

products, *N,N'*-diphenylbenzidines and carbazoles, respectively.^{1,2} If the anodic oxidation of diphenylamines is conducted under the cyanation conditions, the cyanide ion attacks the aromatic nucleus to yield *p*-cyanodiphenylamines³ or the quinoneimine cyanohydrin methyl ether.⁴ Since the aromatic substitution reaction of diphenylamines is uncommon, it was investigated if such a reaction takes place even when other nucleophiles such as acetate or methoxide ion are used.

The anodic oxidation of diphenylamine in methanol containing sodium methoxide was carried out with a constant current. A mixture of *o*- and *p*-methoxydiphenylamines was formed in 7.6% yield (based on unrecovered diphenylamine; *o*:-*p*- 1:20; conversion, 10%) (Scheme I) together with a considerable amount of tarry products.

With methanol containing salts of other anions such as perchlorate or tetrafluoroborate, a small amount of intermolecular coupling product, *N,N'*-diphenylbenzidine, was obtained along with a significant amount of tarry residue. Nuclear substitution product was not detected.

It is apparent from these results that nuclear methoxylation requires the presence of methoxide ion. Because a methoxy substituent lowers the oxidation potential of substrates, the methoxyamines formed are often much less resistant toward oxidation than the starting material, and, besides, the isomers might be oxidized at different rates. However, the isomer ratio did not change practically with the amount of passed electricity and the observed one would therefore represent a close approximation of the true isomer distribution. These orientations in the present methoxylation, para preponderance, are in accord with those in the cyanation.³

Anodic oxidation of diphenylamine in acetic acid containing sodium acetate affords brownish residue exclusively.

Experimental Section

Materials. Methanol was purified by fractional distillation from magnesium methoxide. Reagent grade sodium, sodium perchlorate, and sodium tetrafluoroborate were used.

Diphenylamine and *N,N'*-diphenylbenzidine were obtained commercially and the former substrate was purified by recrystallization. Preparation of *o*- and *p*-methoxydiphenylamines was as previously described.³ *m*-Methoxydiphenylamine was prepared by the method of Dolman and Stewart.⁵

Anodic Oxidation of Diphenylamine in Methanolic Sodium Methoxide. The electrolysis was carried out nonpotentiostatically using a two-compartment cell under a nitrogen atmosphere as described previously.⁶ The anolyte was made up of 0.85 g (5.0 mmol) of diphenylamine in methanol-sodium methoxide (50 ml, 1.0 M). The catholyte was a methanolic sodium methoxide solution. During the electrolysis, the solution was kept stirred magnetically and cooled externally with ice. The reaction was then run with a constant current of 0.05 A for 110 min. The electrolyzed mixture was treated as usual³ and was analyzed by GLC (SE 30, 170°).

Anodic Oxidation in Methanolic Sodium Perchlorate. Diphenylamine (0.85 g, 5.0 mmol) was electrolyzed in methanol containing sodium perchlorate (50 ml, 1.0 M) at 0.05 A for 110 min. The organic material was chromatographed on silica gel using a 3:1 benzene-hexane mixture as an eluent. Unreacted starting material was first eluted, followed by *N,N'*-diphenylbenzidine (0.04 g, 0.12 mmol).

Registry No.—Diphenylamine, 122-39-4; methoxide ion, 3315-60-4.

References and Notes

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Nucleophilic Aromatic Substitution Reactions of Unactivated Aryl Chlorides with Methoxide Ion in Hexamethylphosphoramide

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It has previously been shown by other workers that metal alkoxides react with unactivated aryl halides to give aryl alkyl ethers.¹⁻⁵ Although some procedures gave good yields of products when aryl bromides or iodides were used, unactivated aryl chlorides gave poor yields of ethers.¹⁻³ In some procedures the aryl halides reacted by an aryne mechanism which led to an undesired mixture of isomeric products.³⁻⁵ Recently it was shown that *o*-dichlorobenzene reacted by a bimolecular displacement mechanism with potassium methoxide complexed with a crown ether to give a 40-50% yield of *o*-chloroanisole.⁶











We wish to report that unactivated aryl chlorides react by a bimolecular displacement mechanism with sodium methoxide in hexamethylphosphoramide (HMPA) to give in most cases good yields of methyl aryl ethers. Various examples with reaction conditions and yields of products are shown in Table I. The variation in yields is consistent with the electronic effects of the substituents in the aryl chlorides.

The reactions are proceeding by a bimolecular displacement mechanism (S_NAr)⁷ rather than an aryne mechanism based on the products produced. The fact that the aryl chlorides give single products rather than mixtures of isomeric products indicates that an aryne mechanism is not operating. In the case of 1-chloronaphthalene an aryne mechanism may be operating to a slight extent, since a trace of 2-methoxynaphthalene was produced along with the 1-methoxy isomer. A radical-anion mechanism (SRN1) is not likely since there are no additional products where chloride is replaced by hydrogen⁷ and also since addition of 0.1 molar equiv of *p*-dinitrobenzene, a radical inhibitor, had no effect on the yield of product in the reaction of *o*-dichlorobenzene.⁸

Experimental Section⁹

***m*-Chloroanisole.** A magnetically stirred mixture of 2.94 g (20 mmol) of *m*-dichlorobenzene, 1.30 g (24 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 90° for 20 h in a flask equipped with a condenser and a drying tube. The mixture was then cooled and poured into 80 ml of water which was then extracted with two 75-ml portions of ether. The combined ether extract was washed with three 20-ml portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give 2.74 g of liquid. Analysis of the liquid by GLC (SE-30, 120°, or methyl silicone, 145°) revealed that it consisted only of *m*-chloroanisole and that the yield of *m*-chloroanisole was 87%. *o*-Chloroanisole and *p*-chloroanisole had retention times longer than that of *m*-chloroanisole and were completely absent. Product purified by GLC gave a refractive index of *n*_D²⁰ 1.5353 (lit.¹⁰ *n*_D²⁰ 1.5362)

Table I
Reaction of Aryl Chlorides with Sodium Methoxide in HMPA

Registry no.	Aryl chloride	Reaction conditions			Product	Yield, ^b %	Registry no.
		Temp, °C	Time, h	Molar/ equiv ^a CH ₃ ONa			
541-73-1		90	20	1.2		87	2845-89-8
		90	19	1.1 ^c			
95-50-1		90	19.5	1.1		78 ^d	766-51-8
108-90-7		120	18.5	1.5		50	100-66-3
90-13-1		120	19	1.5		54	2216-69-5
106-43-4		120	24	1.5		13	104-93-8

^a Commercial sodium methoxide used in all cases except where noted. ^b Yields determined by GLC. ^c Sodium methoxide generated in reaction mixture from methanol and sodium hydride. ^d Addition of 0.1 molar equiv of *p*-dinitrobenzene had no effect on yield. ^e Trace of 2-methoxynaphthalene also present.

and an infrared spectrum identical with that of an authentic sample. An alternative procedure involved generation of sodium methoxide from methanol and sodium hydride. A mixture of 0.71 g (22 mmol) of methanol, 1.06 g of a 50% dispersion of sodium hydride in mineral oil (22 mmol), and 40 ml of dry HMPA was stirred at room temperature for 1.5 h before addition of 2.94 g (20 mmol) of *m*-dichlorobenzene and heating at 90° for 19 h. Completion of the reaction as in the above procedure gave a 79% yield of *m*-chloroanisole.

***o*-Chloroanisole.** A magnetically stirred mixture of 2.94 g (20 mmol) of *o*-dichlorobenzene, 1.19 g (22 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 90° for 19.5 h in a flask equipped with a condenser and drying tube. A work-up procedure the same as that described for *m*-chloroanisole gave 2.66 g of liquid. Analysis of the liquid by GLC (SE-30, 120°, or methyl silicone, 145°) revealed that it consisted of *o*-chloroanisole and a small amount of unreacted *o*-dichlorobenzene and that the yield of *o*-chloroanisole was 78%. *m*-Chloroanisole had a shorter retention time than *o*-chloroanisole and was completely absent. Product purified by GLC gave a refractive index of n_D^{20} 1.5440 (lit.¹⁰ n_D^{20} 1.5445) and an infrared spectrum identical with that of an authentic sample. When the above reaction was run in exactly the same manner except that 0.34 g (2 mmol) of *p*-dinitrobenzene was also added, there was no change in the yield of *o*-chloroanisole.

Anisole. A magnetically stirred mixture of 2.25 g (20 mmol) of chlorobenzene, 1.62 g (30 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 120° for 18.5 h in a flask equipped with a condenser and drying tube. A work-up procedure the same as that described for *m*-chloroanisole gave 1.71 g of liquid. Analysis of the liquid by GLC (methyl silicone, 127°) revealed that it consisted of anisole and unreacted chlorobenzene and that the yield of anisole was 50%. Product purified by GLC gave an infrared spectrum identical with that of an authentic sample.

1-Methoxynaphthalene. A magnetically stirred mixture of 3.25 g (20 mmol) of 1-chloronaphthalene, 1.62 g (30 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 120° for 19 h in a flask equipped with a condenser and drying tube. A work-up procedure identical with that described for *m*-chloroanisole gave 2.80 g of liquid. Comparison of GLC (Carbowax 20M, 165°) retention times with those of authentic samples revealed that the liquid consisted of 1-methoxy- and 2-methoxynaphthalene (97:3 ratio), some unreacted 1-chloronaphthalene, and an unidentified product of short retention time. The yield of 1-methoxynaphthalene, which had only a slightly shorter retention time than the 2-methoxy isomer, was 54%. Product purified by GLC gave a refractive index of n_D^{20} 1.6219 (lit.¹⁰ n_D^{20} 1.6220) and an infrared spectrum identical with that of an authentic sample of 1-methoxynaphthalene.

***p*-Methylanisole.** A magnetically stirred mixture of 2.53 g (20 mmol) of *p*-chlorotoluene, 1.62 g (30 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 120° for 24 h in a flask equipped with a condenser and drying tube. A work-up similar to that previously described for *m*-chloroanisole gave 1.98 g of liquid. Analysis of the liquid by GLC (SE-30, 122° or Carbowax 20M,

120°) revealed that it consisted of *p*-methylanisole and much unreacted *p*-chlorotoluene and that the yield of *p*-methylanisole was 13%. Product purified by GLC gave an infrared spectrum identical with that of an authentic sample.

Registry No.—HMPA, 680-31-9; methoxide ion, 3315-60-4.

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- (9) HMPA was dried by distillation from sodium hydride at reduced pressure. Sodium methoxide (Matheson) was used from freshly opened bottles. Refractive indices were determined with a Bausch and Lomb refractometer (type 33-45-58). Infrared spectra were recorded with a Perkin-Elmer Model 237B or Beckman IR-33 spectrometer. Gas chromatography (GLC) was performed on a Hewlett-Packard 5750B or Perkin-Elmer Model 154D chromatograph employing helium as the carrier gas at 50 ml/min. The following 6 ft X 0.25 in. columns were used: 10% SE-30 on 60-80 mesh Chromosorb W (AW-DMCS); 10% methyl silicone oil (SF-96) on 60-80 mesh Chromosorb W; 10% Carbowax 20M on 60-80 mesh Chromosorb W (AW-DMCS).
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An Oxime to Nitro Conversion. A Superior Synthesis of Secondary Nitroparaffins

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We have devised a convenient oxime to nitro conversion which constitutes an improved synthesis of secondary ni-