photochemical activity, presumably caused by rapid internal electron transfer. Their lack of fluorescence is consistent with these properties. Zinc would seem to have been the simpler choice, and it does fluoresce. Zinc is both chelated far more firmly ($\sim 10^4$ times) and enters the ring far more easily. Boucher and Katz²⁹ have pointed out that zinc chlorophylls aggregate less than the magnesium derivatives. This may have been one cause for the selection of magnesium since chlorophyll in vivo is highly aggregated. Our results show that zinc may introduce complications such as two different oxidized species. Moreover, if the aim of the biological system is minimum redox potential combined

(29) L. J. Boucher and J. J. Katz, J. Am. Chem. Soc., 89, 4703 (1967).

with maximum stability in a protonic solvent, then magnesium is a good mini-max solution to these requirements.

Acknowledgments. We thank Professor S. Granick for his constant help, and Professor G. Feher at the University of California at San Diego and Dr. R. Shulman at Bell Laboratories, Murray Hill, N. J., for use of their esr apparatus and help with the measurements. We thank Professors R. H. Felton and J. Fajer for showing us their manuscript prior to publication and for several helpful discussions.

This work was supported by grants from the Public Health Service, GM-14827 and GM-04922 and by a NATO fellowship to J. H. Fuhrhop from the Deutscher Akademischer Austauschdienst.

Anodic Cyanations of Aromatic Compounds

S. Andreades and E. W. Zahnow

Contribution No. 1538 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received January 15, 1969

Abstract: Electrochemical oxidations of cyanide ion solutions containing aromatic substrates result in three types of cyanation reaction: aromatic substitution of hydrogen; replacement of aromatic methoxyl by nitrile; and introduction of a nitrile group in an α position of tertiary amines. Mechanistic evidence indicates all products are derived from initial oxidation of aromatic substrate and subsequent reaction with cyanide ion. The fate of electrochemically generated cyano radical was investigated by esr spectroscopy.

Previous work¹ on the electrochemical oxidation of cyanide ion in aqueous solution suggested an initial irreversible one-electron process leading to cyanogen which, in basic solution, ultimately yielded cyanate ion. Oxidation products were not detected by chronopotentiometry using current reversal techniques. Although cyano radicals have received considerable study spectroscopically in the vapor phase,² relatively few investigations of the chemical fate of cyano radical in the condensed phase have appeared. Cyano radical has been invoked to account for low yields of cyanated products from the photolysis of mercuric cyanides³ or organomercuric cyanides.4

In this paper, we describe results of controlled potential electrochemical oxidations of nonaqueous solutions of cyanide ion in the presence of aromatic substrates to give cyanated products.⁵ Electrolysis of silver cyanide in liquid ammonia or pyridine produces cyanogen as a

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 D. E. Paul and F. W. Dalby, J. Chem. Phys., 37, 592 (1962); D. Schofield, W. Tsang, and S. H. Bauer, *ibid.*, 42, 2132 (1965); M. Jeunehomme, *ibid.*, 42, 4086 (1965); S. H. Bauer and W. S. Watt, *ibid.*, 44, 1327 (1966); K. M. Evenson and H. P. Broida, *ibid.*, 44, 1637 (1966); C. A. Gay, D. H. Shaw, and H. O. Pritchard, J. Phys. Chem., 69, 1504 (1965); J. A. Knight, R. A. Stokes and D. Bouven *ibid.* 60, 678 (1965); (1965); J. A. Knight, R. A. Stokes, and D. Bowen, *ibid.*, **69**, 678 (1965); N. Basco and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A283**, 291 (1965). Esr detection of cyano radical in a solid argon matrix was also reported: E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys., 36, 1938 (1962).

(3) K. Yoshida and S. Tsutsumi, Tetrahedron Letters, 2417 (1965); J. Org. Chem., 31, 3835 (1966).

(4) K. Yoshida and S. Tsutsumi, *Tetrahedron Letters*, 281 (1966).
(5) Part of this work was presented at the Spring Meeting, Electrochemical Society, Dallas, Texas, May 1967: S. Andreades and E. W. Zahnow, Extended Abstracts, I-4, p 15.

primary product.⁶ Recently intervention of cyano radical has been proposed to account for cyanated products obtained from the electrolysis of methanol solutions of sodium⁷ or mercuric⁸ cyanide in the presence of cyclohexene or aromatic compounds, respectively. The interpretation in the former case has been criticized.9

Electroanalytical Studies

To elucidate the primary electrode process or to define intermediate species which might be trapped in subsequent reactions, oxidation of cyanide ion in acetonitrile at a platinum electrode was studied. Chronopotentiometry in CH₃CN revealed a poorly defined, elongated oxidation transition with $E_{1/4} \approx +0.90$ V¹⁰ vs. $Ag-10^{-2} M AgNO_3$. Data in Table I taken over a 30fold change in current level clearly show the over-all process to be diffusion controlled. Current reversal produced a small reduction transition at -2.0 V.

Cyclic voltammetric experiments in the potential range -2.5 to +2.0 V (see) revealed an oxidation process at potentials more positive than +0.5 V. At lower scan rates (≈ 0.9 V/sec) discrete but relatively broad peaks were observed. At higher scan rates (up to 263

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(9) V. D. Parker and B. E. Burgert, *ibid.*, 4065 (1965); 2415 (1968).
(10) The potential of the Ag-10⁻² M AgNO₃ electrode in CH₃CN vs. aqueous sce has been reported as +0.30 V: R. C. Larson, R. T. Iwamoto and R. M. dams Aval. Chim. Acta 5, 371 (1961). moto, and R. N. Adams, Anal. Chim. Acta, 25, 371 (1961).

⁽⁶⁾ H. Schmidt and H. Meinert, Z. Anorg. Allgem. Chem., 295, 156 (1958); A. von Krusenstjern and J. Meier, Metalloberflaeche, 18, 330 (1964).

⁽⁷⁾ K. Koyama, T. Susuki, and S. Tsutsumi, Tetrahedron Letters,

Table I. Chronopotentiometric Data $^{\alpha}$ for Oxidation of CyanideIon at a Platinum Anode

104 <i>i</i> ₀ , A/cm ²	au, sec	$\frac{10^{3}i_{0}\tau^{1/2}}{(A \sec^{1/2})/\text{cm}^{2}}$
2.35	26.2	1.20
2.94	16.6	1.20
3.53	11.5	1.20
4.70	6.6	1.21
9.40	1.64	1.20
17.6	0.455	1.19
35.3	0.120	1.22
71.0	0.030	1.22

 a 3.6 \times 10⁻³ M (C₂H₅)₄NCN, 0.5 M (C₂H₅)₄NClO₄, in acetonitrile.

 Table II.
 Electrode Potential Limits of Solvent-Electrolyte Systems^{a,b}

Solvent	Electrolyte, M	E _A (V vs. sce)	E _C (V vs. sce)
Acetonitrile	$(C_2H_5)_4$ NClO ₄ , 0.5	+2.9	-2.9
Acetonitrile	$CH_{3}(C_{2}H_{5})_{3}NCH_{3}C_{6}H_{4}SO_{3},$ 0.1	+3.3	-2.2
Dimethylformamide	$(C_2H_5)_4NClO_4, 0.5$	+1.9	-2.8
Methanol	LiClO ₄ , 0.5	+1.3	-1.0
Tetrahydrofuran	LiClO ₄ , 0.5	+1.6	-3.1
Dimethyl sulfoxide	$(C_2H_5)_4NClO_4, 0.5$	+1.5	-2.8
Dimethylacetamide	$(C_2H_5)_4NClO_4, 0.5$	+1.6	-2.7
Pyridine	$(C_2H_5)_4$ NClO ₄ , 0.3	+3.3	-2.2

^a Current density maintained at 1.4×10^{-3} A/cm². ^b Quoted values are judged to allow detection of an electron-transfer process due to the presence of 1 mequiv/l. of electroactive material when the separation of quarter-wave potential is 300 mV.

Table III. Peak Potentials^a

tentials were used in combination with peak oxidation potentials (E_p) determined¹¹ for selected aromatic compounds in acetonitrile (Table III).

Product Studies

Electrolysis of Tetraethylammonium Cyanide Solutions in the Presence of Aromatic Substrates. Reactions of prime concern in electrosynthesis are generally the slower reactions of reactants and intermediates at the electrode. These slower reactions do not affect the more rapid electroanalytical techniques described above but generally most closely reflect the conditions present in controlled potential coulometric experiments. Thus, in the preparative runs, large concentrations of reactants were present in stirred solutions at large electrodes and the process was independent of the rate of mass transfer of the electroactive species to the electrode.

Oxidation potentials of the cyanated products in general are substantially higher than the values for the reactants so that isomer and product distributions did not change with the amount of charge passed.¹²

Using smooth platinum gauze electrodes, anhydrous acetonitrile was chosen as the solvent with a good balance of desired properties: a wide spread between anodic and cathodic limits (+2.0 and -2.4 V, respectively, vs. sce) and sufficient solubility for both the cyanide electrolytes and organic substrates. Most product studies were carried out in undivided, three-electrode cells (Figure 1). The cylindrical platinum gauze anode and cathode were arranged concentrically. The

Compound (M)	Scan rate, V/sec	Span, V vs. sce	$E_{\rm p}$, V vs. sce
Anthracene (5.6×10^{-3})	0,80	-1.7 to $+2.3$	+1.2, +1.55
Benzene (4.5×10^{-3})	0.90	-1.7 to $+2.8$	+2.4
Anisole (3.8×10^{-3})	0.80	-1.7 to $+2.3$	+1.7
Naphthalene (7.8×10^{-3})	0.80	-1.7 to $+2.3$	+1.6
<i>p</i> -Dimethoxybenzene (5.9×10^{-3})	0.80	-1.7 to $+2.3$	+1.15, +1.75
Diphenvl (6.6×10^{-3})	0.90	-1.7 to $+2.8$	+1.8.+2.4
N,N-Dimethylaniline (4.8 \times 10 ⁻³)	0.90	-1.7 to $+2.8$	+0.7, +2.25

^{*a*} 0.5 M (C₂H₅)₄NClO₄ in CH₃CN.

V/sec), the peaks merged into a broad plateau. No reduction peaks were observed. If an electroactive intermediate is assumed reducible at potentials more positive than 0 V, the half-life of this oxidation product must be less than 1 msec to escape detection at our maximum scan rate.

Seven coulometric runs at +1.80 V (vs. Ag -10^{-2} M AgNO₃ in CH₃CN) gave *n* values ranging from 0.73 to 0.93 and averaging 0.8 electron per cyanide ion. The solvent-electrolyte medium was preelectrolyzed to eliminate electroactive impurities. Emission spectroscopic determinations showed negligible platinum content in the solution after electrolysis, and the correction for silver ion from the reference electrode was <+5% in the worst case.

Acetonitrile was chosen as a solvent with the widest anodic and cathodic limits as judged from measurements with perchlorate electrolytes (Table II).

Aromatic Substrates

In selecting potentials for cyanide oxidations in the presence of aromatic substrates, reported oxidation pocentral anode was rotated to minimize polarization effects. A saturated calomel electrode, placed close to the rotating anode, was used to monitor and control the anode potential at the desired value (see Experimental Section). To minimize cell resistance, cell dividers were used only for selected experiments. Tetraethylammonium cyanide served as both the supporting electrolyte and as a reactant.

Two types of aromatic cyanation reactions were observed from electrolysis of acetonitrile solutions of tetraethylammonium cyanide containing aromatic substrates, and generally only at anode potentials greater than the oxidation half-wave potential of aromatic substrate. One type was replacement of aromatic hydrogen in orientations typical of electrophilic substitution reactions (*vide infra*). With di- and trimethoxybenzenes, direct replacement of methoxyl occurred

(11) The E_p values were determined under conditions generating electrochemically irreversible processes. Significant oxidation takes place at more negative potentials so that the E_p values represent maximum oxidation potentials.

(12) L. Eberson and S. Nilsson, Abstracts, Faraday Society Meeting, Newcastle-on-Tyne, April 2-4, 1968, No. 45.

Reactant	$E_{1/2},$ +V/sce	Product	Anode potential, +V/sce	Yield,• %	Posi- tion	Spin density ⁷	Position substi- tuted
Anisole	1.76	Anisonitrile o-Methoxybenzonitrile	2.0ª	5	1 2 3 4	0.258 0.122 0.048 0.282	2
<i>p</i> -Dimethoxybenzene <i>p</i> -Dimethoxybenzene <i>p</i> -Dimethoxybenzene	1.34	Anisonitrile Anisonitrile	2.0 ^b 1.3° 0.9 ^d	95 >90 >95	1, 4 2, 3	0.241 0.084	1 (4)
Veratrole	1.45	o-Methoxybenzonitrile	2.0	94	1, 2 3 4	0.233 0.012 0.162	1 (2)
1,3-Dimethoxybenzene	1.38	2,4-Dimethoxybenzonitrile ^a	2.0	12	1, 3 2, 5 4, 6	0.161 0.0 0.270	4 (6)
1,2,3-Trimethoxybenzene	1.4 2	2,6-Dimethoxybenzonitrile ^h	2.0	86	1, 3 2 4, 6	0.113 0.316 0.025	2

^a Ratio 49.3% para, 50.7% ortho. ^{b-d} Current efficiencies (conversions): (b) 20% (47%), (c) 30% (30%), (d) 95% (3%). ^e Corrected for recovered starting material. ^f Of highest filled molecular orbitals. Calculated for the cation radicals [A. Zweig, W. G. Hodgson, and W. H. Jura, J. Am. Chem. Soc., **86**, 4124 (1964)]. ^e Reference 13. ^h Reference 14.

only when methoxy groups were situated in *ortho* and *para* positions. With anisole or *meta*-oriented methoxyl groups, reaction type 1 occurs. With tertiary amines, cyanation at an α position of an alkyl group supplants ring substitution (reaction 3).

$$ArH \xrightarrow{Et,NCN} ArCN \qquad (1)$$

$$CH_{3}O \longrightarrow OCH_{3} \xrightarrow{Et_{4}NCN} CH_{3}O \longrightarrow CN \quad (2)$$

Methoxybenzenes. Under the above conditions, pdimethoxybenzene, veratrole, and 1,2,3-trimethoxybenzene gave anisonitrile, o-methoxybenzonitrile, and 2,6-dimethoxybenzonitrile, respectively (Table IV). After about 50% conversion of aromatic reactant, yields were generally >90% with current efficiencies of $\sim 30\%$.

With anisole and *m*-dimethoxybenzene, methoxyl displacement did not occur. Instead, nuclear substitution produced, generally in much lower yields, methoxybenzonitrile (50.7% ortho, 49.3% para) and 2,4-dimethoxybenzonitrile, respectively.



Electrolytic Oxidation of Tetraethylammonium Cyanide Solutions. Control electrolyses of acetonitrile

(13) H. Baganz and I. Paproth, Naturwissenschaften, 40, 341 (1953);
P. Karver, A. Rebmann, and E. Zeller, Helv. Chim. Acta, 3, 270 (1920),
(14) F. Mauthner, J. Prakt. Chem., 121, 259 (1929); A. Russell and W. G. Tebbens, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 293.

solutions of tetraethylammonium cyanide in the absence of aromatic substrates at the same anode potentials (e.g., +2.0 V vs. sce) revealed a competing cyanation re-



Figure 1. Preparative scale electrolysis cell.

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tion involving the electrolyte cation. The products were  $\alpha$ -diethylaminopropionitrile, ethylene, and hydrogen. Electrolyses using alundum dividers showed both hydrogen and ethylene were evolved at the cathode

Et<sub>4</sub>NCN 
$$\xrightarrow{\text{CH}_3\text{CN}}$$
 Et<sub>2</sub>NCH(CH<sub>3</sub>)CN + CH<sub>2</sub>=CH<sub>2</sub> + H<sub>2</sub>

while the nitrile was isolated from the anolyte. Discharge of tetraethylammonium cation<sup>15</sup> apparently occurs at the prevailing cathode potential (ca. -2.5 V sce) to give triethylamine as well. Migration of triethylamine to the anode, oxidation, and cyanation would account for the results (vide infra). Yields of  $\alpha$ diethylaminopropionitrile increased in undivided cells or when triethylamine was added to the electrolyte solutions. Darkening occurred in these reactions and cathodic discharge of acetonitrile undoubtedly accounted for part of the hydrogen evolution.

Anodic Cyanations of Amines. The reaction noted above was applied to several tertiary amines. In each case, cyanation at an  $\alpha$  position occurred (Table V).

Table V. Anodic Cyanation of Amines

| R <sub>2</sub><br>R <sub>1</sub> NCH                                                       | $ I_2 R_3 \xrightarrow{CN^-}_{anode} R_1 N - CH $ | <b>R</b> 3                                                                                                                        |
|--------------------------------------------------------------------------------------------|---------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| R <sub>1</sub>                                                                             | $R_2$                                             | R <sub>3</sub>                                                                                                                    |
| $\begin{array}{c} Et\\ C_6H_5\\ C_6H_5\\ C_6H_5\\ C_6H_5\\ C_6H_6CH_2\\ C_6H_3\end{array}$ | Et<br>CH3<br>Et<br>Et<br>CH3<br>H                 | $\begin{array}{c} \mathbf{CH}_3\\ \mathbf{H}\\ \mathbf{CH}_3\\ \mathbf{H}^a\\ \mathbf{H}\\ \mathbf{H}\\ \mathbf{H}^b \end{array}$ |

<sup>a</sup> Main product. <sup>b</sup> Only dimer was isolated.

No ring cyanations were observed. In mixed amines, e.g., N-methyl-N-ethylaniline, cyanation occurred preferentially at a primary position to give 64% a and 34%b.



Because of the difference in stability of products a and b, several experiments were run to see if this result was merely due to preferential decomposition of b either during reaction or during work-up. Nmr analyses at different extents of reaction and on reactions run at different potentials showed some variation in the a/b ratio, but always distinctly in favor of a. Furthermore, cyanation of benzyldimethylamine gave exclusive cyanation at a methyl group rather than at a benzyl position. In addition to cyanation of a methyl group in N,N-dimethylaniline as the main reaction, significant amounts of N-methylaniline appeared.

In the presence of secondary amines, the reaction becomes more complex. Attempted cyanation of Nmethylaniline under similar conditions in an undivided cell gave coupled product resulting from a cathodic dimerization.<sup>16</sup> When the same reaction was run in the ano-

$$C_{6}H_{3}NHCH_{3} \xrightarrow{\text{EtaNCN}} C_{6}H_{3}NHCH_{2}CH_{2}NHC_{6}H_{5}$$
  
-2.0 V (anode)  
-2.0 V (cathode)

lyte compartment of a divided cell, no dimer was formed in the anolyte, and a cyanated product was not detected.

Primary amines are cleaved at the C-N bond to give products from the resulting carbonium ion at the amine site. Darkening even with tertiary amines is undoubtedly caused by side reactions resulting from hydrogen abstraction from solvent. In the absence of cyanide ion, oxidation of triethylamine in acetonitrile gives triethylammonium ion resulting from hydrogen abstraction from solvent by triethylamine cation radical.<sup>17-19</sup>

Anodic Cyanation of Other Aromatic Compounds. Ring cyanation of other aromatics generally resulted in moderate to low yields of monocyano product. In general, higher yields were obtained from substrates with lower oxidation potentials. For ring cyanations of compounds with higher oxidation potentials, cyanide salt in methanol was a preferred medium. Biphenyl and diphenyl ether gave p-phenyl- and p-phenoxybenzonitriles, respectively, as the main product. The para to ortho ratio was ca. 3. The nitrile group apparently deactivates aromatic systems toward further cyanation (confirmed by oxidation potential studies).<sup>12</sup> Dicyanation was observed only in the case of anthracene using Et<sub>4</sub>NCN in acetonitrile to give 9,10-dicyanoanthracene in 54% yield. Attempts to cyanate benzonitrile were unsuccessful.

Competing methoxylations of side chains were observed when potassium cyanide-methanol solutions were electrolyzed at higher anode potentials. For example, formation of p-(methoxymethyl)toluene accompanied the formation of 2,5-dimethylbenzonitrile from *p*-xylene (Table VI). As expected, however, formation of the ether decreased at lower anode potentials. No side-chain cyanation was observed.

# Discussion

Although cyanide ion unquestionably is oxidized at the potentials used, the results all point to a mechanism involving oxidation of the aromatic substrate to a cationic species (most likely a cation radical) which subsequently reacts with cyanide ion.

While significant amounts of cyanide ion are oxidized at approximately +0.5 V (sce) or greater, cyanation generally occurs only at potentials in the region of or greater than the oxidation half-wave potential of the aromatic substrate. For p-dimethoxybenzene, with an oxidation potential  $(E_{1/2})$  of +1.15 V (see), no cyanation was observed below +0.9 V (sce). The current efficiency for anisonitrile formation increased from 20 to 95% (based on a 2e process) as the anode potential and conversions were decreased from +2.0 to +0.9 V, and from 47 to 3%, respectively (Table IV). The 95% figure measured at low conversion is subject to considerable error but the results are indicative of a reaction which is most efficient in the vicinity of +1.0 V with more current wasted in side reactions at higher potentials. The fact that oxidation of p-dimethoxybenzene can compete favorably with cyanide ion oxidation at

<sup>(15)</sup> L. Horner and A. Mentrup, Ann. Chem., **646**, 49 (1961). Amide ion produces a similar cleavage of  $R_4N^+$  at low temperatures: W. L. Jolly, J. Am. Chem. Soc., 77, 4958 (1955).

<sup>(16)</sup> A similar reductive dimerization of  $\alpha$ -cyanoamines is produced by sodium in toluene: H. Thies, H. Schonenberger, and P. K. Qasba, *Tetrahedron Letters*, 163 (1965). *Cf.* also the anomalous reductive cleavage of Strecker nitriles: P. Rajagopalan and B. G. Advani, ibid., 2197 (1965). Cathodic dimerization of N-phenylmethylenimine, arising from dehydrocyanation of the expected product, is also a possibility.

<sup>(17)</sup> R. F. Dapo and C. K. Mann, Anal. Chem., 35, 677 (1963).
(18) C. D. Russell, *ibid.*, 35, 1291 (1963).

<sup>(19)</sup> Cf. also C. K. Mann, ibid., 36, 2424 (1964).

| Reactant                      | Medium <sup>a</sup> | Product                                                                 | Anode<br>potential,<br>+V vs. sce | Current<br>yield, <sup>b</sup><br>% | Oxidation<br>potential, <sup>c</sup><br>+V vs. sce | Ref     |
|-------------------------------|---------------------|-------------------------------------------------------------------------|-----------------------------------|-------------------------------------|----------------------------------------------------|---------|
| Anthracene                    | Α                   | 9,10-Dicyanoanthracene                                                  | 2.0                               | 54                                  | 1.14                                               | f, s    |
| Anthracene                    | В                   | 9-Cyanoanthracene                                                       |                                   | Trace                               |                                                    | 7       |
| Naphthalene                   | В                   | 1-Cyanonaphthalene                                                      | 1.6-1.8                           | <5                                  | 1.64                                               | 7, 12   |
| Biphenyl                      | Α                   | p-Phenylbenzonitrile <sup>h</sup>                                       | 2.5                               |                                     | 1.78                                               |         |
| Biphenyl                      | С                   | p-Phenylbenzonitrile                                                    | 1.75                              | 20                                  |                                                    |         |
| Biphenyl                      | В                   | p-Phenylbenzonitrile <sup>k</sup>                                       |                                   |                                     |                                                    | 12      |
| Diphenyl ether                | С                   | p-Phenoxybenzonitrile <sup>1</sup>                                      | 0.5-3.0                           | 27                                  | 1.67 <sup>i</sup>                                  | r, s    |
| Benzene                       | С                   | Benzonitrile                                                            | 2.0-3.5                           | Trace                               | 2.38                                               |         |
| Toluene                       | В                   | Methylbenzonitrile <sup>d</sup>                                         |                                   |                                     | 2.28                                               | 12      |
| Chlorobenzene                 | В                   | Chlorobenzonitrile <sup>e</sup>                                         |                                   |                                     | 2.37                                               | 12      |
| <i>p</i> -Xylene              | С                   | 2,5-Dimethylbenzonitrile                                                | 3.5                               | 23.4                                | 1.86                                               |         |
|                               |                     | p-(Methoxymethyl)toluene                                                |                                   | 28.3                                |                                                    |         |
| $C_6H_5N(CH_3)_2$             | Α                   | C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> )CH <sub>2</sub> CN     | 2.5                               | 37                                  | 0.710                                              | m, s    |
| $C_{6}H_{5}N(C_{2}H_{5})_{2}$ | Α                   | C6H5N(C2H5)CH(CH3)CN                                                    | 1.5-2.0                           | 36                                  | 0. <b>6</b> 4                                      | n, s    |
| $C_6H_5N(CH_3)C_2H_5$         | Α                   | C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> )CH(CH <sub>3</sub> )CN | 2.0                               | 45                                  |                                                    | 0, S    |
|                               |                     | $C_6H_5N(C_2H_5)CH_2CN$                                                 |                                   |                                     |                                                    | o, p, s |
| $C_6H_5CH_2N(CH_3)_2$         | Α                   | $C_6H_5CH_2N(CH_3)CH_2CN$                                               | 2.0                               | 20                                  | 1.0 <sup><i>i</i></sup>                            | q, s    |

<sup>a</sup> A = Et<sub>4</sub>NCN, CH<sub>3</sub>CN; B = NaCN, CH<sub>3</sub>OH; C = KCN, CH<sub>3</sub>OH. <sup>b</sup> Assuming a 2e process. <sup>c</sup> E<sub>1/2</sub> for reactant; Pt electrode in CH<sub>3</sub>CN. <sup>d</sup> 40% ortho, 8% meta, 52% para. <sup>e</sup> 50% ortho, 50% para. <sup>f</sup> R. O. C. Norman and P. D. Ralph, J. Chem. Soc., 2221 (1961); H. Beyer and H. Fritsch, Ber., 74, 494 (1941). <sup>e</sup>  $E_{p/2}$ , ref 20. <sup>h</sup> 30% ortho. <sup>i</sup> Estimated, electrode badly coated. <sup>i</sup> Estimated E from tri-ethylamine and tribenzylamine which have essentially the same oxidation potentials. <sup>k</sup> 25% ortho. <sup>i</sup> 35% ortho. <sup>m</sup> D. B. Luten, Jr., J. Org. Chem., 3, 588 (1939). <sup>n</sup> W. McMeeking and T. S. Stevens, J. Chem. Soc., 347 (1933). <sup>o</sup> F. Sachs and W. Kraft, Ber., 36, 757 (1903); A. Weissberger, et al., J. Am. Chem. Soc., 73, 3100 (1951). P. F. Epstein, J. Org. Chem., 24, 68 (1959). M. Freifelder, J. Am. Chem. Soc., 82, 2386 (1960). C. M. Suter, ibid., 51, 2584 (1929). Reference for product only.

potentials well above +0.5 V is consistent with electrode adsorption of the aromatic before charge transfer.<sup>12, 20, 21</sup>

Studies of other anodic aromatic substitution reactions have also implicated a mechanism involving oxidation of the aromatic to a cationic species and subsequent reaction with a nucleophile. Pertinent examples are methoxylation<sup>20, 22</sup> and acetoxylation<sup>21</sup> of aromatic compounds. Mechanisms involving dications, cation radicals, or concerted nucleophile-assisted two-electron transfer have been proposed.<sup>20, 21, 23</sup> Primarily from isomer distribution studies, the last mechanism has been favored as most closely analogous to homogeneous electrophilic aromatic substitution reactions.<sup>21</sup> The three mechanisms presently cannot be unambiguously distinguished since they all eventually involve the cationic intermediate



in the product-forming step. Recently, formation of dications as the primary electrode process in aromatic hydrocarbon oxidations has been challenged.<sup>24,25</sup> Evidence has been presented supporting the cation-radical mechanism in the cases studied.<sup>24,25</sup>

Observed orientations in all cases in the present work are in accord with the well-known patterns for electrophilic substitutions. For the cyanation of methoxybenzenes, the proposed mechanism in Scheme I involves a le oxidation to cation radical 1, attack by cyanide ion, and a subsequent le oxidation to the usual cationic intermediate, 3, associated with aromatic elec-

(20) N. L. Weinberg and H. R. Weinberg, Chem. Rev., 68, 449 (1968).
(21) L. Eberson, J. Am. Chem. Soc., 89, 4669 (1967).
(22) B. Belleau and N. L. Weinberg, *ibid.*, 85, 2525 (1963).
(23) C. L. Perrin, Progr. Phys. Org. Chem., 3, 220 (1965).
(24) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, J. Am. Chem.

Soc., 89, 5766 (1967).

(25) M. E. Peover and B. S. White, J. Electroanal. Chem., 13, 93 (1967).





trophilic substitutions. According to this mechanism, the position of attack by cyanide ion will be determined by orientation effects operating in the cation radical. That these orientation effects are the same as those generated from the neutral molecule is supported by the spin-density distributions calculated from esr spectra of the observed cation radicals<sup>26</sup> (Table IV). These spin densities should also reflect the electron distribution of the highest filled molecular orbital of the corresponding neutral molecule, according to the one-electron MO approximation that removal of one electron does not affect the distribution of the remaining electrons. The data in Table IV support the suggestion that the electron distribution of the hfmo in the cation radical determines the path of normal electrophilic substitution reactions<sup>27</sup> considering the anode as the electrophile. In each case, the methoxyl displacement occurs at the position of highest spin density. Finally, loss of the methoxyl group as formaldehyde from 3 or 3' can occur either before or after desorption.<sup>28</sup>

Scheme II is an attempt to describe the electrode process in more detail. The steps are initial adsorption of the aromatic substrate, a 1e oxidation to cation radical, and a cvanide ion assisted le oxidation to the cation intermediate 3', followed by desorption. This sequence differs essentially from that proposed by Eberson<sup>21</sup> for acetoxylation in that 2e electron transfer is depicted as

<sup>(26)</sup> See Zweig, Hodgson, and Jura, footnote f, Table IV.

<sup>(27)</sup> K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, J. Chem. Phys., 22, 1433 (1954).

<sup>(28)</sup> A less likely sequence in which methoxyl radical is lost from 2 to give methoxyl radical and eventually unstable methyl cyanate cannot be ruled out.

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Scheme II



occurring by two discrete le steps<sup>26</sup> and attack by cyanide ion is on a cation-radical intermediate 1'. Distinct evidence for cyanide ion participation is not at hand but is reasonable in view of the greater nucleophilicity of cyanide ion relative to acetate ion.<sup>29</sup> If the first electron transfer is cyanide ion assisted, 1' might resemble radical 2. If the second step is cyanide assisted, 2 is an unnecessary intermediate.

Schemes I or II also apply to the substitution by cyanide of aromatic hydrogen, *i.e.*,  $CH_3O = H$  at the point of attack. Thus, attack of anisole gives 49.3% *para* and 50.7% ortho at the two ring H positions of highest spin-density<sup>26</sup> characteristic of an electrophilic process.



In contrast, cyanation of anisole by photochemically generated cyano radicals gives 58% ortho, 14% meta, and 28% para attack.<sup>12,30</sup>

Orientations of cyanations of anthracene, naphthalene, chlorobenzene, biphenyl, diphenyl ether, and toluene are also consistent<sup>12</sup> with a mechanism involving intermediate 3'' (Table VII). Displacement of methoxyl in anisole does not compete with ring hydrogen substitution because an intermediate such as 1' or 3' (p- $CH_3O = H$ ) would be of higher energy than 1'' or 3''. The hydrogen substitution reactions are generally lower yield processes involving aromatic substrates with oxidation potentials above ca. +1.3 V. Cleanest cyanations were obtained on aromatic substrates with oxidation potentials below +1.3 V. Thus, anthracene (oxidation peak potential, +1.2 V (sce)) gave 9,10-dicyanoanthracene<sup>31</sup> in 54% yield, while only 5% conversion to methoxybenzonitriles occurs under the same conditions (Et<sub>4</sub>NCN-CH<sub>3</sub>CN, anode potential +2.0 V (sce)) from anisole ( $E_{1/2} = +1.76$  V).

Table VII. Isomer Distributions for Anodic Cyanations

| Et_NCN-CH_3CN, %            |       |       |      | NaC             | N-CH₃C | )H, % |
|-----------------------------|-------|-------|------|-----------------|--------|-------|
| Compound                    | ortho | meta  | para | ortho           | meta   | para  |
| Anisole                     | 50.7  |       | 49.3 | 53°             | <0.1   | 47    |
| Toluene                     | 31.9  | 3.1   | 65   | 40°             | 8      | 52    |
| Biphenyl                    | 30    |       | 70   | 24 <sup>5</sup> | 0.4    | 75.5  |
| Diphenyl ether <sup>a</sup> | 28    | Trace | 72   | 39.5            | Trace  | 60.5  |

<sup>a</sup> Solvent: CH<sub>3</sub>CN-CH<sub>3</sub>OH, 50:50 vol %. <sup>b</sup> Data from ref 12.

(31) Monocyanoanthracene was not found.<sup>7</sup> According to Scheme I, a dicationic intermediate<sup>32</sup> is not necessary.<sup>23,24</sup>

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

The use of KCN-CH<sub>3</sub>OH gives more cyanated products from the more difficultly oxidized reactants but the products are generally contaminated with methoxylated products. Isomer distributions do not change<sup>12</sup> significantly (Table VII) with medium (Et<sub>4</sub>NCN-CH<sub>3</sub>CN compared to KCN-CH<sub>3</sub>OH) so that involvement of cyano radicals as the nitrile product precursors is also ruled unlikely in methanol.

Cyanation of Amines. Cation radicals have been implicated clearly in anodic oxidation of amines. Esr spectra and cyclic voltammograms for the cation radical of 2,4,6-tri-*t*-butylaniline have been observed.<sup>33</sup> Oxidation of N,N-dimethylaniline at a planinum anode in CH<sub>3</sub>CN<sup>34</sup> is best interpreted in terms of initial formation of a cation radical<sup>12,35</sup> followed by fast chemical reactions.<sup>35</sup> In KOH-CH<sub>3</sub>OH, initial adsorption of this amine has been deduced from a fractional reaction order.<sup>36</sup>

Anodic cyanation of amines appears related to methoxylation of amines and analogous mechanisms are likely (Scheme III). A one-electron oxidation of ad-



sorbed amine to planar cation radical 4 would force closer approach of the alkyl substituents to the electrode surface. Proton removal either before or during the second le oxidation eventually produces cation 5 which gives product by reaction with cyanide ion. Normally Scheme III via a cation of type 5 in homogeneous solution predicts predominant cyanation at the secondary position of the ethyl group. However, steric constraints imposed by the electrode surface make the methyl protons more accessible in 4 and the  $-N^+=CH_2$  more stable in 5, even if desorption begins during formation of the incipient cation. This proposed mechanism accommodates the preference for attack on methyl group compared to the methylene positions.

In methoxylation of N,N-dimethylbenzylamine in which an even greater preference for generating the benzyl carbonium ion would be expected, attack at a methyl group was favored by a factor of 4.<sup>37</sup> A steric explanation was proposed,<sup>12,37</sup> but the actual stereochemical configuration around nitrogen was not considered. Anodic cyanation of N,N-dimethylbenzylamine gives exclusive attack at a methyl group. Chemical oxidations of N,N-dimethylbenzylamine with Nbromosuccinimide, manganese dioxide, benzoyl peroxide, and alkaline potassium permanganate give ex-

(33) G. Cauquis, G. Fauvelot, and J. Rigaudy, Compt. Rend., 264, 1758 (1967).

(34) V. Dvorak, I. Nemec, and J. Zyka, Microchem. J., 12, 99 (1967). (35) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, J. Am. Chem. Soc., 88, 3498 (1966). Oxidation of  $CN^{-}$  to  $CN \cdot only$  by a very stable cation radical such as tri-panisylamine was recently reported: L. Papouchado, R. N. Adams, and S. W. Feldberg, J. Electroanal. Chem. 21, 408 (1969).

(36) N. L. Weinberg and T. B. Reddy, ibid., 90, 91 (1968).

(37) N. L. Weinberg and E. A. Brown, J. Org. Chem., 31, 4058 (1966). Involvement by methoxyl radicals was also postulated [P. J. Smith and C. K. Mann, *ibid.*, 33, 316 (1967)] but was subsequently ruled out: N. L. Weinberg, *ibid.*, 33, 4326 (1968).

<sup>(29)</sup> K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1963, p 424.

<sup>(30)</sup> Photochemical cyanations of methoxynitrobenzenes presumably involve anion radicals: R. L. Letsinger and J. H. McCain, J. Am. Chem. Soc., 88, 2884 (1966).



Figure 2. Esr spectrum. Anodic oxidation of tetraphenylarsonium cyanide in DMSO.

pected attack at the benzyl position to produce benzaldehyde.<sup>38</sup> During anodic cyanation of N,N-dimethyl-



benzylamine, abstraction of a proton and oxidation at the benzyl position (adjacent to two positive centers) are probably rendered more difficult than abstraction from a methyl position (Scheme IV). Adsorption of the aromatic ring may not be necessary in this case, however.

Scheme IV



Fate of Cyano Radical. Electrochemical oxidations of cyanide ion at a Pt electrode were carried out in an esr cavity to elucidate the fate of the cyano radical. Although cyano radical was not detected, a basic 13line signal (Figure 2) characteristic only of the cyanide oxidation process was observed. This was confirmed by variation of cation and solvent. Thus, aside from differences in resolution, the same signal was obtained with  $Et_4NCN$ ,  $(CH_3)_4NCN$ , and  $(C_6H_5)_4AsCN$  in oxygen-free acetonitrile, dimethyl sulfoxide, pyridine, or dimethyl- $d_6$  sulfoxide. Involvement of hydrogen is ruled out in the deuterated solvent. Best resolution was obtained with 0.4 M (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsCN in DMSO or DMSO- $d_6$ . Esr signals with good signal-to-noise ratios appeared at electrode potentials greater than +1.0 V. Addition of  $\sim 1\%$  water had little effect, producing only a slight decrease in signal-to-noise ratio.

The spectrum in Figure 2 is interpreted in terms of four nitrogen atoms, three of which give almost identical hyperfine splittings. The hyperfine splitting ratio is ca. 3:1, with the single nitrogen having the larger splitting. The postulated tricyanomethylenimine anion-radical structure shown in the proposed scheme below accounts for these data. Total reaction via this



Figure 3. Esr spectrum. Anodic oxidation of tetraphenylarsonium cyanide-<sup>16</sup>N in DMSO.

sequence predicts consumption of 0.75 electron per cyanide ion in accord with the coulometric data.



Structural elements were checked by isotopic substitution. Anodic oxidation of  $(C_6H_5)_4AsC^{15}N$  containing only nitrogen-15 in DMSO achieved the simplification shown in Figure 3. Since <sup>16</sup>N has a spin of <sup>1</sup>/<sub>2</sub>, the spectrum indicates four nitrogens, two of which are equivalent and a third with a slightly smaller coupling constant. The fourth N gives a splitting approximately three times greater than the other three. There is good agreement between the <sup>14</sup>N and <sup>15</sup>N spectra. The presence of other magnetic nuclei can be ruled out.

Information on the structural features of the carbon atoms were obtained by anodic oxidation of  $(C_6H_5)_4$ -AsCN enriched with 10% and 20% <sup>13</sup>C in separate experiments. Two sets of <sup>13</sup>C splittings were observed with a relative intensity ratio of 2:1. The relative intensity of the more intense <sup>13</sup>C resonance lines to that of the <sup>12</sup>C spectrum, when considered with the known <sup>18</sup>C enrichment level, implies that two carbon atoms are involved in this set.

Thus, at least three carbon atoms are present in the radical, two of which are equivalent. Since little is known about <sup>13</sup>C splittings, it is not surprising that splittings from all four carbon atoms are not seen. Reliable calculation of expected <sup>13</sup>C splittings<sup>39</sup> was not possible, and near zero <sup>13</sup>C splittings have been observed previously.

With the electrolyzing current turned off, signal intensity decreased by a factor of 0.5 in *ca*. 0.5 hr. This includes diffusion of the radical out of the esr cavity setting a minimum value on its half-life which is probably much longer. The esr parameters are summarized in Table VIII.

Table VIII. Summary of Esr Parameters

| Solvent               | g value                                                                                    | Hyperfine<br>splitting <sup>a</sup>                                                                                                                                      | No. of<br>nuclei      |
|-----------------------|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| CH₃CN<br>DMSO<br>DMSO | $\begin{array}{r} 2.0038 \pm 0.0002 \\ 2.0030 \pm 0.0002 \\ 2.0036 \pm 0.0002 \end{array}$ | $\begin{array}{l} A(^{14}\mathrm{N}) = 1.86\\ A(^{14}\mathrm{N}) = 5.90\\ A(^{15}\mathrm{N}) = 2.68\\ A(^{15}\mathrm{N}) = 2.52\\ A(^{15}\mathrm{N}) = 8.22 \end{array}$ | 3<br>1<br>2<br>1<br>1 |

 $^{a} \pm 0.01.$ 

(39) M. T. Jones and W. R. Hertler, J. Am. Chem. Soc., 86, 1881 (1964).

<sup>(38)</sup> D. Buckley, S. Dunstan, and H. B. Henbest, J. Chem. Soc., 4901 (1957); E. F. Curragh, H. B. Henbest, and A. Thomas, *ibid.*, 3559 (1960); S. Dunstan and H. B. Henbest, *ibid.*, 4905 (1957); R. Stewart, "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 60. In oxidations with platinum and molecular oxygen, however, methyl groups are favored over benzyl positions: G. T. Davis and D. H. Rosenblatt, *Tetrahedron Letters*, 4085 (1968).



Figure 4. Esr electrolysis cell.

An additional test for electrochemically generated cyano radical was carried out by running a simultaneous cyanide ion oxidation and a Kolbe oxidation of propionate ion. Propionitrile was obtained in ca. 7%



yield. This experiment is ambiguous in that the propionitrile might be formed via oxidation to ethyl carbonium ion followed by reaction with cyanide ion. However, formation of ethyl cation is unlikely under the conditions used. 40

#### **Experimental Section**

All potentials are referred to a saturated calomel electrode unless otherwise noted. All experiments were performed under dry nitrogen. Acetonitrile was purified by refluxing over P2O5, over K<sub>2</sub>CO<sub>3</sub>, and distillation through a packed column with a conductivity cell built into the receiver for monitoring impurities.

Apparatus for Electroanalytical Studies. The cell used for chronopotentiometry and cyclic voltammetry consisted of a compartment containing the working electrode and a side arm of this compartment isolated by a fritted glass disk containing the auxiliary electrode, commonly a spiral of platinum wire. A platinum wire sealed in the bottom of the main compartment was used to make contact when a mercury pool was used as the working electrode. The cap for the main compartment had a gas inlet, a gas outlet, and a sleeve through which a solid working electrode was positioned. In a third compartment, the reference electrode was connected to the main compartment by a Luggin capillary which terminated near the working electrode. The reference electrode was a solution of silver nitrate  $(10^{-2} M)$  in acetonitrile contained in a salt-bridge tube available from Corning Glass as a combination of a glass tube and a bulb on one end of unfused Vycor (part no. 749303-7900-7930). A silver wire in the solution was sealed through a serum cap. The solid working electrode was a circular platinum sheet sealed in a glass jacket and spot welded to a platinum wire. The electrode areas were determined by chronopotentiometry through the reduction of ferricyanide ion in aqueous 1 M potassium chloride solution using 7.67  $\times$  10<sup>-6</sup> cm<sup>2</sup>/sec for the diffusion coefficient<sup>41</sup> of ferricyanide ion.

The cell for controlled-potential coulometry was the usual type constructed from a 250-ml heavy-walled beaker and a Teflon lid fabricated to hold gas dispersion tubes, bridges, etc.

The cell used for the esr measurements (Figure 4) provides reasonably efficient separation of the working and auxiliary electrodes without unduly high resistances. The salt-bridge tubes have been described above. The cell was tailored to fit the probe area of the Varian V-4500 esr spectrometer. The working electrode was platinum. The esr cell was loaded in the drybox and then sealed.

The instrument used to control potential or current for electroanalytical studies employed an operational amplifier circuit design. An output of 0.80 A at 40 V was available. The response time of this instrument was about 1 msec under ideal conditions and may be longer depending on the load.

The triangular-wave generator used for cyclic voltammetry had a maximum output of +10 V and a continuously variable period of  $5 \times 10^{-3}$  to  $6 \times 10^{2}$  sec. Either a single or multisweep scan could be selected.

A Tektronix 564 oscilloscope and a Speedomax recorder were used as read-out devices.

Apparatus for Preparative Studies. The three-electrode cell depicted in Figure 1 was used for all preparative studies. Anode and cathode were constructed of concentric platinum gauze cylinders. The central anode was rotated to minimize polarization effects by an insulated connection to a stirring motor. Electrical contact was made to the mercury seal around the rotating metal shaft.

Constant electrode potential was maintained using a modified American Instrument Company Redox-O-Trol 4-3965, which employed a 190-W dc generator with a maximum output of 27 V and 7.0 A, in conjunction with an integrating recorder for measurement of charge. The working electrode potential was set by a manually adjusted reference potential variable from 0.4 to 9.0 V.

Synthesis of Electrolytes. Tetraphenylarsonium Cyanide. A solution of 49.0 g (1.0 mol) of sodium cyanide in 1500 ml of warm methanol was added over 0.5 hr to a stirred solution of 200.0 g (0.495 mol) of tetraphenylarsonium chloride in 500 ml of methanol under an atmosphere of dry nitrogen. The mixture was stirred for an additional 0.5 hr and filtered to remove the precipitated sodium chloride (9.8 g of precipitate). The filtrate was evaporated to dryness and the residue was extracted with 400 ml of warm dry acetonitrile. The extract was filtered from the residue of 42.4 g (NaCl + excess NaCN) and the filtrate was concentrated to 360 ml giving crop 1 (46.6 g) of tetraphenylarsonium cyanide. Addition of tetrahydrofuran precipitated additional salt to give a total yield of 161.9 g (83%) of tetraphenylarsonium cyanide monohydrate. Anal. Calcd for  $C_{23}H_{20}NAs \cdot H_2O$ : C, 70.26; H, 5.19; N, 3.28; As, 17.53. Crop 3, Found: C, 69.93; H, 5.30; N, 3.14; As, 17.88.

Arsenic was termined by a Parr bomb technique since standard digestion with nitric acid gave only 0.3% arsenic. A sample was dried at  $110^{\circ}$  (0.1 mm) for 2 hr. Anal. Calcd for  $C_{25}H_{20}NAs$ : C, 73.35; H, 4.93; N, 3.42; As, 18.30. Found: C, 73.27; H, 4.99; N, 3.06; As, 18.18; H<sub>2</sub>O (Karl Fisher), 0.07.

Tetramethylammonium Cyanide. Using the above procedure, 50 g (1.0 mol) of sodium cyanide and 54 g (0.5 mol) of tetramethylammonium chloride were combined in 1.8 l. of methanol to give 22.2 g of tetramethylammonium cyanide. Since the salt was not very soluble in acetonitrile, the initial precipitate (NaCl + (CH<sub>3</sub>)<sub>4</sub>NCN, 74 g) was reextracted with three 500-ml portions of warm methanol, filtered, and worked up as before to obtain another 7.8 g of tetramethylammonium cyanide. Anal. Calcd for  $C_5H_{12}N_2$ : C, 59.95; H, 12.08; N, 27.96. Found: C, 59.85; H, 72.06; N, 28.26; Cl, <0.03%.

Tetraethylammonium Cyanide.<sup>42</sup> Under dry nitrogen, a solution of 50 g of sodium cyanide (Mallinckrodt AR) in 1.5 l. of methanol

<sup>(40)</sup> E. J. Corey and J. Casanova, Jr., J. Am. Chem. Soc., 85, 165 (1963); E. J. Corey, N. L. Bauld, R. T. Londe, J. Casanova, Jr., and E. T. Kaiser, ibid., 82, 2645 (1960); L. Eberson, Acta Chem. Scand., 17, 1196 (1963).

<sup>(41)</sup> M. von Stackelberg, M. Pilgram, and V. Tomme, Z. Elektrochem., 57, 342 (1953). (42) O. W. Webster, W. Mahler, and R. E. Benson, J. Am. Chem.

Soc., 84, 3678 (1962).

was added to a stirred solution of 100 g of tetraethylammonium chloride (RSA Corp., anhydrous) in 200 ml of methanol. The reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with 1 l. of dry acetonitrile. The extract was evaporated under reduced pressure, and crystals of product formed. When about 200 ml of solution remained, 47 g of tetraethylammonium cyanide was collected on a filter and was washed with acetonitrile. Anal. Calcd for  $C_9H_{20}N_2$ : C, 69.17; H, 12.90; N, 17.93. Found: C, 69.82; H, 12.96; N, 17.77. On dilution with tetrahydrofuran the filtrate yielded an additional 28 g of product, which was recrystallized from acetonitrile before use.

Tetraphenylarsonium Cyanide-<sup>13</sup>C. Using the procedure described above, 0.5 g (0.01 mol) of sodium cyanide-<sup>13</sup>C (50.5% <sup>13</sup>C, Merck and Co., Ltd.) in 15 ml of methanol was added to a solution of 4.1 g (0.01 mol) of tetraphenylarsonium chloride in 10 ml of methanol. A total of 3.6 g of tetraphenylarsonium cyanide-<sup>13</sup>C was obtained. Mass spectral analysis by direct introduction of the sample into the isatron indicated *ca.* 50% <sup>13</sup>C, based on the weak parent ions at *m/e* 409 and 410.

Tetraphenylarsonium Cyanide-<sup>15</sup>N. Using the procedure described above, 0.70 g (0.0106 mol) of potassium cyanide-<sup>15</sup>N (97% <sup>15</sup>N, Merck and Co., Ltd.) in 15 ml of methanol was added under dry nitrogen to a solution of 4.44 g (0.0106 mol) of tetraphenylarsonium chloride in 10 ml of methanol. Totals of 0.74 g of sodium chloride and 3.63 g of tetraphenylarsonium cyanide were obtained. The arsonium salt was assayed for cyanide-<sup>15</sup>N content by acidifying a sample in a gas sampling bulb for mass spectral analysis. Based on *m/e* 26 and 27 ions corrected for nitrogen and assuming the same sensitivity of both isotopic molecules, values of 97.5% HC<sup>15</sup>N and 2.4% HC<sup>14</sup>N were found.

Electrolyses. Typical electrolyses are summarized below.

Electrochemical Cyanation of p-Dimethoxybenzene. A solution of 30.0 g (0.192 mol) of tetraethylammonium cyanide and 10.0 g (0.0725 mol) of p-dimethoxybenzene in 375 ml of acetonitrile was electrolyzed at an anode potential of +2.0 V for 15 hr. The current decreased slowly from 1.0 to 0.5 A. A total of 0.5 faraday was passed. Approximately 75% of the acetonitrile was removed under vacuum on a rotary evaporator and the remaining crude liquid was diluted with 100 ml of water. The aqueous mixture was then extracted five times with 50-ml portions of ether. The combined ether layers were dried and distilled. After removal of the ether, the remaining 9.5 g of crude liquid product was shown to be 47% anisonitrile and 53% dimethoxybenzene by vapor phase chromatographic analysis. The product contained at least 95% of the above mixture. The anisonitrile was isolated by preparative vpc and shown to be identical with an authentic sample (Eastman Kodak Co.) by its infrared spectrum. The total conversion was 47% and the yield was 95%.

When the experiment was conducted in acetonitrile containing 5% water, 0.73 faraday was passed and, in addition to the anisonitrile, 1 g of *p*-methoxybenzamide was isolated.

Cyanation of Anisole. A solution of 10.0 g (0.093 mol) of anisole and 30.0 g (0.192 mol) of tetraethylammonium cyanide dissolved in 375 ml of acetonitrile was electrolyzed at an anode potential of +2.0 V for 18 hr. The initial total potential across the cell was 5.2 V and the average current level was  $\sim 0.6$  A giving a total current consumption of 0.313 faraday. The mixture was worked up as above. After removal of the ether, the crude undistilled liquid showed weak CN absorption and was largely unreacted anisole by vapor phase chromatography and infrared analysis. The methoxybenzonitriles (total yield 5% by vpc) were concentrated by distillation. Analysis by vpc gave an isomer distribution of 50.7% o-, 49.3% p-, and no m-methoxybenzonitrile using a 1-m stainless steel column packed with butanediol succinate on 60-80 Chromosorb W, a column temperature of 174° (preheater 225°), and a flow rate of 10 cc/7 sec. Using a column temperature of 148° (preheater  $215^{\circ}$ ) and a flow rate of 10 cc/4.2 sec, retention times for the ortho and para isomers were 6.85 and 5.45 min, respectively. Each nitrile was isolated by preparative vpc and shown to be identical with an authentic sample<sup>43</sup> by infrared spectra.

Electrochemical Cyanation of Anthracene. A solution containing 0.53 g (3 mmol) of anthracene and 6.0 g (38.5 mmol) of tetraethylammonium cyanide in 300 ml of acetonitrile and 100 ml of ether was electrolyzed for 0.6 hr at an anode potential of 2.0 V. Total current passed was 0.027 faraday. After half the acetonitrile

(43) Samples were obtained from K & K Laboratories, Inc., Plainview, N. Y.

and ether was evaporated, the mixture was diluted with water and filtered to give 0.373 g of crude 9,10-dicyanoanthracene. This solid was dissolved in boiling benzene and the solution was filtered to remove some dark amorphous impurities. An analytical sample was obtained by recrystallization from benzene to give 73 mg of greenish yellow needles, mp  $340-341^{\circ}$  dec (sealed capillary, lit.<sup>44</sup> mp  $334^{\circ}$ ). The infrared spectrum was identical with that of an authentic sample.<sup>44</sup> Anal. Calcd for C<sub>18</sub>H<sub>8</sub>N<sub>2</sub>: C, 84.19; H, 3.53; N, 12.28; mol wt, 228. Found: C, 84.30; H, 3.88; N, 12.35; mol wt, 228 (mass spectroscopy).

Electrochemical Oxidation of Tetraethylammonium Cyanide. A solution of 30 g of tetraethylammonium cyanide in 375 ml of acetonitrile was electrolyzed at an anode potential of 2.0 V for 12 hr. The current decreased from 1.2 to 0.16 A (0.435 faraday). The total initial voltage across the cell was 5.0 V and the cathode potential was -2.5 V. After electrolysis, the mixture was worked up as usual to give 9.4 g (39%) of  $\alpha$ -diethylaminopropionitrile,<sup>45</sup> bp 43-45.5° (1.0 mm).

Electrochemical Cyanation of Biphenyl in Methanol. A solution of 10.0 g (0.065 mol) of biphenyl and 10.0 g (0.153 mol) of potassium cyanide in 110 ml of methanol was electrolyzed using an anode potential of +1.75 V. The current dropped from 2.5 to 0.3 A in 2 hr. Total current consumed was 0.5 faraday in 23 hr. The mixture slowly turned orange as electrolysis proceeded. At the end of the electrolysis, the current level had dropped to 0.03 A. The mixture was worked up in the usual manner and the final distillation gave 2.0 g of starting biphenyl and 2.8 g of phenylbenzonitriles, bp  $120-139^{\circ}$  (0.5 mm), with a residue of 2.1 g. Vpc analysis indicated 70% para and 30% ortho cyanation. The distillate could also be purified by careful chromatography on alumina using benzene as the eluent. Chromatographic cuts of pphenylbenzonitrile43 were combined and recrystallized from hexane to give an analytical sample, mp  $83-84^{\circ}$ . Anal. Calcd for C<sub>13</sub>H<sub>9</sub>N: C, 87.12; H, 5.06; N, 7.82. Found: C, 86.97; H, 4.96; N, 7.75. The nmr and ir spectra were compared with spectra of authentic samples.

Electrochemical Cyanation of p-Xylene in Methanol. In the rotating anode cell, 20.0 g of p-xylene, 10 g of potassium cyanide, and 110 ml of methanol were electrolyzed using an anode potential of 3.5 V for 3 hr and 3.0 V for 18 hr. Applied voltage across the cell varied from 5.5 to 4.0 V during the reaction. Total current consumed was 1.3 faraday. The methanol was evaporated from the dark orange mixture. The residue was treated with 100 ml of water and extracted four times with 50-ml portions of ether. The combined ether layers were dried and distilled. (Filtration and acidification of the basic aqueous layer gave only a trace of brown solid.) After removal of the ether, distillation of the extract gave: fraction 1, bp 67-69° (1.5 mm), 7.6 g; fraction 2, bp 70-113° (1.5 mm), 2.0 g; fraction 3, bp 113-140° (1.5 mm), 1.3 g; fraction 4, bp 140-182° (1.5 mm), 1.3 g; fraction 5, bp 183° (1.5 mm), 0.5 g. Fractions 1 and 2 were colorless, 3 and 4 were yellow, and 5 was orange. Slight decomposition occurred during the distillation of 4 and 5. Fractions 2-5 showed strong nitrile infrared absorption and were largely 2,5-dimethylbenzonitrile, while fraction 1 showed only weak nitrile absorption. Fraction 1 was almost pure *p*-(methoxymethyl)toluene. A sample was purified by preparative vpc. Anal. Calcd for  $C_9H_{12}O$ : C, 79.38; H, 8.88; mol wt, 136.19. Found: C, 79.34; H, 8.90; mol wt, 136 (mass spectroscopy).

The nitrile products were also purified by liquid chromatography on neutral alumina (activity grade 1) in benzene to give 2,5-dimethylbenzonitrile as the predominant product. Hydrolysis product, 2,5-dimethylbenzamide, eluted from the column later.

The experiment was repeated using 10.0 g of potassium cyanide, 110 ml of methanol, 0.1 g of cuprous cyanide, and 20.0 g of *p*xylene. Electrolysis was carried out at 30-55° at a potential of +3.5 V and a total current consumption of 1.11 faradays over a 19-hr period. The usual work-up gave 2.2 g [bp 50-60° (3 mm)] and a red residue of 22 g. The distillate was a mixture of *p*-(methoxymethyl)toluene and *p*-tolualdehyde. The structure of the aldehyde was confirmed by treatment of 0.5 g of distillate with 2,4dinitrophenylhydrazine. The dinitrophenylhydrazone derivative of *p*-tolualdehyde was obtained (0.3 g) as a red crystalline solid, mp 243-244°, after recrystallization from a solution of 95% ethanol and ethyl acetate (lit.<sup>46</sup> mp 232.5-234.5° from nitrobenzene). Anal.

<sup>(44)</sup> See footnote f, Table VI.

<sup>(45)</sup> C. Malen and J. R. Boissier, Bull. Soc. Chim. France, 923 (1956).
(46) H. H. Strain, J. Am. Chem. Soc., 57, 758 (1935); cf. also E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIA, Elsevier Publishing Co., New York, N. Y., 1954, p 88.

| Table IX. | Proton Chemical | Shifts in | Cvanoamines. | Ŧ | Valuesa |
|-----------|-----------------|-----------|--------------|---|---------|

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|                                                                                                  | NCH <sub>3</sub> | NCH <sub>2</sub> CN | NCH <sub>2</sub> CH <sub>3</sub> | NCH   | NCHCH3 | NCH <sub>2</sub> CH <sub>3</sub> |
|--------------------------------------------------------------------------------------------------|------------------|---------------------|----------------------------------|-------|--------|----------------------------------|
| (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH(CN)CH <sub>3</sub>                             | .,               |                     | 7.44 <sup>b</sup>                | 6.25° | 8.594  | 8.95                             |
| C <sub>4</sub> H <sub>5</sub> N(CH <sub>3</sub> )CH <sub>2</sub> CN                              | 7.18             | 6.08                |                                  |       |        |                                  |
| C <sub>6</sub> H <sub>5</sub> N(CH <sub>2</sub> CH <sub>3</sub> )CH(CN)CH <sub>3</sub>           |                  |                     | 6.695                            | 5.66° | 8.53ª  | 8.88"                            |
| C <sub>4</sub> H <sub>5</sub> N(CH <sub>2</sub> CH <sub>3</sub> )CH <sub>2</sub> CN              |                  | 6.08                | 6.69°                            |       |        | 8.89*                            |
| C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> )CH(CN)CH <sub>3</sub>                           | 7.16             |                     |                                  | 5.46° | 8.53d  |                                  |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> CN <sup>7</sup> | 7.61             | 6.42                |                                  |       |        |                                  |
|                                                                                                  |                  |                     |                                  |       |        |                                  |

<sup>a</sup> Measured at 60 MHz in CCl<sub>4</sub>. <sup>b</sup> Center of ABX<sup>3</sup> multiplet. <sup>c</sup> Quadruplet. <sup>d</sup> Doublet. <sup>d</sup> Triplet. <sup>f</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N at  $\tau$  6.66.

Calcd for  $C_{14}H_{12}N_4O_2$ : C, 56.00; H, 4.03; N, 18.66. Found: C, 56.18; H, 4.20; N, 18.57.

The 22 g of residue from the distillation was eluted from a column of 300 g of neutral alumina (activity grade 1) with benzene to obtain fraction 2 (0.674 g) and fraction 3 (10.24 g). Elution with ether gave fraction 4 as 2.18 g. Elution with methanol gave fraction 5 as 0.31 g and fraction 6 as 9.44 g of dark red material. Fractions 2–4 showed strong nitrile absorption at 4.5  $\mu$ . By vpc analysis, fraction 2 was 31% *p*-(methoxymethyl)toluene and 34% 2,5-dimethylbenzonitrile. Fraction 3, which contained about 50% nitrile and 50% of the ether, was rechromatographed on 300 g of alumina to obtain 3.5 g of pure 2,5-dimethylbenzonitrile, established by comparison of its infrared spectrum and its vpc retention time with that of an authentic sample.<sup>43</sup> An additional 5.1 g of the nitrile was obtained.

The total yields under these conditions were 2,5-dimethylbenzonitrile (23%), *p*-tolualdehyde (2.6%), and *p*-(methoxymethyl)toluene<sup>47</sup> (42.4%).

A similar electrolysis was carried out using tetraethylammonium cyanide instead of potassium cyanide. The products consisted mainly of the methyl ether but cyanation again occurred in much lower yield. In addition, it appeared that oxidation of a methyl group to an aldehyde increased when the tetraethylammonium salt was used in place of the potassium salt.

Electrochemical Cyanation of N,N-Dimethylaniline. A solution of 50 g of dimethylaniline and 30 g of tetraethylammonium cyanide in 350 ml of acetonitrile was electrolyzed at an anode potential of +2.5 V. The total output voltage across the cell was 4.8 V. A total of 0.35 faraday was passed. After the usual work-up, the final distillation gave fraction 1, bp 49-50° (0.6 mm), fraction 2, bp

(47) C. D. Gutsche and H. E. Johnson, J. Am. Chem. Soc., 77, 109 (1955).

51-61° (0.6 mm), 2.2 g; and fraction 3, bp 161-168° (0.6 mm), 7.4 g. Infrared analysis of fractions 1 and 2 indicated they were dimethylaniline. Fraction 3 had strong nitrile absorption at 4.57  $\mu$  and weak absorption at 2.95  $\mu$ . Gas chromatographic analysis of fraction 3 indicated *ca*. 10% N-methylaniline, 12% dimethylaniline, and 65% N-phenyl-N-methylaminoacetonitrile.<sup>48</sup> The proton nmr spectrum clearly showed the presence of the C<sub>6</sub>H<sub>6</sub>N(CH<sub>3</sub>)-CH<sub>2</sub>- grouping (see Table IX). *Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>: C, 73.93; H, 6.89; N, 19.17; mol wt, 146.19. Found: C, 73.65; H, 7.05; N, 19.37: mol wt, 146 (mass spectroscopy); 141 (freezing point, C<sub>6</sub>H<sub>6</sub>).

Electrochemical Cyanation of N,N-Diethylaniline. In a similar procedure, electrolytic cyanation of N,N-diethylaniline after consumption of 0.13 faraday gave 4.0 g of  $\alpha$ -(N-phenyl-N-ethylamino)propionitrile.<sup>49</sup>

Electrochemical Cyanation of N-Methyl-N-ethylaniline. Similarly, at an anode potential of +2.0 V after consumption of 0.09 faraday, 3.5 g of a mixture of N-phenyl-N-ethylaminoacetonitrile<sup>50</sup> and  $\alpha$ -(N-phenyl-N-methylamino)propionitrile was obtained in a ratio of *ca*. 1:2.

Electrochemical Cyanation of Benzyldimethylamine. Similarly, at an anode potential of +2.0 V, after consumption of 0.285 faraday in 10 hr, 5.4 g of N-benzyl-N-methylaminoacetonitrile,<sup>51</sup> bp 70-76° (0.3 mm), was obtained.

Acknowledgment. The authors are indebted to Dr. M. T. Jones, formerly of these laboratories, for measurement of the esr spectra and considerable help with the interpretation.

- (48) See footnote m, Table VI.
- (49) See footnote n, Table VI.
- (50) See footnote o, Table VI.(51) See footnote q, Table VI.