95-54-5; isopropylamine, 75-31-0; cyclohexanone, 108-94-1; 3-pentanone. 96-22-0; acetonitrile, 75-05-8; phosgene, 75-44-5; allyl alcohol, 107-18-6; ethyl alcohol, 64-17-5; acetone, 67-64-1; oxalyl chloride, 79-37-8; ethanethiol, 75-08-1; Cl_2DISN, 33420-44-9; 2,2-dimethoxypropane, 77-76-9; 2-pentanone, 107-87-9; 2-butanone, 78-93-3; cyclohexanone dimethyl ketal, 933-40-4; sodium ethoxide, 141-52-6; 3-methyl-2-butanone, 563-80-4; hexafluoroacetone, 684-16-2; chloral, 75-87-6.

Anodic Oxidations. VI.[1] Para-Cyanation of Diphenylamines

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Electrochemical oxidation of diphenylamine and its monosubstituted derivatives in methanol containing sodium cyanide yields nuclear cyanation products in good yield. In the cases of the ortho- and meta-substituted diphenylamines as well as the unsubstituted, cyanation took place preferentially at the para position. Para-substituted diphenylamines showed quite different behaviors; *p*-methoxydiphenylamine remained almost intact while *p*-cyanodiphenylamine gave a product cyanated exclusively at the para position of the other phenyl ring. Coulometric data showed that on an average two electrons were lost per organic molecule. The overall reaction involves the initial oxidation of organic substrates.

Anodic cyanation is expected to provide a promising method for synthesis of nitriles by reason of its simple operation. However, the reaction is conducted in most cases in methanol owing to the limited solubility of cyanide salt, leading thus to the competitive formation of methoxylated products.[2-4] To avoid a concurrent methoxylation, tetraethylammonium cyanide–acetonitrile system has been examined.[5] The latter system is suitable for replacement of aromatic methoxyl by nitrile and introduction of a nitrile group in an α position of tertiary amines. For replacement of aromatic hydrogen, however, cyanide salt in methanol is a preferred medium.

Originally,[2] this reaction was depicted as a homolytic substitution reaction by anodically generated cyano radicals, but it was later shown[6] that the cyanation of anisole involved anodic oxidation of the aromatic species followed by reaction with cyanide ion as shown for anodic acetoxlation.[7] This is supported by the results of controlled potential anodic cyanation of other organic compounds[5,8] and by the comparative experiments with the photochemical cyanation.[9] It seems that methoxylation also proceeds *via* an analogous mechanism.[10]

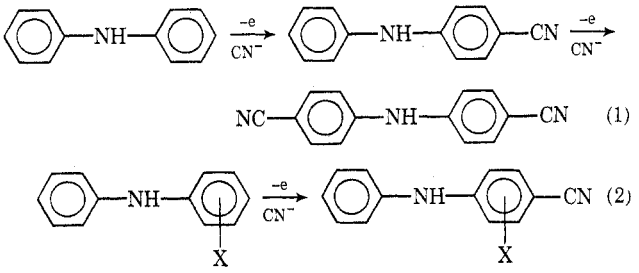
According to this mechanism, a factor controlling the relative prevalence of the two pathways leading to cyanation and side reaction, methoxylation, is ascribable to the relative reactivity of initially generated cation radicals toward different nucleophiles.[10] Stable (or less reactive) cationic species would react selectively with the stronger nucleophile, cyanide ion. Although the stability of cation radicals may not precisely be correlated with oxidation potential of the parent substrates, it does appear that substrates with lower oxidation potential are able to produce the more selective cation radical. A very stable cation radical such as tri-*p*-anisylamine cannot undergo cyanation but oxidizes cyanide ion to radical.[11]

With this practical view in mind, anodic oxidation of aromatic amines, which seem to have moderate oxidation potentials, was carried out in methanol containing sodium cyanide. It was found that nuclear cyanation took place effectively.

Results

Electrolyses were all conducted at anode potentials between 0.3 and 0.6 V. At these potentials only organic substrates are oxidized.[8] It was observed that nuclear cyanation occurred exclusively at a para position (Table I[12-14]).

With diphenylamine cyanation occurred at a para position to give *p*-cyanodiphenylamine (61% yield). In diphenylamines with methoxyl or methyl group in ortho or meta position, substitution occurred at the para position of the substituted phenyl group. *p*-Methoxydiphenylamine remained almost intact under the reaction conditions adopted. In diphenylamine



X = *o*- or *m*-CH_3 and OCH_3

with cyano group (strongly electron-withdrawing substituent) at a para position, cyanation occurred

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TABLE I

ANODIC CYANATION OF DIPHENYLAMINES[a]

Reactant	Decomposition[b] potential, V vs. sce	Oxidation potential, V vs. sce	Preparative anode potential, V vs. sce	Electricity, F	Product	Registry no.	Current efficiency, %	Yield,[g] %	n, F/mol
Diphenylamine	0.40	0.835[c]	0.42	0.017	4-Cyanodiphenylamine	36602-01-4	69	61 58[h]	1.7
2-Methoxydiphenylamine	0.33		0.35	0.008	2-Methoxy-4-cyano-diphenylamine	36602-02-5	34	44	2.6
4-Methoxydiphenylamine	0.28	0.59[d]	0.3–1.1	0.017	[f]				7.3
2-Methyldiphenylamine	0.40		0.40–0.42	0.011	2-Methyl-4-cyano-diphenylamine	36602-03-6	57	53	2.0
3-Methyldiphenylamine	0.35		0.33–0.40	0.012	3-Methyl-4-cyano-diphenylamine	36602-04-7	43	49	2.3
4-Cyanodiphenylamine	0.40		0.60	0.011	4,4'-Dicyanodiphenyl-amine	36602-05-8	29	31	2.2
N-Methyldiphenylamine	0.49	0.84[e]	0.60	0.013	*N*,*N*-Diphenylamino-acetonitrile	36602-06-9	57	65	2.3
					Diphenylamine		5	6	

[a] [NaCN], 0.8 *M*; [amine], 0.4 *M* (4-methoxydiphenylamine is less owing to its limited solubility); temp, 25°. [b] Data read from current–potential curve. [c] $E_{1/2}$, value from ref 12. [d] $E_{p/2}$, value from ref 13. [e] $E_{p/2}$, value from ref 14. [f] A small amount of unidentified nitrile. [g] Based on amine consumed. [h] Nonpotentiostatic oxidation (conversion, 50%; see Experimental Section).

at the para position of the other phenyl group; *viz.*, dicyanation is possible in the case of diphenylamine. Coulometric data showed an average of 2.2 electrons lost per organic molecule.

With *N*-methyldiphenylamine, cyanation occurred at a methyl group to give *N*,*N*-diphenylaminoacetonitrile in high yield. In addition, a small amount of diphenylamine was produced. These types of reaction in tertiary amines have already been observed by Andreades and Zahnow.[5] *N*,*N*-Dimethylaniline showed the same behavior as did *N*-methyldiphenylamine. Triphenylamine was almost inert under these conditions (cpe 0.78 V, n = 16.3) and aniline polymerized.

Discussion

One major advantage of the present reaction lies in its high selectivity with regard to the position of attack. The reaction products were para-cyanated phenylamines exclusively. Thus the reaction is the most convenient method for the syntheses of *p*-cyanodiphenylamine. It is not necessary to control an anode potential for the purpose of organic syntheses (see Table I). Other methods of synthesizing these compounds are troublesome and of poor yield in some cases (see the preparation of authentic sample in Experimental Section).[15]

Earlier electrochemical studies of diphenylamines have been concerned with the effects of structure on $E_{1/2}$, *i.e.*, the ease of oxidation.[16,17] It has recently been reported that diphenylamine gives diphenylbenzidine in acetonitrile.[12,18] In aqueous acetone the electrochemical oxidation of diphenylamines leads to benzoquinone and the corresponding amine.[19] In no case has an aromatic substitution by a nucleophile been reported.

In the electrochemical oxidation of diphenylamines, the first step is the oxidation of amines to cation radicals.[19] Oxidation with lead tetraacetate also gives cation radicals.[20] In view of these studies and the present results of controlled potential electrolyses, the primary electrode process is considered to be the oxidation of diphenylamine to a cation radical which subsequently reacts with cyanide ion. However, an unequivocal explanation for the attacking position is still lacking. Probably, it would be necessary to consider both the reactivity of initially generated cation radicals and the nature of nucleophiles.

As has already been described, both *p*-methoxydiphenylamine and triphenylamine are apparently inert under the present conditions even though they discharge practically. This phenomenon would be ascribable to the regeneration of aromatic amines by redox reaction between anodically generated cation radicals and cyanide ion, as has already been indicated by Papouchado, Adams, and Feldberg.[11]

There are two essentially important stages for anodic cyanation of organic compounds. The first stage is the electrochemical oxidation of organic compounds to cation radicals. We can readily obtain the information concerning this stage by voltammetry. The second step is the reaction of the anodically generated cation radical with cyanide ion. The information concerning this step is at present lacking. We cannot forecast precisely what structure of cation radicals will trap cyanide ion effectively prior to reactions with other nucleophiles such as the solvent methanol. In view of earlier successful anodic cyanation,[1–6,8,9] it seems that relatively stable (but, not too stable) cation radicals efficiently react with cyanide ion.

Experimental Section

The electrochemical and spectroscopic instrumentation and techniques were as previously described.[8]

Materials.—Methanol was purified by fractional distillation from magnesium activated with iodine. Reagent grade sodium cyanide was used with no purification other than drying.

Aniline, *N*,*N*-dimethylaniline, and *N*-methyldiphenylamine were obtained commercially and were purified by distillation before use. Diphenylamine and triphenylamine were purified by recrystallization. *o*-Methoxydiphenylamine was prepared

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by decarboxylation of *N*-*o*-anisylanthranilic acid:[21] bp 146–148° (2 mm); ir 3420 (NH), 2840 (OCH_3), 1595 (NH), 1240, 1120, 1025 (COC), 745, and 695 cm^{-1} (mono- and 1,2 substitution); nmr (CCl_4) τ 2.7–3.4 (9 H, m), 4.02 (1 H, broad), and 6.23 (3 H, s). *p*-Methoxydiphenylamine was prepared by treating acetyl-*p*-anisidine with excess bromobenzene[22] and was purified by column chromatography and recrystallization: mp 106–107° (from ethanol, lit.[22] mp 106°); ir 3410, 1600 (NH), 1245, 1185, 1035 (COC), 850, 755, and 695 cm^{-1} (mono- and 1,4 substitution); nmr ($CDCl_3$) τ 2.7–3.3 (9 H, m), 5.15 (1 H, broad), and 6.22 (3 H, s). *o*-Methyldiphenylamine was prepared by decarboxylation of *N*-*o*-tolylanthranilic acid:[21] bp 117° (3 mm); ir 3420, 1600 (NH), 750, and 695 cm^{-1} (mono- and 1,2 substitution); nmr (CCl_4) τ 2.8–3.9 (9 H, m), 4.85 (1 H, broad), and 7.83 (3 H, s). *m*-Methyldiphenylamine was prepared from potassium *m*-toluidide and bromobenzene:[23] bp 117–119° (3 mm); ir 3420, 1600 (NH), 870, 770, 750, and 690 cm^{-1} (mono- and 1,3-substitution); nmr (CCl_4) τ 2.8–3.5 (9 H, m), 4.70 (1 H, broad), and 7.80 (3 H, s).

An authentic sample of *p*-cyanodiphenylamine was prepared from *p*-aminobenzonitrile and iodobenzene by a modification of the method of Gilman and Shirley.[22] Attempts to prepare this compound from *p*-cyanohalobenzenes and aniline or by Sandmeyer reaction from *p*-aminodiphenylamine were unsuccessful, and numerous amounts of tarry substance were produced.

Potentiostatic Oxidations.—The organic compound (0.02 mol) in 50 ml of methanol–sodium cyanide (0.80 *M*) was electrolyzed at an controlled anode potential. The electrolyzed mixture was treated with water, and the organic material was extracted with ether as described earlier.[8,10] The ether was removed by distillation, and the residue was chromatographed on alumina using benzene as an eluent. Unreacted starting material was first eluted, followed by cyanated products. *N*-Phenylaminoacetonitriles were partially hydrolyzed to amides on column chromatography, which were eluted with ethyl acetate. *p,p'*-Dicyanodiphenylamine was also eluted by ethy acetate.

Nonpotentiostatic Oxidations.—Preparative-scale electrolysis was carried out in a two compartment H-type cell with glass frit separating the compartments fitted with platinum foil electrodes (20 × 30 mm^2). The anolyte was made up of 20.3 g (0.12 mol) of diphenylamine, 7.8 g (0.16 mol) of sodium cyanide, and 180 ml of methanol. The catholyte was a methanolic solution of sodium cyanide. The electrolysis was carried out at the terminal voltage of 24–32 V to maintain the current of 0.1 A for 32 hr under a nitrogen atmosphere. During the electrolysis, the solution was stirred magnetically and cooled externally with ice. The electrolyzed mixture was treated as usual.

Identification of Product.—Cyanated products were identified by elemental analyses, by ir, nmr, and mass spectra, and by comparison with authentic samples.

4-Cyanodiphenylamine: mp 101–102° (from ethanol); ir 3340 (NH), 2240 (CN), 825 (1,4 substitution), 760, and 690 cm^{-1} (monosubstitution); nmr ($CDCl_3$) τ 2.4–3.1 (9 H, m) and 3.85 (1 H, broad). *Anal.* Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42; mol wt, 194.24. Found: C, 80.25; H, 5.22; N, 14.36; mol wt, 194 (mass spectroscopy).

2-Methoxy-4-cyanodiphenylamine: mp 80–81° (from ethanol); ir 3345 (NH), 2235 (CN), 1266, 1134, 1032 (COC), 848, 810 (1,2,4 substitution), 750, and 688 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.60–3.15 (8 H, m), 3.58 (1 H, broad), and 6.08 (3 H, s); *Anal.* Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.48; mol wt, 224.26. Found: C, 74.69; H, 5.31; N, 12.46; mol wt, 224 (mass spectroscopy).

2-Methyl-4-cyanodiphenylamine: mp 116–116.5° (from carbon tetrachloride); ir 3380 (NH), 2240 (CN), 890, 825 (1,2,4 substitution), 750, and 695 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.6–3.1 (8 H, m), 4.35 (1 H, broad), and 7.75 (3 H, s). *Anal.* Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45; mol wt, 208.26. Found: C, 80.72; H, 5.82; N, 13.37; mol wt, 208 (mass spectroscopy).

3-Methyl-4-cyanodiphenylamine: mp 116.5–117° (from carbon tetrachloride); ir 3380 (NH), 2240 (CN), 870, 820 (1,2,4 substitution), 750, and 700 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.6–3.35 (8 H, m), 3.95 (1 H, broad), and 7.60 (3 H, s). *Anal.* Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45; mol wt, 208.26. Found: C, 80.87; H, 5.82; N, 13.44; mol wt, 208 (mass spectroscopy).

4,4'-Dicyanodiphenylamine: mp 265–266° (from ethyl acetate, lit.[24] mp 240–246°); ir 3360 (NH), 2230 (CN), and 825 cm^{-1} (1,4 substitution); nmr ($(CD_3)_2CO$) τ 1.37 (1 H, broad), 2.34 (4 H, d, J = 8.9 cps), and 2.66 (4 H, d, J = 8.9 cps). *Anal.* Calcd for $C_{14}H_9N_3$: C, 76.70; H, 4.14; N, 19.17; mol wt, 219.25. Found: C, 76.98; H, 4.06; N, 18.95; mol wt, 219 (mass spectroscopy).

N,N-**Diphenylaminoacetonitrile**: bp 130° (1 mm); ir 2230 cm^{-1} (CN); nmr (CCl_4) τ 2.7–3.4 (10 H, m) and 5.80 (2 H, s); mol wt, 208 (mass spectroscopy).

N,N-**Diphenylaminoacetamide**: mp 149–150° (from ethanol); ir 3470, 3360 (NH_2), and 1690 cm^{-1} (CO); nmr ($CDCl_3$) τ 2.6–3.1 (10 H, m), 3.55 (2 H, broad), and 5.57 (2 H, s). *Anal.* Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38; mol wt, 226.28. Found: C, 74.11; H, 6.26; N, 12.36; mol wt, 226 (mass spectroscopy).

N-**Phenyl**-*N*-**methylaminoacetonitrile**: bp 100° (1 mm) (lit.[5] bp 161–168° (0.6 mm)); ir 2245 (CN), 758. and 690 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.65–2.95 (2 H, m), 3.10–3.30 (3 H, m), 6.07 (2 H, s), and 7.13 (3 H, s). *Anal.* Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16; mol wt, 146.19. Found: C, 73.65; H, 6.96; N, 19.07; mol wt, 146 (mass spectroscopy).

N-**Phenyl**-*N*-**methylaminoacetamide**: mp 167.5–168.5° (from ethanol); ir 3360, 3200 (NH_2), 1650 (CO), 752, and 690 cm^{-1} (monosubstitution); nmr ($CDCl_3$) τ 2.55–2.80 (2 H, m), 3.05–3.30 (3 H, m), 3.50 (2 H, broad), 6.15 (2 H, s), and 6.97 (3 H, s). *Anal.* Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06; mol wt, 164.21. Found: C, 66.03; H, 7.50; N, 17.12; mol wt, 164 (mass spectroscopy).

Registry No.—*N,N*-Diphenylaminoacetamide, 36602-07-0; *N*-phenyl-*N*-methylaminoacetonitrile, 36602-08-1; *N*-phenyl-*N*-methylaminoacetamide, 21911-76-2.

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