conductivities measured on compactions of 14 and 15 are 15 and 5×10^{-5} (Ω cm)$^{-1}$, respectively [TTF–TCNQ: 25 (Ω cm)$^{-1}$]. The wide difference in electrical behavior is likely associated with different crystallographic linear chain stacking of donors and acceptors in the two salts, segregated in 14 and alternating in 15.[9]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and ultraviolet–visible spectra were determined on a Perkin-Elmer 202 spectrophotometer. Mass spectra were obtained on a Perkin-Elmer 270B mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Cyclopenteno-1,2,3-thiadiazole (4). Improving on the procedure of Meier,[2] 176.65 g (0.7 mol) of cyclopentanone tosylhydrazone was treated cautiously at 0° with 450 ml (6.2 mol) of thionyl chloride. The dark solution was stirred at room temperature for 3 h or until gas evolution ceased. The excess thionyl chloride was removed by rotary evaporation at 60°. The resulting residue was treated with 78.55 g (1.4 mol) of potassium hydroxide in 400 ml of water, warmed gently on a steam bath for 45 min, and filtered. The solution was extracted twice with ether, the ether layers being combined, dried over MgSO$_4$, and concentrated. The resulting dark oil was distilled at 60–62° (0.05 mm) to give 30.0 g (34%) of 4 as a slightly yellow liquid [lit.[2] bp 42–46° (0.01 mm)].

Cyclohexeno-1,2,3-thiadiazole (5) was prepared as described above for the preparation of 4 using 133.19 g (0.5 mol) of cyclohexanone tosylhydrazone, 320 ml of thionyl chloride, and 56.11 g of potassium hydroxide. The dark oil was distilled at 70–71° (0.05 mm) to give 63.7 g (91%) of 5 as a colorless liquid [lit.[2] bp 51–55° (0.01 mm)].

Cyclopentenotrithiocarbonate (8). A solution of 11.0 g of 4 in 60 ml of carbon disulfide was heated to 205° for 6 h in a glass-lined stainless steel autoclave. After cooling, the excess carbon disulfide was removed by rotary evaporation. The residue was dissolved in chloroform and filtered and the chloroform solution concentrated to a dark oil. The oil was chromatographed on silica gel using hexane as eluent. The highly colored impurities (<4.5%) were discarded and the remaining yellow fractions were combined and concentrated to a yellow solid. The solid was crystallized from hexane to give 6.29 g (41.4%) of 8 as long, yellow needles: mp 105–108°; ir (KBr) 1110 and 1040 cm^{-1}; λ_{max} (hexane) 232 nm (log ϵ 3.79), 268 (3.07), and 380 (4.02); mass spectrum m/e 174.

Anal. Calcd for C$_6$H$_6$S$_3$: C, 41.34; H, 3.47; S, 55.18. Found: C, 41.26; H, 3.56; S, 55.20.

Cyclohexenotrithiocarbonate (9). Following the above procedure for the preparation of 8, a solution of 15 g of 5 in 60 ml of carbon disulfide was heated for 7 h at 215°. The dark oil was chromatographed using hexane–chloroform as eluent. The colorless fractions (<4%) were discarded and the remaining yellow fractions were combined and concentrated to a yellow solid. The solid was crystallized from hexane–chloroform to give 8.52 g (42.6%) of 9 as short, yellow needles: mp 81–82° (lit.[3] mp 82–83°); ir (KBr) 1055 and 899 cm^{-1}; λ_{max} (hexane) 234 nm (log ϵ 3.84), 273 (3.15), and 372 (4.072); mass spectrum m/e 188.

Bis(cyclopenteno)tetrathiafulvalene (12). *Caution should be exercised with perchlorate salts.*[10] A solution of 0.500 g (2.87 mmol) of 8 in 20 ml of acetone was cooled to 0°. A cold solution of 2.38 g (11.72 mmol) of m-chloroperbenzoic acid (85%) in 20 ml of acetone was added dropwise with stirring. After 30 min, no 8 could be detected by TLC (silica gel HF, chloroform, R_f 0.86). Perchloric acid (60–62%) (3 ml) was added to the dark solution precipitating the light tan perchlorate salt 10. Further salt precipitated on addition of 200 ml of ether and the salt was filtered, washed with ether, and dried.[10] The perchlorate salt was directly dissolved in 20 ml of acetonitrile. The solution was degassed with argon and cooled to 5°. Triethylamine, 1.0 g, was added dropwise and immediately a solid formed. After stirring for 30 min, 20 ml of water was added and the solid filtered and dried. The crude product, mp 242–245°, was sublimed at 200° (0.05 mm) to give 0.284 g (70%) of 12 as a yellow-brown solid, crystallized from acetonitrile–trichlorobenzene: mp 244°; ir (KBr) 1450, 1325, and 769 cm^{-1}; λ_{max} (1,2-DCE) 307 nm (log ϵ 4.02), 327 sh (3.968), and 462 (2.248); mass spectrum m/e (rel intensity) 284 (M, 100), 142 (M/2, 17).

Anal. Calcd for C$_{12}$H$_{12}$S$_4$: C, 50.66; H, 4.26; S, 45.08. Found: C, 50.64; H, 4.13; S, 45.27.

Bis(cyclohexeno)tetrathiafulvalene (13). *Caution should be exercised with perchlorate salts.*[10] Following the above procedure for the preparation of 12, 2.0 g of 9 was oxidized with 10.781 g of peracetic acid (30%) to give the hydrosulfate salt as a red oil. Treatment with 12 ml of perchloric acid (60–62%) gave the solid tan perchlorate salt 11.[10] The perchlorate salt was directly dissolved in 30 ml of acetonitrile and treated with 1.51 g of triethylamine to give 1.49 g (90%) of 13 as a yellow solid, mp 245° dec, purified by sublimation at 190° (0.05 mm) to give 13 (82%) as a redbrown solid, crystallized from chlorobenzene: mp 247.6–248.2°; ir (KBr) 1448, 1340, and 779 cm^{-1}; λ_{max} (CH$_3$CN) 297 nm (log ϵ 4.025), 323 sh (3.98), and 472 (2.283); mass spectrum m/e (rel intensity) 312 (M, 100), 156 (M/2, 9).

Anal. Calcd for C$_{14}$H$_{16}$S$_4$: C, 53.80; H, 5.16; S, 41.04. Found: C, 53.86; H, 5.15; S, 41.30.

Bis(cycloalkeno)tetrathiafulvalene–tetracyanoquinodimethane (14 and 15). Charge transfer salts 14 and 15 were formed by the known procedure[7] using rigorously purified acetonitrile under an argon atmosphere. The two solutions were mixed, heated for an additional 15 min, and allowed to cool over several hours to yield the respective salts as black needles.

For 15: Anal. Calcd for C$_{26}$H$_{20}$N$_4$S$_4$: C, 60.43; H, 3.91; N, 10.85; S, 24.82. Found: C, 59.37; H, 4.09; N, 10.60; S, 24.29.

For 14:[8] Anal. Calcd for C$_{14}$H$_{16}$N$_4$S$_4$: C, 58.98; H, 3.31; N, 11.47; S, 26.24. Found: C, 59.05; H, 3.35; N, 11.46; S, 26.36.

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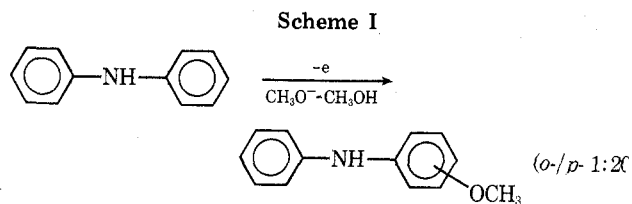
Anodic Oxidation of Diphenylamine in the Presence of Methoxide Ion

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The electrochemical oxidation of diphenylamines produces the intermolecular and intramolecular coupling

Scheme I

$(o\text{-}/p\text{-} 1{:}2C$

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-cyanodiphenylamines[3] 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 usual[3] 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.

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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 (SNAr)[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 hydrogen[7] 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 Section[9]

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^{20}D 1.5353 (lit.[10] n^{20}D 1.5362)