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Free Radical Reactions in Organic Electrode Processes. V*[1] Anodic Cyanation of Some Monosubstituted Benzenes*[2]

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The anodic reaction between cyanide ions and monosubstituted benzenes in methanol has been investigated. An examination of the products has indicated that the reaction proceeded by means of the formation of nucleus-cyanated products. The solvent perhaps also participates concurrently in this anodic reaction leading to the formation of methoxylated compounds. The results offer a striking contrast in isomer distribution between these two substitutions. The substituents on the benzene rings had a pronounced effect on the yield of the cyano compounds. The reactivity of the aromatic compounds toward the anodic cyanation decreased in the following order:

anisole $\gg$ toluene $>$ ethylbenzene $>$ cumene $\gg$ benzene $\gg$ methyl benzoate.

These results have been interpreted as resulting from the generation of an aromatic ion radical at an anode by the loss of a π-electron from each molecule.

In a previous paper,[1] we have demonstrated that the anodic reaction of sodium cyanide with some aromatic hydrocarbons, leading to the formation of cyano compounds, could be carried out in methanol by using a platinum anode. The anodic cyanation occurred only on the aromatic nuclei. The situation in this substitution closely resembles that of the electrophilic aromatic substitutions, even though napthalene and anthracene are reactive at the same position in their respective molecules toward both homolytic and electrophilic substitutions.

Two possible intermediates, *i. e.,* an electrophilic cyano radical or an aromatic cation radical, were conceivable for this anodic aromatic cyanation, but at that time we had not found conclusive evidence for making any particular choice between these two species.

In the present work, monosubstituted benzenes were chosen as the organic substrates, and the effect of substituents on the yield and on the variety of the products formed in the electrochemical reaction was investigated in order to elucidate the mode of the anodic cyanation.

Results and Discussion

All the electrolyses were conducted between a platinum anode and a mercury-pool cathode in an undivided cell under essentially similar conditions.

In the experiment with anisole added, a mixture (3 g) of *o*- and *p*-anisnitriles was obtained. From the gas chromatographic analysis, an isomer distribution of 40% *ortho* and 60% *para* was obtained. The *meta* isomer was not detected. The fractional crystallization of the mixture from ethanol led to the isolation of the *p*-isomer. The saponification of the mother liquor with alcoholic potassium hydroxide afforded *o*-anisic acid. These isolated compounds were identified by a mixed melting-point test, elemental analyses, and a study of the infrared spectra.

When toluene was added as an organic substrate, the anodic reaction proceeded by means of the formation of tolunitirles (0.78 g), methoxytoluenes, and an isonitrile. A sharp infrared absorption band at 2180 cm^{-1} and the foul odor of the crude product suggested the formation of an isonitrile. Gas chromatography indicated that the isomer distribution for tolunitriles consisted of 27% *ortho*, 5.4% *meta*, and 67.5% *para*. It yielded no indication of the formation of benzyl cyanide. Among these products, *o*- and *p*-tolunitriles could be separated by chromatography; they were identified, after treatment with alcoholic potassium hydroxide, as *o*-toluamide and *p*-toluic acid respectively.

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*[1] Part IV: K. Koyama, T. Susuki and S. Tsutsumi, *Tetrahedron,* **23**, 2675 (1967).

*[2] Presented partly at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964, and the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

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[1] a) K. Koyama, T. Susuki and S. Tsutsumi, *Tetrahedron,* **23**, 2675 (1967). b) K. Koyama, T. Susuki and S. Tsutsumi, *Tetrahedron Letters,* **1965**, 627.

TABLE 1. ISOMER DISTRIBUTION IN THE PRODUCT OBTAINED FROM THE ANODE REACTION OF CYANIDE ION WITH ETHYLBENZENE

	Isomer distribution			
	Methoxyethylbenzene		Cyanoethylbenzene	
	Retention time* min	%	Retention time* min	%
α-	4.3	80.3	—	—
o-	6.3	3.3	13.5	33
m-	7.4	8.4	21.2	10
p-	8.1	8.0	24.3	57

* Conditions: 3 m-column of 25% polyethyleneglycol 6000 on Shimalite; carrier gas, He, 46 ml/min; column-temp.. 180°C.

A detailed study of isomer distributions, including those of methoxylated products, was made by experiments with ethylbenzene added. The results obtained are summarized in Table 1.

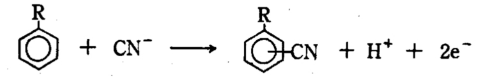
As is indicated in Table 1, it is quite evident that there is a marked difference in isomer distribution between methoxyethylbenzenes and cyanated products. Side-chain methoxylation took place in preference to nuclear methoxylation, while hydrogen atoms on the aromatic ring preferred to undergo substitution with the cyano group. This product analysis was performed by gas chromatography. Several other unidentified peaks were observed on the gas chromatogram; some of them might be assignable to those of isonitriles. The precipitation of silver cyanide in an aqueous silver nitrate solution, through which evolved gases were passed, may provide evidence for the formation of hydrogen cyanide.

The anodic reaction of cyanide ions in the presence of cumene gave considerable amounts of a product arising from the side-chain substitution of cumene with the methoxy group, but it failed to give any side-chain cyanation product. The isomer distribution of the nucleus-cyanated products consisted of 35.6% *ortho*, 13.8% *meta*, and 50.6% *para*. *p*-Cumic acid was isolated from the saponification products obtained by treatment with alcoholic potassium hydroxide.

The anodic reaction of cyanide ions with benzene in methanol afforded a small amount of benzonitrile, together with anisole, but it failed to yield any cyano product when benzene was replaced with methyl benzoate.

The results obtained from the present work are summarized in Table 2.

TABLE 2. CURRENT YIELDS OF NITRILE FORMATION



Substituent R	Half-wave oxidation potential* $E_{1/2}$(ox), V	Current yield (Y), %	Current yield for		
			Ortho	Meta	Para
$-OCH_3$	1.76a)	12.1	4.9	—	7.2
$-CH_3$	1.98b)	1.38	0.4	0.08	0.9
$-C_2H_5$		1.16	0.4	0.12	0.68
$-CH(CH_3)_2$		1.16	0.42	0.16	0.58
-H	2.30b)	0.1			
$-CO_2CH_3$		—	—	—	—

* *vs.* SCE.

a) A. Zwig, W. G. Hodgson and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964).

b) E. S. Pysh and N. C. Yang, *ibid.*, **85**, 2124 (1963).

The substituent on the aromatic ring had a pronounced effect on the yield of aromatic cyano products. The order of the reactivity of the aromatic compounds toward this anodic aromatic cyanation decreases as follows:

anisole $\gg$ toluene $>$ ethylbenzene $>$ cumene
$>$ benzene $\gg$ methyl benzoate.

This order is in good agreement with that of the ability of the substituents to supply electrons to the ring. The results indicate that the substitution reaction took place at electron-rich sites in the ring. In addition, the isomer distributions in the cyano products are in striking contrast to those in the methoxylated compounds obtained together with nitriles.

In order to elucidate the mode of the anodic aromatic cyanation, a graphical plot of the logarithms of current yield against the half-wave polarographic oxidation potential is represented in Fig. 1.

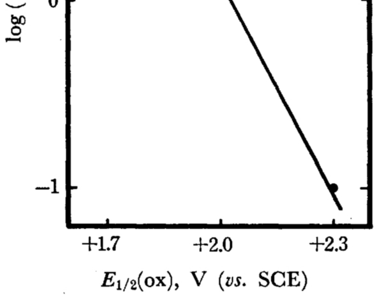


Fig. 1. Correlation of log (Y) and $E_{1/2}$(ox) for the anodic aromatic cyanation.

If cyano radicals are formed at the anode, then diffuse into the bulk solution, and finally attack the aromatic substrates, the current yield would not be expected to be related to the half-wave polarographic oxidation potential. Therefore, the good linear correlation with the half-wave oxidation potential suggests that the electrochemical behavior of the aromatic compounds at the anode plays an important part in the formation of the nitriles.

The reaction has a high sensitivity to substituent influence. The substituent-effect seems larger than that expected for homolytic reactions, even if electrochemically-generated cyano radicals behave as strong electron acceptors. This suggestion is derived from plotting the relative current yield as a function of the σ-constant (Fig. 2), even though competition experiments should be used in the evaluation of the relative current yields.[2]

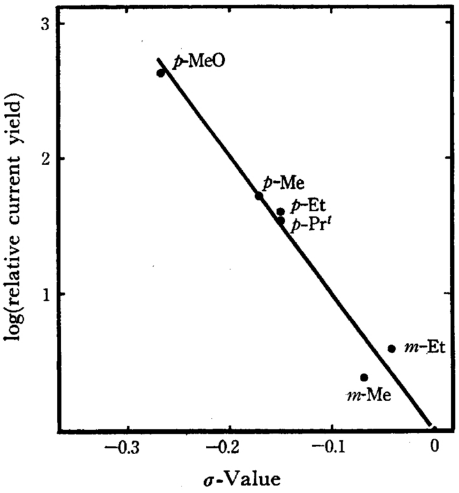
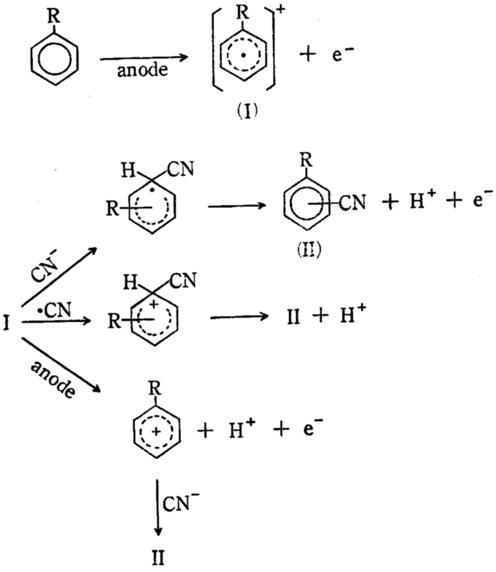


Fig. 2. Correlation of log (relative current yield) and τ for the anodic aromatic cyanation.

From the considerations described above, we would like to suggest that such good linear correlations are not to be interpreted as resulting from the attack of an electrophilic cyano radical on the aromatic substrate, but as resulting from the direct reflection of the electrochemical behavior of the aromatic compounds at the anode. The aromatic ion radical generated on the anode surface reacts immediately, or through the formation of as aryl or benzyl cation by the loss of a proton and an electron, with either cyanide ion or the radical, resulting in the formation of an aromatic cyano compound. However, if the two anodic substitution reactions, *i. e.*, cyanation and methoxylation, occurs concurrently in this reaction system, and if they proceed *via* a common intermediate, the difference in the isomer distribution between these two substitutions will have to be ascribed to the differences in the electrochemical and chemical behavior of cyanide and methoxide anions.



Experimental

All the melting points and boiling points are uncorrected. The infrared spectra were obtained with a Shimadzu infrared spectrophotometer IR-27C. Gas chromatograms were obtained with a Shimadzu gas chromatograph GC-2A, and a Toyo gas chromatograph GC-S-7.

Materials. Commercially-available methanol (special grade) was dried over calcium hydride and then distilled (bp 64.5°C). Anisole was obtained commercially, washed with aqueous sodium hydroxide, then with water, dried over anhydrous magnesium sulfate, and distilled from sodium; bp 154°C, n_D^{15} 1.5196. Benzene, toluene, ethylbenzene, and cumene were treated with sulfuric acid in a usual manner, and were distilled from sodium through a helices-packed column. The fractions collected had bp's of 80, 111, 135—136, and 151—153°C respectively. Methyl benzoate was obtained commercially, and then distilled; bp 78.5°C/11 mmHg.

Electrolysis of Methanol Solution of Sodium Cyanide in the Presence of Anisole. A solution of sodium cyanide (8.6 g) and anisole (36 g, 0.33 mol) in methanol (200 m*l*, 160 g) was electrolyzed between a platinum anode (2.5×6.0 cm^2) and a mercury-pool cathode (surface area: *ca.* 50 cm^2), at 0—5°C with an applied potential of 6 V, at a current of 0.5 A for 20 hr while a slow stream of nitrogen was passed through the solution. The electrodes were spaced *ca.* 1.3 cm apart. At the end of the electrolysis, the current passed through amounted to 9.92 A-hr. Additional sodium cyanide was introduced, portion by portion, as the electrolysis proceeded, until finally 14.9 g of the cyanide had been added by the time the current was stopped. After a

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[2] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York (1960), pp. 220—230, 434.

usual work-up of the electrolyzed solution, the residue (18 g) was distilled to yield the following fractions: (A), wt 9.7 g, bp 47—49°C at 15 mmHg; (B), 4.1 g, bp 50—125°C at 15 mmHg.

The former fraction was found by gas chromatography to consist of unreacted anisole. The infrared spectrum of the latter fraction exhibited a characteristic absorption band at 2240 cm^{-1}. The cyano products present in fraction B were determined by gas chromatography, and found to be *o*- and *p*-anisnitriles. The yields of *o*- and *p*-anisnitriles were 1.2 and 1.8 g respectively. The gas chromatography was carried out by using a 3 m column packed with 20% polyester DA on fire brick C-22, and hydrogen carrier gas, at a column temperature of 175°C. The retention times of *o*- and *p*-anisnitriles were 24.2 and 22.5 min respectively. The *m*-isomer, whose retention time would be 14.6 min under the conditions employed, could not be detected. The re-distillation of fraction B under reduced pressure gave 2.0 g of an oily distillate; bp 100—128°C at 12 mmHg. The distillate was partially crystallized on cooling, and then separated on a filter.

The solid melted at 59—60°C after recrystallization from ethanol; it was identified as *p*-anisnitrile by a mixed melting point measurement and by a comparison of its infrared spectrum with that of an authentic sample. (Found: C, 72.00; H, 5.48%. Calcd for C_6H_7NO: C, 72.16; H, 5.30%.)

The filtrate was saponified with alcoholic potassium hydroxide to give, after recrystallization from aqueous ethanol, a small amount of *o*-anisic acid, mp 94—96.5°C; mixed mp with authentic *o*-anisic acid, 99—100°C. (Found: C, 63.84; H, 5.82%. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30%.)

No further attempt was made to investigate other products, *e. g.*, the methoxylated compounds.

Electrolysis of Methanol Solution of Sodium Cyanide in the Presence of Toluene. A solution of sodium cyanide (12.2 g) and toluene (46.1 g, 0.5 mol) in methanol (300 m*l*, 240 g) was electrolyzed between a platinum foil anode (6.0×5.0 cm^2) and a mercury-pool cathode (*ca.* 50 cm^2) at 0—5°C with an applied potential of 7 V and at a current of *ca.* 1 A for 24 hr. By the end of the electrolysis, the additionally-used sodium cyanide amounted to 22.1 g and the current passed through, to 26.8 A-hr.

The solvent and the bulk of the toluene were removed from the electrolyzed solution and collected in a trap immersed in a dry ice-acetone bath. The gas chromatography of the low-boiling fraction indicated that it contained 39 g of unreacted toluene. The residue emitted a foul odor, and gave an infrared spectrum displaying an absorption band at 2180 cm^{-1}. However, treatment with diluted hydrochloric acid destroyed the odor and gave an infrared absorption band at 3300—3500 cm^{-1}, while the band at 2180 cm^{-1} disappeared. The residue was extracted with ether, and an ether-insoluble solid was removed by filtration. The solid separated on a filter was found to be unchanged sodium cyanide. The filtrate was distilled under reduced pressure to yield, after the removal of the solvent, the following fractions: (A), wt 3.1 g, bp 63—75°C at 13 mmHg; (B), 3.9 g, bp 76—110°C at 13 mmHg; (C), 2.8 g, bp 70—120°C at 0.6 mmHg; (D), 4 g of higher-boiling residue.

The infrared spectroscopic examination of these fractions revealed the presence of some cyano compounds (2240—2260 cm^{-1}), together with methoxylated compounds (1095—1110 and 1250 cm^{-1}) and isonitriles (2180 cm^{-1}). The gas chromatography was carried out by using two columns. The conditions employed and the retention times of the three isomeric tolunitriles identified are listed in Table 3.

TABLE 3. GAS-CHROMATOGRAPHIC ANALYSIS OF ISOMERIC TOLUNITRILES

	P. E. G. 6000, 3 m Column temp., 163°C H_2, min	Polyester DA, 3 m 175°C H_2, min
o-Tolunitrile	8.7	22
m-Tolunitrile	10.4	25.8
p-Tolunitrile	11.4	28.8

The quantitative determination of these three isomers was accomplished by an internal standard method; it indicated that they amounted to 0.221 g (*ortho*), 0.044 g (*meta*), and 0.515 g (*para*), respectively.

Fraction B was chromatographed over alumina. Elution with benzene gave two fractions. The first-eluted oil was heated under reflux with 10% potassium hydroxide in ethanol to yield trace amounts of a white solid, mp 137—140°C. After recrystallization from water, the solid melted at 139—140°C, and it failed to depress the melting point of authentic *o*-toluamide. Moreover, the infrared spectrum was identical with that of an authentic sample. (Found: C, 70.63; H, 6.35%. Calcd for C_8H_9NO: C, 71.09; H, 6.71%.)

The hydrolysis of the second fraction with alcoholic potassium hydroxide gave *p*-toluic acid, mp 178—179°C, undepressed by admixture with an authentic sample. The infrared spectrum was in good agreement with that of an authentic sample. (Found: C, 70.98; H, 5.86%. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92%.)

Electrolysis of Methanol Solution of Sodium Cyanide in the Presence of Ethylbenzene. A solution of sodium cyanide (14.2 g) and ethylbenzene (0.5 mol) in methanol (300 m*l*) was electrolyzed at a temperature of 0.5°C with an applied potential of 6—7 V and at a current of 1 A under a slow stream of nitrogen. The nitrogen, accompanied by the gases evolved, was washed with a 1 N acidic silver nitrate solution, and then with a 2 N aqueous sodium hydroxide solution. Additional sodium cyanide (25.8 g) was introduced, portion by portion, into the solution during the electrolysis. The electrolysis was continued until 1.016 faraday had been passed through the solution. As the reaction proceeded, a white precipitate was formed in the silver nitrate solution when portions of it were placed in a washing bottle. After the electrolysis has stopped, the alkaline solution was acidified with diluted nitric acid and silver nitrate was added, thus yielding trace quantitites of silver cyanide.

The electrolyzed solution was worked up in a manner similar to that used for toluene. Distillation gave the following fractions: (A), wt 3.4 g, bp 60—62°C at 14 mmHg; (B), 2.0 g, bp 80—85°C at 14 mmHg; (C), 8.9 g of a residue.

The compounds in each fraction were examined by gas chromatographic and infrared analyses. The infrared spectra of fractions A and B exhibited characteristic absorption bands at 1100—1120, 1250 (C–O–C), and 2260 (–C≡N) cm^{-1}. The infrared analysis also indicated the presence of some cyano products in the residue. The gas chromatographic analysis was accomplished by using a 3 m column of 25% polyethyleneglycol 6000 on Shimalite, the carrier gas was He (flow rate: 46 m*l*/min) and the column-temperature, 180°C.

The product distributions in all the fractions are summarized in Table 4.

TABLE 4. PRODUCT DISTRIBUTION IN THE ELECTROLYSIS OF METHANOL SOLUTION OF SODIUM CYANIDE IN THE PRESENCE OF ETHYLBENZENE

	Weight (g) in		
	Fraction A	Fraction B	Residue
α-Methoxyethylbenzene	2.708	0.086	—
o-Methoxyethylbenzene	0.078	0.036	—
m-Methoxyethylbenzene	0.095	0.199	—
p-Methoxyethylbenzene	0.073	0.205	—
o-Cyanoethylbenzene	0.044	0.18	0.043
m-Cyanoethylbenzene	0.013	0.043	0.022
p-Cyanoethylbenzene	0.037	0.175	0.243

Authentic cyanoethylbenzenes were prepared by the Sandmeyer reaction of aminoethylbenzenes. The infrared spectrum of authentic *o*-cyanoethylbenzene exhibited characteristic absorption bands at 760 and 2260 cm^{-1}, while *p*-cyanoethylbenzene showed them at 840 and 2260 cm^{-1}. These two samples were further characterized by gas chromatography. The aminoethylbenzenes used in the Sandmeyer reaction were synthesized by the high-pressure catalytic hydrogenation of a nitroethylbenzene or by the action of zinc on a nitrobenzene in hydrochloric acid. These had bp's of 100—101°C at 17 mmHg (*ortho*) and 57°C at 2 mmHg (*para*). α-Phenylpropionitrile was prepared from hydratripic aldehyde *via* the oxime according to the procedure of Newman and Closson.3) The nitrile was distilled at 113—116°C at 18 mmHg.

α-Methoxyethylbenzene bp 56—57°C at 9 mmHg, was prepared from methylphenylcarbinol, *n*-buthyllithium, and dimethyl sulfate. The infrared spectrum showed absorption bands at 700, 750, and 1110 cm^{-1}, and the gas chromatogram displayed a single peak. Ring-methoxylated ethylbenzenes were prepared from the corresponding ethylphenols by methylation with dimethyl sulfate.

Electrolysis of Methanol Solution of Sodium Cyanide in the Presence of Cumene. A solution of sodium cyanide (15.3 g) and cumene (0.5 mol) in methanol was electrolyzed under conditions similar to those described for toluene. By the end of the electrolysis, 1.033 faraday had been passed through the solution. The total of sodium cyanide used was 40 g. After the electrolyzed solution had been sorked up in a manner similar to that used with toluene, the following fractions were obtained by vacuum-distillation: (A), wt 4.3 g, bp 40—44°C at 8 mmHg; (B), 3.4 g of residue. The infrared spectrum of fraction A exhibited absorption bands at 1100 and 2260 cm^{-1}. The gas chromatography was carried out by using a 3 m column packed with 25% Polyethyleneglycol 6000 on Shimalite; He was the carrier gas (40 m*l*/min), and the column temperature, 180°C. No evidence for the presence of α-cyanocumene in any fraction could be obtained from the gas chromatographic analysis. The product distributions in all the fractions are given in Table 5.

TABLE 5. PRODUCT DISTRIBUTION IN THE ELECTROLYSIS OF METHANOL SOLUTION OF SODIUM CYANIDE IN THE PRESENCE OF CUMENE

	Retention time min	Product (g) in	
		Fraction A	Residue
α-Methoxycumene	6.3	0.09	0.12
o-Cyanocumene	18.8	—	0.31
m-Cyanocumene	24.3	—	0.12
p-Cyanocumene	28.4	—	0.44

A portion (2.2 g) of the residue was chromatographed over silica gel. The fractions eluted with benzene were examined by thin-layer chromatography, and were combined on the basis of their thin-layer chromatographic behavior. The combined oil (0.4 g) was saponified in an autoclave with 10% alcoholic potassium hydroxide at 140°C for 14 hr; it gave, after recrystallization from benzene, a small amount (less than 0.1 g) of *p*-cumic acid, mp 116—118°C, undepressed by admixture with an authentic sample. (Found: C, 73.35; H, 7.18%. Calcd for $C_{10}H_{12}O_3$: C, 73.14; H, 7.37%.)

Authentic *o*- and *p*-cyanocumenes were synthesized by a route similar to that used for the preparation of cyanoethylbenzenes, but the Sandmeyer reaction was carried out using the method given in "Organic Syntheses"4) for the preparation of *o*- and *p*-tolunitriles. α-Cyanocumene was prepared according to the directions of Hauser *et al.*5,6) These samples were characterized by gas chromatography and infrared analysis. The method used for the preparation of α-methoxycumene, bp 65—68°C at 8 mmHg, was virtually identical with that described for α-methoxyethylbenzene. The other isomeric methoxycumenes were also prepared by the action of dimethyl sulfate on the corresponding sodium phenolates.

Electrolysis of Methanol Solution of Sodium Cyanide in the Presence of Benzene. A solution of sodium cyanide (15.5 g) and benzene in methanol was electrolyzed until 1.0 faraday had been passed through the solution. Additional sodium cyanide (29.2 g) was then added. A usual work-up of the electrolyzed solution left an oil (0.15 g), bp 30—120°C at 10 mmHg. The infrared spectrum of the oil showed characteristic absorption bands at 700, 760, 1250, and 2250 cm^{-1}. Gas chromatography (columns: 20% Polyester DA on fire brick C-22, 3 m, 25% Apiezon L on Shimalite, 3 m; carrier gas, H_2, 0.5 kg/cm^2; column temperature, 170°C) indicated the presence of benzonitriles with retention times of 5.6 and 2.2 min

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3) M. S. Newman and R. D. Closson, *J. Am. Chem. Soc.,* **66**, 1553 (1944).

4) H. T. Clarke and R. R. Read, "Organic Syntheses," Coll. Vol. I, 2nd Ed., 514 (1956).

5) A. Brodhang and C. R. Hauser, *J. Am. Chem. Soc.,* **77**, 3024 (1955).

6) C. R. Hauser and W. R. Brasen, *ibid.,* **78**, 494 (1956).

under these two sets of conditions respectively. Moreover, it gave a peak with the same retention time as that of anisole on the gas chromatogram. The yield of the nitrile was 0.05 g. The treatment of the oil with an alcoholic potassium hydroxide solution under reflux for 24 hr afforded, after purification by sublimation, a trace amount of benzoic acid; mp 121—122°C, undepressed by admixture with an authentic sample. The infrared spectrum of this derivative was identical in all respects with that of an authentic sample.

Electrolysis of Methanol Solution of Sodium Cyanide in the Presence of Methyl Benzoate. The electrolysis was conducted in a manner similar to that used in the experiment with benzene until 1.0 faraday had been passed through the solution. The total amount sodium cyanide used was 39.4 g. After a usua work-up, the following fractions were obtained; (A), wt 3.0 g, bp 44—47°C at 0.8 mmHg; (B), 18.6 g, bp 47—50°C at 0.8 mmHg; (C), 1.6 g, bp 50—90°C at 0.8 mmHg; (D), 5 g of a residue.

The gas chromatographic and infrared analyses of these fractions indicated the absence of any cyano product. Each fraction gave a negative Lassigne sodium decomposition test for nitrogen,7) and unreacted methyl benzoate was recovered from all of the fractions except the higher-boiling residue.

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7) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York (1948), p. 52.