

Nucleophilic Substitution Reactions on Haloazobenzenes

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Cuprous cyanide and cuprous alkoxides (methoxide, ethoxide, isopropoxide, and *tert*-butoxide) readily underwent substitution reactions with 2-iodoazobenzene to yield 2-cyanoazobenzene and the 2-alkoxyazobenzenes, respectively. Similar reactions with the corresponding sodium salts gave either no reaction or reduction of 2-iodoazobenzene to azobenzene with one exception, sodium methoxide, which gave 2-methoxyazobenzene. The reactivities of 2-bromo-, 2-chloro-, 3-iodo-, and 4-iodoazobenzene are contrasted to that of 2-iodoazobenzene. Substitution reactions of 2,6-diiodo- and 2,2'-diiodoazobenzene are discussed.

Very few electrophilic substitution reactions of azobenzene give 2-substituted azobenzenes and when they do the yields are very low.¹ Thus to obtain 2-substituted azobenzenes the most convenient method is the condensation of an aromatic nitroso compound with an aniline.² The limitations of such reactions are the availability of the necessary two starting materials. In this paper there are described nucleophilic substitution reactions of 2-iodoazobenzene (2a) that lead to a number of 2-substituted azobenzenes (Scheme I). The 2-iodoazobenzene (2a) can be synthesized by a condensation reaction³ (Scheme I) or through direct⁴ (Scheme I) mercuriation of azobenzene (1) or through indirect⁵ formation of the same mercurial and subsequent iodination of this mercurial. Such reaction sequences can be

extended to other azobenzenes where an R group (or groups) is present on the azobenzene. This has been done for two examples in this paper.

Examples of aromatic nucleophilic substitution reactions are numerous in the literature. Substitution is easiest when the ring is activated with an electron-withdrawing group or groups in the ortho and/or para position(s) to the leaving group.⁶ For unactivated aromatics the use of the copper salts either as catalysts or in themselves leads to substitution; however, the conditions of reaction are usually rather severe.⁷⁻⁹ A few cases of nucleophilic substitution of chlorohydroxyazobenzenes are reported in which alkoxides, with cupric salts as catalysts, replace the chlorine.¹⁰

Results and Discussion

The results of the substitution reactions on monohaloazobenzenes are listed in Table I. The ratio of nucleophilic reagent to haloazobenzene was always kept large to drive the reaction to completion where possible. No difficulty was experienced in isolating the monocyno compounds from the reaction mixtures as other workers have found.⁹

The cyanide ion is a good nucleophile, but with the sodium ion in methanol, it did not substitute for the iodine of 2-iodoazobenzene (2a). When dimethylformamide was used as the solvent and the temperature of the reaction was 100°, then a very small yield of 2-cyanoazobenzene (3a) was obtained. At reflux no product was obtained. However, with the cuprous ion, in methanol, the substitution of 2a with cyanide proceeded smoothly and essentially quantitatively to yield 3a. The reaction of cuprous cyanide with 3-

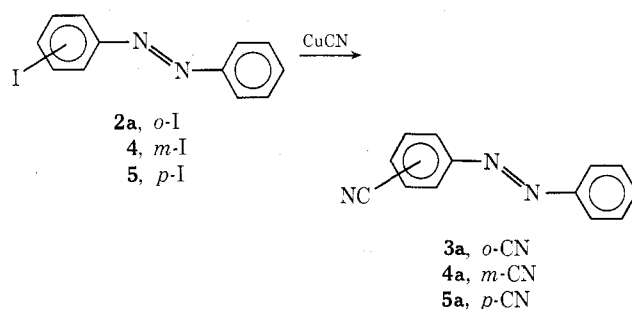
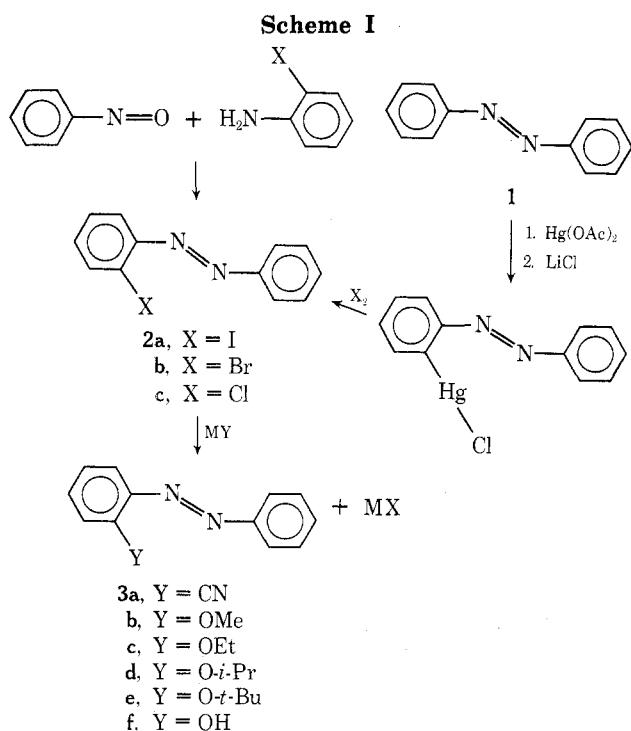


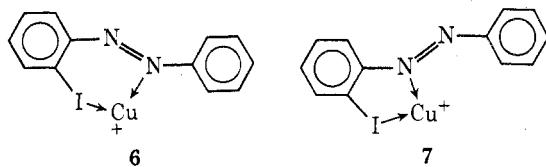
Table I
Nucleophilic Substitution Reactions on Haloazobenzenes

Nucleophilic reagent (MY)	Haloazobenzene	Molar ^a ratio	Solvent	Method	SM	% Yield ^b products
NaCN	2a	3	Methanol	A	100	0
NaCN	2a	3	DMF, 100° ^c	A	50	1
NaCN	2a	3	DMF, 152°	A	0	0, 10 (1)
CuCN	2a	3	Methanol	A	1	94
CuCN	4	3	Methanol	A	95	1
CuCN	4	3	None	C	6	52
CuCN	5	3	Methanol	A	91	1
CuCN	5	3	None	C	33	34
CuCN	2b	4	Methanol	A	15	81
CuCN	2c	4	Methanol	A	95	0
NaOMe	2a	3	Methanol	B	3	95
NaOMe	2b	13	Methanol	B	94	0
CuOMe	2b	13	Methanol	B	32	49
NaOEt	2a	10	Ethanol	B	0	0, 90 (1)
NaO- <i>i</i> -Pr	2a	13	2-Propanol	B	0	0, 100 (1)
NaO- <i>t</i> -Bu	2a	13	<i>tert</i> -Butyl alcohol	B	70	0
CuOEt	2a	7	Ethanol	B	1	89, 1 (3f)
CuO- <i>i</i> -Pr	2a	13	2-Propanol	B	0	62, 10 (1), 16 (3f)
CuO- <i>i</i> -Pr ^d	2a	13	2-Propanol	B	0	62, 13 (1), 20 (3f)
CuO- <i>t</i> -Bu	2a	13	<i>tert</i> -Butyl alcohol	B	21	18, 42 (3f)
CuCl	2a	3	Methanol	A	0	100
NaOH	2a	12	Methanol	A	90	0
CuOH	2a	3	Methanol	B	0	0, 93 (3b)
CuOH	2a	16	<i>tert</i> -Butyl alcohol	B	64	11
Cu ₂ O	2a	2	Methanol	A	70	29 (3b)
Cu ₂ O	2a	2	2-Propanol	A	74	3 (3d)

^a Ratio of moles of nucleophilic reagent to moles of haloazobenzenes. ^b The percent recovery of starting material (SM) is given. Under products is listed the percent yield of the expected product and then additional products with identification numbers in parentheses. ^c Heated for only 1.5 hr. ^d Reagent made with a 10% molar excess of cuprous chloride.

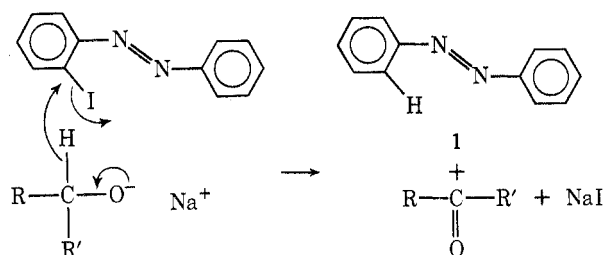
iodo- (4) and 4-iodoazobenzene (5) in methanol gave only slight yields of the corresponding cyano compounds (4a and 5a). However, with no solvent and a much higher temperature 4 and 5 reacted partially with cuprous cyanide to give 4a and 5a, respectively, along with some apparent decomposition. The substitution of 2-bromoazobenzene (2b) was slower than that of 2-iodoazobenzene (2a) and 2-chloroazobenzene (2c) did not react at all under these conditions.

The above results suggest that the essential part of the reaction is the chelation of the cuprous ion by an azo nitrogen and by the iodo group as illustrated (6 and 7). The cop-



per would then assist in removing the iodine, thus allowing for easy substitution of the cyano group. The sodium ion does not chelate and the 3-iodo- and 4-iodoazobenzenes (4 and 5) cannot form such chelates. If chelation were not favored then the 2-iodo- and 4-iodoazobenzenes should be expected to react at about the same rates.⁶

The methoxide ion is generally a better nucleophile¹¹ than the cyanide ion and this is seen in the case of the reaction of sodium methoxide with 2a to give a high yield of 2-methoxyazobenzene (3b). Reaction between sodium methoxide and 2-bromoazobenzene (2b) did not take place, indicating that possibly this is on the borderline of reactivity. Reaction of sodium ethoxide and sodium isopropoxide gave exclusively reduction of 2a to azobenzene (1). Possible reaction mechanisms are a hydride transfer of the α hydro-



gen of the alkoxide or hydrogen abstraction by aryl radicals or, in copper reactions, copper-associated radicals generated through an electron transfer mechanism to give reduction of 2a and to give a carbonyl compound. The carbonyl compounds, acetaldehyde and acetone, in these reactions were not searched for. Under these mild conditions, the sodium *tert*-butoxide did not undergo the reduction reaction, having no α hydrogen atom, and did not undergo substitution. Bacon and Rennison¹³ similarly found that sodium alkoxides, with cuprous oxide as catalyst, gave reduction of 1-bromonaphthalene to naphthalene. In their case, sodium methoxide gave between 5 and 50% substitution and about 10% reduction. Sodium ethoxide gave 5 to 10% substitution and the rest reduction while sodium isopropoxide gave reduction and no substitution. They also found that sodium *tert*-butoxide gave some reduction and no substitution. They surmised that, at their conditions of over 100°, copper-associated radicals possibly were involved and these can remove β hydrogens from a *tert*-butyl group for the reduction. They did show that when the sodium salt of benzyl alcohol was used in the reaction that benzaldehyde resulted.

Two cuprous alkoxides have recently been described. Cuprous methoxide¹⁴ was made by the reaction between methylcopper and methanol and the cuprous *tert*-butox-

Table II
Nucleophilic Substitution Reactions on Dihaloazobenzenes

Nucleophilic reagent (MY)	Dihaloazobenzene	Molar ^a ratio	Solvent	Method	SM	% Yield ^b	
						Mono-	Di-
CuCN	8	1	Methanol	A	11	75 (9a)	12 (10a)
CuCN	8	7	Methanol	A	0	0	94 (10a)
CuCN	11	7	Methanol	A	3	20 (12a)	45 (13a)
NaOMe	8	1	Methanol	B	20	51 (9b)	20 (10b)
NaOMe	8	9	Methanol	B	0	1 (9b)	81 (10b)
NaOMe	11	15	Methanol	B	100	0	0
CuOMe	11	9	Methanol	B	36	15 (12b)	47 (13b)

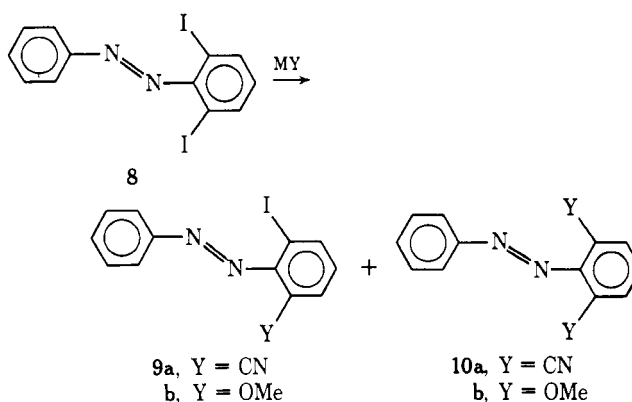
^a Ratio of moles of nucleophilic reagent to moles of dihaloazobenzene. ^b The percent recovery of starting material (SM) is given. Under mono- and di- are listed the percent yields of the expected products and in parentheses are the identification numbers.

ide¹⁵ was obtained by reaction of lithium *tert*-butoxide and cuprous chloride. For this work the cuprous alkoxides were made in situ and used immediately. The method of making the cuprous alkoxides was to react equal molar amounts of sodium alkoxide with cuprous chloride under reflux for 30 min. The 30-min reflux period was found to be essential since without it no expected products resulted. The reaction of cuprous isopropoxide with **2a** seemed to show no difference in the ratio of products whether the cuprous isopropoxide was made with a slight excess of cuprous chloride or a slight excess of sodium alkoxide. Thus it appears that both sodium and cuprous isopropoxide can give reduction.

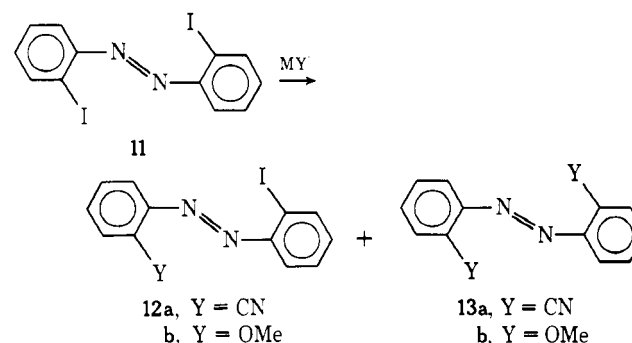
Since the sodium methoxide reacted completely with **2a**, cuprous methoxide was not treated with **2a** but was treated with 2-bromoazobenzene (**2b**) to give a fair yield of 2-methoxyazobenzene (**3b**). Cuprous ethoxide reacted with **2a** to give a good yield of 2-ethoxyazobenzene (**3c**) and no detectable reduction product, azobenzene (1). Reaction between cuprous isopropoxide and **2a** gave a fair yield of 2-isopropoxyazobenzene (**3d**) in addition to the reduction product, azobenzene (1), and some 2-hydroxyazobenzene (**3f**). Cuprous *tert*-butoxide and **2a** gave a low yield of 2-*tert*-butoxyazobenzene (**3e**) along with recovered **2a** and a fair yield of **3f**.

The 2-hydroxyazobenzene (**3f**) that was observed in the case of the reaction between cuprous isopropoxide (or *tert*-butoxide) and **2a** could be due to the decomposition of **3d** (or **3e**) or formation directly by substitution with cuprous hydroxide. 2-Isopropoxyazobenzene (**3d**) was refluxed for 22 hr with cuprous isopropoxide. On work-up, no 2-hydroxyazobenzene (**3f**) was detected, thus suggesting that decomposition of the alkoxyazobenzene is not the path to **3f**. Sodium hydroxide and **2a** were refluxed in methanol but no reaction was observed after 22 hr. This is not surprising, since the hydroxide ion generally is less nucleophilic than cyanide.¹² However, when 1 equiv of cuprous chloride was added to the sodium hydroxide and this refluxed for 30 min, to make cuprous hydroxide, there was obtained on reaction with **2a** an excellent yield of 2-methoxyazobenzene (**3b**) but no **3f**. The reaction of cuprous hydroxide and **2a** in *tert*-butyl alcohol did yield **3f**. This suggests that in methanol there is an equilibrium between the hydroxide and methoxide ions and that the methoxide reacts faster to form **3b**. In *tert*-butyl alcohol the hydroxide ion apparently reacts faster than the *tert*-butoxide ion, giving **3f** and no **3e**. The formation of cuprous hydroxide in the cuprous alkoxide reactions could be generated by decomposition of the cuprous isopropoxide or *tert*-butoxide into cuprous hydroxide and alkene. Commercial cuprous oxide when treated with **2a** in methanol gave a small yield of **3b**, and in isopropyl alcohol a slight amount of **3d**.

In Table II are listed the results of substitution reactions on diiodoazobenzenes. 2,6-Diiodoazobenzene (**8**) with 1 mol of cuprous cyanide gave predominantly the product of monosubstitution, 2-cyano-6-iodoazobenzene (**9a**). When a



large excess of cyanide was used, then the only product was the disubstituted compound, 2,6-dicyanoazobenzene (**10a**). 2,2'-Diiodoazobenzene (**11**) is not as reactive as **8** and even with an excess of cuprous cyanide reaction did not proceed completely to the dicyano compound, 2,2'-dicyanoazobenzene (**13a**), and some 2-cyano-2'-iodoazobenzene (**12a**) was left. A fair amount of what appeared to be decomposition



material was observed on working up this reaction. In the reactions of diiodo compounds some loss of cyano compounds resulted if the reaction mixtures were not worked up with the ammonia solution. This is unlike the cases noted earlier in Table I but similar to what others have noted.⁹

Reaction between **8** and sodium methoxide proceeded as with cuprous cyanide. In the equal molar case there was, however, obtained more disubstituted product, 2,6-dimethoxyazobenzene (**10b**), than in the cyanide case, and less monosubstituted product, 2-iodo-6-methoxyazobenzene (**9b**). The 2,6-dimethoxyazobenzene (**10b**) obtained in

Table III
Properties of the Compounds^a

Compd	Mp °C		Ir $\nu_{C=N}$, cm ⁻¹	Nmr, δ values ^b	
	Found	Lit.		Aromatic region ^c	Aliphatic region
1	65-67	68 ^d		8.1-7.3	
2a	60-61.5	62 ^e		8.1-7.0 ^f	
2b	39-40	36 ^e		8.1-7.3	
2c	27-28	33 ^e		8.1-7.3	
3a	61.5-63		2210	8.1-7.3	
3b	34-36	40 ^h		8.1-6.8	s 4.0 ⁱ
3c	130-135 ^j			8.1-6.8	q 4.2 ($J \cong 6$) t 1.5 ($J \cong 6$)
3d	130-135 ^j			8.2-6.7	sep 4.5 ($J \cong 6$) d 1.3 ($J \cong 6$)
3e	62-64			8.1-6.9	s 1.4
3f	79-80	81 ^h		8.3-6.7	s 12.8 ^{i, h}
4	69-70	71 ^e		8.0-7.3	
				d 8.2 ($J \cong 2$) t 7.2 ($J \cong 8$)	
4a	90.5-91		2210	8.3-7.3	
5	105-106	106 ^e		8.1-7.3	
5a	120-121	120.5-121.5 ^d	2207	8.2-7.3	
8	118-119	118-119 ^f		8.2-7.3 ^f	
				t 6.6 ($J \cong 8$)	
9a	73-74		2206	8.3-7.5	
				t 7.2 ($J \cong 8$)	
9b	63.5-64.5			8.2-7.3	s 3.8
				7.0-6.9	
10a	178-179		2210, 2208 ^m	8.3-7.4	
10b	113-115	96-97 ⁿ		8.0-7.0	s 3.8 ⁱ
				6.8-6.5	
11	158-159	158-158.5 ^p		8.1-7.0 ^f	
12a	141.5-143		2207	8.2-7.2	
12b	99-100			8.1-6.9	s 4.0
13a	235.5-237		2208	8.2-7.5	
13b	154-155	155 ^t		7.9-6.9	s 4.0 ⁱ

^a Satisfactory analytical data ($\pm 0.4\%$ for C, H, N) were reported for all new compounds listed in the table. ^b Integrations were correct for all compounds. ^c Multiplets unless otherwise specified. ^d Reference 21. ^e Reference 3. ^f For further elucidation of the NMR spectra see ref 4. ^g Reference 20. ^h Reference 17. ⁱ These values compare favorably with the values in ref 17. ^j Boiling points at 0.75 mm. ^k Hydroxyl proton. ^l Reference 4. ^m Shoulder peak. ⁿ References 16 and 17. ^p Reference 22.

this study was found to have a melting point 20° higher than that previously reported.^{16,17} An elemental analysis shows a formulation consistent with that of **10b**. In an effort to prove conclusively the structure, **10b** was made by an independent route. 2-Nitroresorcinol was dimethylated,¹⁸ the nitro group reduced,¹⁹ and the resulting aniline condensed with nitrosobenzene to give **10b**. The melting point of this **10b** was identical with that of the **10b** above and a mixture melting point was undepressed. Repeated crystallizations from different solvents failed to change the melting point. The NMR spectrum is also consistent with **10b**.

2,2'-Diiodoazobenzene (**11**) gave no methoxy compounds when treated with sodium methoxide. Moreover, reduction of one of the iodo groups was sometimes observed although this was erratic. Reaction did take place when cuprous methoxide was used, but not all of the starting material was used up in the reaction even though a large excess of cuprous methoxide was used. These results are consistent with those of reaction with cuprous cyanide. Also a very small amount of reduction was noted in the form of 2-methoxyazobenzene (**3b**) contaminating the mono product, 2-iodo-2'-methoxyazobenzene (**12b**).

In conclusion, a number of cuprous salts can be used to effect substitution of ortho iodoazobenzenes in good yield under mild conditions.

Experimental Section

NMR spectra were recorded on a Varian T-60 spectrometer in 5-10% CDCl₃ solutions with Me₄Si as the internal standard. IR spectra were taken in chloroform solution on a Perkin-Elmer IR-257.

The alumina used throughout this work was of activity grade of about 3 and was made by shaking 1000 g of neutral, Fisher alumina (Alcoa F-20) with 75 ml of water. All solvents used in this work were reagent grade and were used without further purification. The ligroin used was of boiling range 63-75°. The cuprous chloride used was Fisher C-457.

Melting points were taken on a Mel-Temp apparatus and are uncorrected. All microanalyses were carried out by the Galbraith Laboratories, Inc., Knoxville, Tenn.

Chromatography of all compounds was as follows. Azobenzene and all monohaloazobenzenes were eluted with a 9:1 mixture of ligroin-benzene. Monoalkoxyazobenzenes were eluted with a 1:1 mixture of ligroin-benzene, diiodoazobenzenes with a 4:1 mixture of ligroin-benzene, monosubstituted diiodoazobenzenes with a 1:1 mixture of ligroin-benzene, and the dicyano- and dimethoxyazobenzenes with benzene.

All monosubstituted azobenzenes were crystallized from ligroin and all disubstituted azobenzenes from benzene.

The concentrations of the reactions were between 0.10 and 0.06 M in haloazobenzene.

Method A. 2-Iodoazobenzene (**2a**, 1.00 g, 3.3 mmol), 1.0 g (11 mmol) of cuprous cyanide, and 40 ml of methanol were refluxed for 20 hr. The reaction mixture was then poured into 400 ml of water and extracted with ether. The ether was evaporated and the residue was taken up in ligroin and chromatographed on 100 g of alu-

mina. Elution with a 9:1 mixture of ligroin-benzene gave 0.01 g (1%) of 2-iodoazobenzene. Further elution with a 1:1 mixture of ligroin-benzene gave 0.63 g (94%) of 2-cyanoazobenzene (**3a**). Crystallization from ligroin yielded 0.58 g (87%) of **3a**.

Further reactions of this type are listed in Tables I and II. The properties of all compounds used and made are listed in Table III.

In experiments on compounds **8** and **11**, the reaction mixture was poured into 400 ml of 1 *N* ammonium hydroxide solution instead of 400 ml of water.

Method B. Sodium metal (1.0 g, 43 mmol) was treated with 50 ml of refluxing *tert*-butyl alcohol. When all of the sodium was reacted 4.0 g (40 mmol) of cuprous chloride was added and refluxing was continued for 0.5 hr. Then 1.00 g (3.3 mmol) of 2-iodoazobenzene (**2a**) was added and the reaction mixture was refluxed for an additional 20 hr. At the end of the reflux period, the reaction mixture was poured into 300 ml of water and 200 ml of ether. The mixture was made slightly acidic, stirred for 5 min, and filtered to remove the black residue. The filtrate was separated and the ether was extracted three times with 150-ml portions of 1 *N* sodium hydroxide. The aqueous extracts were combined, acidified, extracted with ether, dried over anhydrous sodium sulfate, evaporated, and crystallized from ligroin to yield 0.27 g (42%) of 2-hydroxyazobenzene (**3f**). The ether layer, after base extractions, was evaporated to yield an oil which was dissolved in ligroin and chromatographed on 75 g of alumina. The first band was eluted with a 9:1 mixture of ligroin-benzene to yield 0.21 g (21%) of recovered 2-iodoazobenzene (**2a**). Elution with a 1:1 mixture of ligroin-benzene gave 0.15 g (18%) of 2-*tert*-butoxyazobenzene (**3e**). Crystallization from ligroin by means of a Dry Ice-acetone bath gave red crystals of **3e**.

Further reactions of this type are listed in Tables I and II. The properties of all compounds used and made are listed in Table III.

A similar reaction, but without the cuprous chloride, gave only recovered **2a**.

Method C. 3-Iodoazobenzene (**4**, 1.00 g, 3.3 mmol) and 1.0 g (11 mmol) of cuprous cyanide were placed in a Schlenk tube and heated in an oil bath to 188° for 18 hr. Sublimation occurred. At the end of the reaction time the reaction mixture was extracted with hot chloroform until the extracts were colorless, leaving a black residue. The solvent was evaporated and the work-up of the reaction then proceeded as in method A.

2,6-Dimethoxyazobenzene (10b). At room temperature were mixed 6.1 g (40 mmol) of 2,6-dimethoxyaniline¹⁹ in 50 ml of 95% ethanol and 5.3 g (50 mmol) of nitrosobenzene in a mixture of 95% ethanol and 50 ml of glacial acetic acid. This mixture was allowed to stand for 20 hr. It was then poured into 1 l. of water and extracted three times with 200-ml portions of ether which was washed three times with 250-ml portions of 2 *N* hydrochloric acid and three times with 150-ml portions of water. The ether layer was dried over anhydrous sodium sulfate and evaporated and the residue was taken up in a 3:2 mixture of ligroin-benzene. This was placed on a column of 150 g of alumina and elution with a 3:2 mixture of ligroin-benzene gave a light yellow colored fraction which was discarded. Elution with a 1:4 mixture of ligroin-benzene gave 2.5 g (26%) of an orange compound which after crystallization from benzene-ligroin gave 2.3 g (24%) of **10b**, mp 113–115°. A mixture

melting point with the 2,6-dimethoxyazobenzene made by methoxylation of **8** was 113.5–115.5°.

Anal. Calcd for C₁₄H₁₄N₂O₂: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.06; H, 5.92; N, 11.34.

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Registry No.—**1**, 103-33-3; **2a**, 51343-11-4; **2b**, 4103-29-1; **2c**, 18264-99-8; **3a**, 38302-59-9; **3b**, 6319-21-7; **3c**, 55669-54-0; **3d**, 55669-55-1; **3e**, 55669-56-2; **3f**, 2362-57-4; **4**, 23377-17-5; **4a**, 55669-57-3; **5**, 6639-27-6; **5a**, 1837-93-0; **8**, 52221-99-5; **9a**, 55669-49-3; **9b**, 55669-50-6; **10a**, 55669-51-7; **10b**, 29418-48-2; **11**, 5486-04-4; **12a**, 55669-52-8; **12b**, 613-55-8; **13a**, 16288-72-5; **13b**, 613-55-8; sodium cyanide, 143-33-9; copper cyanide, 544-92-3; sodium methoxide, 124-41-4; copper methoxide, 18213-24-6; sodium ethoxide, 141-52-6; sodium isopropoxide, 683-60-3; sodium *tert*-butoxide; copper ethoxide, 55669-53-9; copper isopropoxide, 53165-38-1; copper *tert*-butoxide, 35342-67-7; cuprous chloride, 7758-89-6; sodium hydroxide, 1310-73-2; cuprous hydroxide, 12125-21-2; cuprous oxide, 1317-39-1; *tert*-butyl alcohol, 75-65-0; 2,6-dimethoxyaniline, 2734-70-5; nitrosobenzene, 586-96-9.

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