sodium thiosulfate solution (2 g of $Na_2S_2O_3$/25 ml of water) was added and a precipitate formed. The precipitate was filtered, washed with water, and dried under vacuum to give pure phenanthrene-10-carboxylic acid (85%). The filtrate was concentrated, and ammonium hydroxide solution was added (10%) and filtered. The filtrate was acidified to give a precipitate which, after washing and drying, was identified as 2-iodo-α-phenylcinnamic acid (*ca.* 10%), mp 175–177° from ethyl acetate (lit.[21] 179–180°).

Using Tetrapropylammonium Bromide for Reduction.—Two sets of reactions were performed, one over a mercury pool and the other without mercury. The technique described for the iodide reaction was followed with no attempt to separate the 2-bromo-substituted products. At 0° the mercury reaction gave 82% phenanthrene-10-carboxylic acid in *ca.* 2.5 hr. The reaction without mercury was allowed to warm to room temperature overnight and gave 78% of cyclized product in *ca.* 22 hr. In both cases free bromine was produced.

Acid Reaction.—The diazonium salt was suspended in fluoroboric acid (10%) at room temperature with fast stirring. The temperature was raised gradually over 1 hr to 70° and kept at 70° for 10 min, at which time the test for the diazonium ion was negative. The reaction mixture was cooled and filtered. The solid was washed several times with water and then dried under vacuum. Fractional crystallization from glacial acetic acid gave the cyclized product (62%), 2-fluoro-α-phenylcinnamic acid (10%), mp 179° (lit.[22] 178°), 2-hydroxy-α-phenylcinnamic acid (3%), mp 198° (lit. 202–204°),[23] and 3-phenylcoumarin (~9%), mp 138.9°.

Acid and Copper Reaction.—The dry diazonium salt was added to a stirred suspension of copper in fluoroboric acid (10%). The reaction commenced at room temperature and the mixture was warmed to 70°. The cyclized products were isolated by the method described for the acid reaction.

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[16] R. Pschorr, *ibid.*, **39**, 3112 (1906).

[17] R. Pschorr, O. Wolfes, and W. Buckow, *ibid.*, **33**, 162 (1900).

[18] C. K. Bradsher, F. C. Brown, and P. H. Leake, *J. Amer. Chem. Soc.*, **79**, 1471 (1957).

[19] R. Pschorr, *Ber.*, **39**, 3118 (1906).

[20] R. Pschorr, *Justus Liebigs Ann. Chem.*, **391**, 48 (1912).

[21] S. M. Kupchan and H. W. Wormser, *J. Org. Chem.*, **30**, 3792 (1965).

[22] K. Bowden and D. C. Parkin, *Can. J. Chem.*, **46**, 3909 (1968).

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Electroorganic Chemistry. VII. Anodic Oxidation of Cyclopropanes

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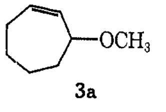
The electrochemical oxidation of bicyclo[4.1.0]heptane (1) and bicyclo[3.1.0]hexane (2) gave products in which the cyclopropane ring was opened. The structures or distributions of the products were completely different from those observed in the acidic solvolyses, metallic oxidations, and radical reactions of 1 and 2. It thus appeared that this electrochemical reaction was initiated by the direct oxidation of the carbon-carbon single bond of the cyclopropane ring. The bond cleavage was observed exclusively on the internal bond.

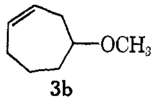
Synthetic reactions initiated by the anodic oxidation of the aromatic nucleus or aliphatic multiple bonds have been studied extensively,[1] while the electrochemical oxidations have never been studied on cyclopropanes in which the characters of the cyclopropane ring are considered to be similar, to a certain extent, to those of the olefinic bond. It was found in our laboratory that in the anodic oxidation of some arylcyclopropanes the aromatic nucleus rather than the cyclopropane ring was oxidized at the anode.[2] In the present study, we wish to report the first evidences that the carbon–carbon single bond in a cyclopropane ring could be anodically oxidized to yield ring-opened products which may be difficultly synthesized by the other methods.

Results

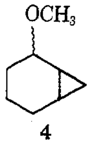
Bicyclo[4.1.0]heptane (1) and bicyclo[3.1.0]hexane (2) were selected as the starting cyclopropyl compounds. In the preparative experiment, the methanolic solution of **1** was oxidized at room temperature using tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte. A carbon rod was used as the electrode and 2 *F*/mol of electricity was passed. The analysis of the reaction products indicated the formation of compounds **3a**, **3b**, **4**, **5a**, **5b**, **6** and a small amount



3a



3b



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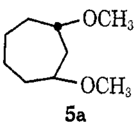

5a

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