Reaction of Haloazoxybenzenes with Sulfuric Acid

Ichiro SHIMAO,* Ken FUJIMORI,† and Shigeru OAE†

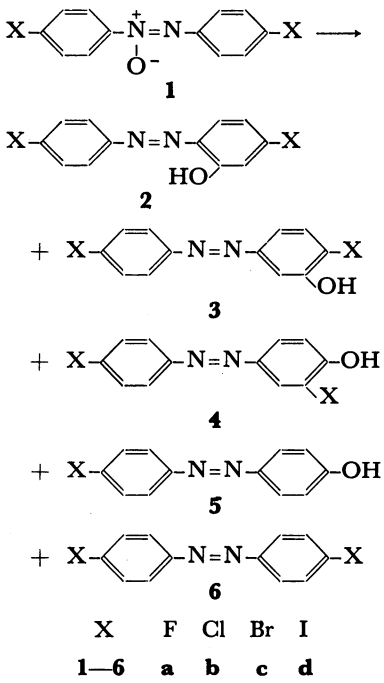
Department of Industrial Chemistry, Faculty of Engineering, Toyama University, Takaoka, Toyama 933
†Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari, Ibaraki 305

(Received June 27, 1981)

Treatment of 4,4′-dihaloazoxybenzenes with sulfuric acid afforded 4,4′-dihaloazobenzenes (**6**) as the major product and 5-halo-2-(*p*-halophenylazo)phenols, the Wallach rearrangement products as minor products, besides 2-halo-5-(*p*-halophenylazo)phenols, 2-halo-4-(*p*-halophenylazo)phenols, and 4-(*p*-halophenylazo)phenols as abnormal rearrangement products. The reaction of fluoro compound gave the azophenols (**3a** or **5a**) in the best yields. However, the ratio of **3a** to **5a** was found to vary with the concentration of sulfuric acid. Treatment of 4-haloazoxybenzenes with sulfuric acid gave 4-(*p*-halophenylazo)phenols and 4-haloazobenzenes (**13**) as major products together with 2-(*p*-halophenylazo)phenols and 5-halo-2-(phenylazo)phenols as minor products. Yields of reduction products **6** and **13** increased as the halosubstituent became heavier in the following sequence: F→Cl→Br→I.

In 1951, Gore and Hughes[1] reported that a treatment of 4,4′-dichloroazoxybenzene (**1b**) with concentrated sulfuric acid yielded 5-chloro-2-(*p*-chlorophenylazo)-phenol (**2b**) and 4,4′-dichloroazobenzene (**6b**). Recently, Cox and Buncel[2] reported briefly that a reaction of 4,4′-dihaloazoxybenzene (**1**) with concentrated sulfuric acid produced their corresponding 5-halo-2-(*p*-halophenylazo)phenols (**2**) together with a large amount of 4,4′-dihaloazobenzenes (**6**), except in the case of the iodo compound (**1d**).

Our recent study[3] on reactions of 4,4′-dialkylazoxybenzenes with sulfuric acid revealed that the major product was 2-alkyl-5-(*p*-alkylphenylazo)phenols and not 4,4′-dialkyl-2-hydroxyazobenzenes as early workers[1] had reported; formation of 4,4′-dialkylazobenzenes was observed as rather a minor reaction. Thus, it is anticipated that a detailed investigation of the Wallach rearrangement of various *p*-halo-substituted azoxybenzenes may provide vital information useful for understanding the nature of the Wallach hydroxyl migration as well as that of the deoxygenation which often predominates. This paper describes results of our reinvestigation and presents our new interpretation of reactions of **1** and 4-haloazoxybenzenes (**11**) with sulfuric acid.



Results and Discussion

Reaction of **1** with 92% sulfuric acid gave a mixture of azophenols and **6**. **6** was separated from azophenols by column chromatography on alumina. Azophenols were separated from one another by chromatography on a deactivated silica-gel column in most cases. Some unidentified resinous materials also were formed in the reaction. The results are shown in Table 1.

In all cases, the main reaction was the reduction of **1** to give **6**; especially, **1d** gave **6d** predominantly. **1d** was reported[2] to be reduced exclusively to **6d** on treatment with sulfuric acid. However, the rearrangement product **2d** also was found to be formed, though in a small amount.

In general, azoxy group is known[1,4] to be reduced partially to azo group in reaction of azoxybenzenes with

TABLE 1. REACTION OF 4,4′-DIHALOAZOXYBENZENE (**1**) WITH SULFURIC ACID
(**1**: 0.5 g, 92% H_2SO_4: 25 cm³, temp: 50 °C, time: 30 min)

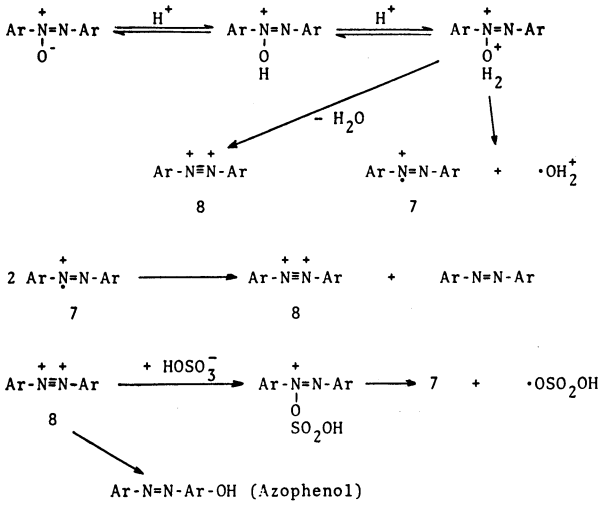
	X	Yield/%				
		2	**3**	**4**	**5**	**6**
1a	F	0.6	7.4		25	40
1b	Cl	12	3.6	2.4	0.2	59
1c	Br	11		1.5	0.2	69
1d[a]	I	1				83

a) 92% H_2SO_4: 75 cm³.

TABLE 2. REACTION OF AZOXYBENZENE WITH SULFURIC ACID
(Azoxybenzene: 0.1 g, temp: 50 °C, time: 30 min)

V[a] / cm³	Yield/%	
	Azobenzene	4-(Phenylazo)phenol
0.5	45	35
0.75	39	40
1.0	36	43
5.0	21	65
10	15	72
50	5	83

a) V is the volume of 92% H_2SO_4.

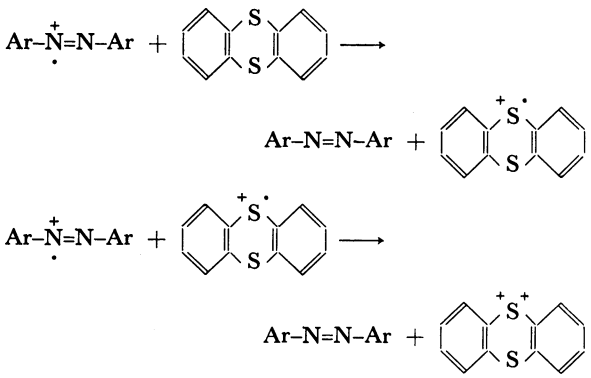


Scheme 1.

sulfuric acid. In order to understand the nature of the formation of azoarene, the reaction of azoxybenzene with 92% sulfuric acid was carried out with varying amounts of sulfuric acid used. The results are shown in Table 2. The yield of azobenzene depends clearly on the ratio of azoxybenzene to sulfuric acid. The extent of reduction decreases as the concentration of azoxybenzene decreases.

Earlier, we[5] noticed predominat reduction to azobenzene in a reaction of azoxybenzene with acetic anhydride around 190 °C, presuming the reduction to proceed *via* a radical cation species. In the present reaction, the reduction to azobenzene is presumed to proceed *via* radical cation **7** shown in Scheme 1. Diprotonation of the azoxy group followed by heterolysis of the N–O bond gives dicationic intermediate **8**, whereas homolytic fission of the N–O bond affords radical cation **7** similarly to an oxygen exchange[6] of diaryl sulfoxide in concentrated sulfuric acid. Disproportionation of **7** gives both an azo compound and dicationic intermediate **8**. This must be a bimolecular process in view of the observation that the amount of the reduction product, azobenzene, increases as the amount of sulfuric acid used decreases. One-electron reduction of **8** can also afford cation radical **7**.[7] There would be a possibility that **7** is partly reduced to give the azo compound by one-electron transfer. Of course, **8** can also formed by diprotonation and subsequent dehydration of the azoxy group.[2] The resulting $\cdot OH^+$ radical cation may be consumed in the oxidation of phenolic substance formed during the reaction to give a resinous material which would also be formed in the reduction of **7** or **8** with phenolic substance. Actually, the yield of reduced products increases under the conditions in which the yield of resinous material increases.[1]

The amount of the reduction product from **1b** increased somewhat in the presence of thianthrene, a good electron transfer agent, as shown in Table 3. Since the cation radical is known to be formed when thianthrene is dissolved in concentrated sulfuric acid, eventually affording thianthrene *S*-oxide,[8] both thianthrene and its radical cation would be involved in the electron transfer to afford azoarene.



When an equimolar mixture of **1b** and 4-(phenylazo)-phenol was treated with 92% sulfuric acid, **1b** was reduced to **6b** nearly quantitatively, though with 65% of 4-(phenylazo)phenol recovered. Thus azophenol acts as a reducing agent. The azophenol would be oxidized by radical cations, such as H_2O^+ or **7**, and/or dication **8**, to form resinous material.

The amount of the reduction product, azoarene, seems to be related to the relative stability of the cation radical **7**. Within the same series in the periodic table, heavier atoms are known to stabilize the α-carbon radical to a higher extent.[9]

In the cases of **1b** and **1c**, *o*-hydroxy azo compounds, **2b** and **2c**, were obtained in substantial yields, in accordance with earlier reports.[1,3] However, **1c** gave a small amount of **4c** and **5c**, and **1b** yielded **3b**, **4b**, and **5b**. Although **3b** and **4b** were not separated from each other by column chromatography, they were partially separated by fractional crystallization described in the Experimental, while the ratio of **3b** to **4b** was determined by high-speed liquid chromatographic analysis.

The reaction of **1a** is peculiar. The yield of *o*-hydroxy azo compound, **2a**, the normal Wallach rearrangement product, was only 0.6%. Beside the reduction product, azophenol **5a** which is also a rearrangement product, was the second main product, accompanied with a comparable amount of **3a**.

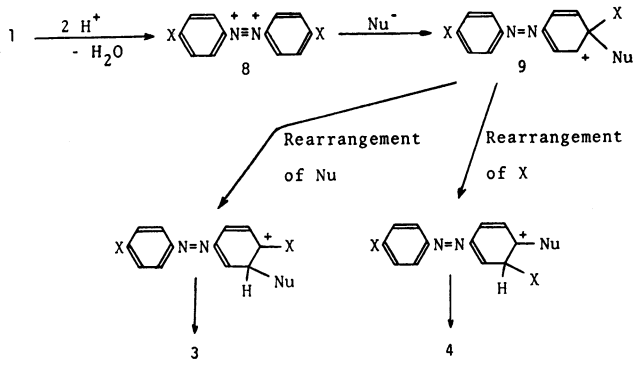
These reaction products, **2**, **4**, **5**, and **6**, were identified by comparison with authentic samples, respectively, while **3b** was acetylated, and the resulting acetate was identified by comparing physical properties with those of the authentic sample obtained independently. Attempts to obtain the authentic sample of **3a** were unsuccessful. The mass spectrum of **3a** showed *m/e* values: 234 (M^+), 139 ($C_6H_4FN_2O$), 123 ($C_6H_4FN_2$), and 111 (C_6H_4F). Chemical shift of the OH proton in $CDCl_3$ was δ 5.60 ppm. A characteristic NMR absorption signal of *o*-hydroxyazobenzene (hydrogen bonded OH, δ about 13 ppm) was not observed.

Table 3. Reaction of 4,4′-dichloroazoxybenzene (**1b**) and thianthrene with sulfuric acid

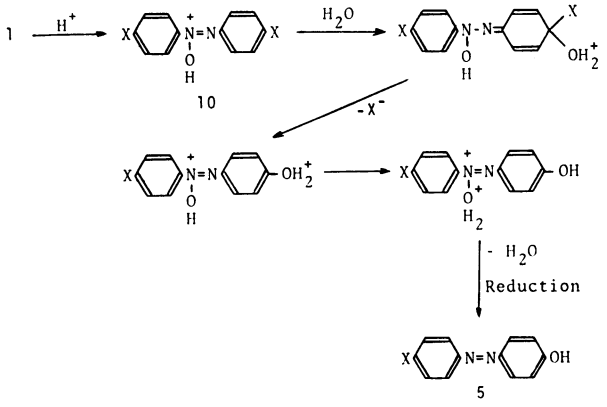
	Yield/%	
	6b	Thianthrene *S*-oxide
1b	54	
1b+Thianthrene	70	56
Thianthrene		42

Further, mp and IR spectrum of this compound are different from those of **4a** obtained by diazo-coupling reaction. Consequently, this compound was ascribed to 2-fluoro-5-(*p*-fluorophenylazo)phenol (**3a**), by analogy with the reaction of **1b**.

Shemyakin *et al.*[10] and we[11] reported independently on the basis of ^{18}O-tracer experiment that the rearrangement leading to *o*-hydroxy azo compound, **2**, is intramolecular. However, the formation of azophenols, **3** and **4**, is considered to be effected by a rearrangement similar to that in the reaction of 4,4'-dialkylazoxybenzenes described previously.[3] Either halide or an other nucleophile, *e.g.*, hydroxysulfonyloxy group or water, is shifted to the adjacent carbon atom in the intermediate (**9**) formed by nucleophilic attack on the dicationic intermediate **8**,[2,3] eventually affording **3** or **4** as shown in Scheme 2. Apparently the shift of chloride is more facile than that of fluoride, while bromide is more readily shifted than hydroxysulfonyloxy or hydroxyl group.



Scheme 2.



Scheme 3.

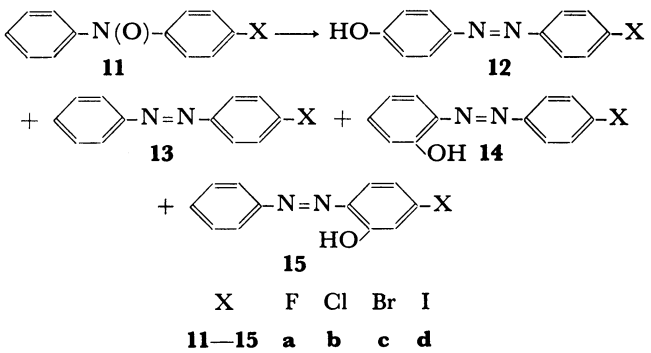
TABLE 4. REACTION OF 4,4'-DIFLUOROAZOXYBENZENE (**1a**) WITH SULFURIC ACID
(**1a**: 0.5 g, sulfuric acid: 25 cm³)

H_2SO_4 Concn %	Temp °C	Time h	Yield/% 2a	3a	5a	6a
92	25	4	0.4	8.8	18	42
92	50	0.5	0.6	7.4	25	40
92	80	1/6	0.9	6.8	27	38
85	80	1	0.6	0.6	58	15
98	25	1	1.2	30	3	43

Compound **5** may be formed by the aromatic nucleophilic substitution on the monoprotonated azoxybenzenes as shown in Scheme 3, *i.e.*, the replacement of halide by nucleophile in the intermediate (**10**). The mechanism of Wallach rearrangement appears to change with chang of concentration of sulfuric acid and structure of azoxy compound. At higher acid concentrations, the dicationic intermediate is generally considered to be formed; in some cases, at lower acid concentrations, a mechanism *via* a quinonoid intermediate formed from monoprotonated azoxybenzenes has been proposed.[2]

In the reaction of **1a**, the distribution of products changed markedly by change of reaction conditions, particularly of the concentration of sulfuric acid. Table 4 shows these results. When a concentrated sulfuric acid was used, **3a** was the main rearrangement product probably because fluoride, which is certainly not a good leaving group, is not a good nucleophile to compete in the migration. On the other hand, **5a** was formed as the major product when a dilute sulfuric acid (85%) was used.[23] The leaving of fluoride is obviously facilitated by the presence of water. In the cases of **1b** and **1c**, however, the acid concentration had little effect on the product distribution. The natures of neither chloride nor bromide ion is much changed by the small change in acid concentration.

4-Haloazoxybenzenes (**11**) were allowed to react with 92% sulfuric acid at 50 °C. The sample **11** was an equimolar mixture of α- and β-isomers. The distribution of products in the reaction of **11** with sulfuric acid are listed in Table 5.



11—15 **a** **b** **c** **d**

Main products were corresponding 4-(*p*-halophenylazo)phenols (**12**) and 4-haloazobenzenes (**13**), while no

TABLE 5. REACTION OF 4-HALOAZOXYBNZENES (**11**) WITH SULFURIC ACID
(**11**: 0.5 g, 92% H_2SO_4: 25 cm³, temp: 50 °C, time: 30 min)

	X	Yield/% 12	13	14	15
	H	65	20	0.3	
11a	F	54	26	0.5	0.3
11b	Cl	34	46	1.4	0.2
11c	Br	27	55	1.7	0.3
11d	I	5	72	2.0	0.3
11cα		30	56	0.14	0.35
11cβ		27	52	2.0	0.1

abnormal rearrangement product, such as 2-halo-4-(phenylazo)phenol or 2-halo-5-(phenylazo)phenol, was obtained. The *p*-halosubstituent did not allow the ipso nucleophilic attack which was observed in the reaction of 4-alkylazoxybenzenes.[12]

Hahn and Jaffe[13] reported that treatment of 4-bromoazoxybenzenes (**11c**) with sulfuric acid gave only 4-(*p*-bromophenylazo)phenol (**12c**). However, under the same reaction conditions the rearrangement product **12c** was a minor product, the major product being the reduction product, *i.e.*, azo compound **13c**. The yield of reduction product **13** was found to increase in the following sequence for substituents: H→F→Cl→Br→I. The same trend was observed in the reactions of 4,4'-dihaloazoxybenzenes. Apparently the *p*-halo substituent facilitates the formation of radical cation intermediate **7** which is stabilized by resonance interaction with the *p*-halo substituent, especially with heavy halo substituents. The radical cation is considered to give eventually the azo compound **13**, as mentioned above.

When both α- and β-isomers of **11c** and their mixture were treated separetely with 92% sulfuric acid, the two isomers and the mixture gave practically the same products (**12c** and **13c**), except the *o*-hydroxy azo compounds (**14c** and **15c**). Interconversion between α- and β-isomers, **11cα** and **11cβ**, was not observed by high-speed liquid chromatographic analysis of the unchanged azoxy compound recovered at about 25% conversion of the reaction, thus supporting the mechanism that *p*-hydroxy azo compound **12** is formed *via* the dicationic intermediate, $C_6H_5N^+{\equiv}N^+C_6H_4X(p)$. The ratio of the rates of **11cα** and **11cβ**, $k\alpha/k\beta$, was determined as about 0.85 from the α/β ratio of the starting material and that of the azoxy compound recovered at 60% conversion. Duffey and Hendley[14] also reported through UV spectrographic experiments that the value of $k\alpha/k\beta$ was 0.9.

In all cases, *o*-hydroxy azo compounds, **14** and **15**, also were obtained in very low yields. The ortho rearrangement to a benzene ring having a *p*-halo substituent is more difficult than that to the other rings. However, the products obtained by UV irradiation of these samples **11** consisted of nearly equal amounts of **14** and **15**.

Experimental

No melting points were corrected. IR spectra were recorded on a JASCO-IRA-1 spectrophotometer. NMR spectra were obtained with a JEOL MH-100 spectrometer using TMS as the internal standard, and mass spectra with a JEOL-OlSG spectrometer. High-speed liquid chromatographic analyses were carried out with a JASCO-FLC 150 apparatus on a 0.5 m×2.1 mm column packed with JASCODAC SV-02 (the solvent was methanol–water).

4,4'-Dihaloazobenzenes, **6a** and **6d**, were obtained from their corresponding *p*-haloanilines by oxidation with active manganese dioxide.[24] **6b** and **6c** were prepared by air oxidation of their corresponding hydrazo compounds which had been obtained by reduction of *p*-nitrohalobenzenes with zinc powder and sodium hydroxide.[24] 4-Haloazobenzenes, **13**, were prepared by condensation of nitrosobenzene with *p*-haloanilines.[24]

4,4'-Dihaloazoxybenzenes, **1a** and **1d**, and 4-haloazoxybenzenes, **11**, were prepared by oxidation of their corresponding azoarene with hydrogen peroxide.[15] Compounds **1b** and **1c** were obtained by reduction of *p*-halonitrobenzenes with D-glucose.[16] Isomeric *p*-bromoazoxybenzenes, **11cα** and **11cβ**, were prepared by the well known method described in the literature.[17,18]

Reaction of 4,4'-Dihaloazoxybenzenes (1) with Sulfuric Acid. A mixture of **1** (0.5 g) and 92% sulfuric acid (25 cm^3) was heated at 50 °C for 30 min. The reaction mixture was poured into cold water and then extracted with benzene. After removal of the solvent, the residue was chromatographed on an alumina column using benzene as the eluent. The eluate gave **6** which was recrystallized from benzene or toluene.

Azophenols remaining at the top of column were extracted with ethanol–water. The extract was chromatographed on a silica gel column using benzene as the solvent.

The first fraction gave **2** which was recrystallized from hexane or benzene.

The second fraction gave **3** and/or **4**. Compound **3a** was recrystallized from hexane, mp 119—121 °C. Found: C, 61.34; H, 3.40; N, 11.83%. Calcd for $C_{12}H_8F_2N_2O$: C, 61.53; H, 3.45; N, 11.96%. IR (KBr): 3480, 1595, 1459, 1280, and 1230 cm^{-1}. In the reaction of **1b**, this fraction gave a mixture of **3b** and **4b**. High-speed liquid chromatographic analysis of the mixture showed that the ratio of **3b** to **4b** was 3 : 2. The mixture was recrystallized from benzene to yield **3b**. The mother liqour was evaporated and the resulting crystalline mass was dissolved in methanol. When the methanol solution was allowed to stand for a long time open in air, two kinds of crystals were formed. The crystals were extracted with boiling hexane for a short time and then the hexane solution was quickly separated by decantation. After removal of the solvent, the residue was recrystallized from hexane–benzene to give **4b**. Compound **3b**: mp 197—198 °C. Found: C, 54.23; H, 2.87; N, 10.52%. Calcd for $C_{12}H_8Cl_2N_2O$: C, 53.96; H, 3.02; N, 10.49%. IR (KBr): 3480, 1580, 1490, and 1410 cm^{-1}. In the case of **1c**, **4c** was obtained.

The third fraction gave **5** which was recrystallized from hexane or toluene.

Compounds **3a** and **3b** were acetylated with acetic anhydride and pyridine. Acetate of **3a**: mp 65—66 °C. Found: C, 60.71; H, 3.38; N, 10.14%. Calcd for $C_{14}H_{10}F_2N_2O_2$: C, 60.87; H, 3.65; N, 10.14%. IR (KBr): 1780 and 1495 cm^{-1}. Acetate of **3b**: mp 116.5—118 °C. The mp and IR spectra of **3b** acetate were identical with those of an authentic sample.

Reaction of 1b and Thianthrene with Sulfuric Acid. A solution of **1b** (0.267 g) and thianthrene (0.216 g) in 98% sulfuric acid (50 cm^3) was stirred at 27 °C for 3 h. The reaction mixture was poured into cold water, and then extracted with benzene. The extract was chromatographed on an alimina column using benzene as the solvent. The eluate geve a mixture of **6b** and thianthrene. **6b** was separated from thianthrene by recrystallization from acetone. The residue on the column was eluted with a mixture of ethanol, benzene, and water, and then the eluate chromatographed on a silica-gel column using benzene as the solvent. The first fraction gave **2b** in 2% yield. Treatment of the second fraction with dilute sodium hydroxide solution gave thianthrene *S*-oxide. Acidification of the mother liquor yielded a mixture of **3b** and **4b** (1%).

Reaction of 4-Haloazoxybenzene (11) with Sulfuric Acid. Compound **11** (0.5 g) was treated with 92% sulfuric acid

(25 cm^3) at 50 °C for 30 min. The reaction mixture was poured into excess cold water and then extracted with benzene. When the extract was chromatographed on an alumina column using benzene as the eluent, 4-haloazobenzene **13** was eluted out. The residue on the column was then eluted with a mixture of ethanol, benzene, and water, to give azophenols. The mixture of azophenols was chromatographed on silica gel. The first fraction was a mixture of **14** and **15** as analyzed by GLPC, while the second fraction was **12**.

In the case of **11c**, when the reaction was stopped in a few min, the unchanged azoxy compound was eluted out together with **13c** by the chromatography on alumina of the reaction mixture, and then the eluent was separated by chromatography on alumina using hexane–benzene as the solvent. The azoxy compound was analyzed by high-speed liquid chromatography.

Preparation of the Authentic Samples. 5-Halo-2-(*p*-halophenylazo)phenols (**2**) were prepared by irradiation of an ethanolic solution of **1**.[25] **2a**: mp 126—126.5 °C. Found: C, 61.40; H, 3.20; N, 11.79%. Calcd for $C_{12}H_8F_2N_2O$: C, 61.53; H, 3,45; N, 11.96%. IR (KBr): 1595 and 1495 cm^{-1}. **2b**: mp 178—180 °C. (lit,[19] 176.5 °C). **2c**: mp 182—184 °C. (lit,[19] 181.5 °C). **2d**: mp 213—215 °C. Found: C, 32.18; H, 1.60; N, 6.22%. Calcd for $C_{12}H_8I_2N_2O$: C, 32.02; H, 1.79; N, 6.23%. IR (KBr): 1590, 1460, and 1395 cm^{-1}.

2-Halo-4-(*p*-halophenylazo)phenols (**4a—4c**) and 4-(*p*-halophenylazo)phenols (**5**) were obtained by diazo-coupling of the corresponding phenols and diazonium salts.[24] **4a**: mp 153—155 °C. Found: C, 61.43; H, 3.23; N, 11.89%. Calcd for $C_{12}H_8F_2N_2O$: C, 61.53; H, 3.45; N, 11.96%. IR (KBr): 3480 and 1495 cm^{-1}. **4b**: mp 141—142 °C. Found: C, 53.77; H, 3.24; N, 10.72%. Calcd for $C_{12}H_8Cl_2N_2O$: C, 53.96; H, 3.02; N, 10.49%. IR (KBr): 3480 and 1480 cm^{-1}. **4c**: mp 158—159.5 °C. Found: C, 40.66; H, 2.26; N, 8.05%. Calcd for $C_{12}H_8Br_2N_2O$: C, 40.48; H, 2.27; N, 7.87%. IR (KBr): 3480, 1485, and 1475 cm^{-1}. **5a**: mp 157—159 °C. Found: C, 66.55; H, 4.17; N, 12.85%. Calcd for $C_{12}H_9FN_2O$: C, 66.66; H, 4.20; N, 12.96%. IR (KBr): 1585 and 1495 cm^{-1}. **5b**: mp 158—160 °C (lit,[20] 154 °C). **5c**: mp 161—163 °C (lit,[21] 162 °C). **5d**: mp 174—176 °C (lit,[22] 172 °C).

3-Acetoxy-4,4'-dichloroazobenzene (3b Acetate): 2-Chloro-5-nitrophenol was acetylated with acetic anhydride and pyridine. Recrystallization from hexane–benzene gave 2-chloro-5-nitrophenyl acetate, mp 78—79 °C. Found: C, 44.82; H, 2.55; N, 6.58%. Calcd for $C_8H_6ClNO_4$: C, 44.56; H, 2.78; N, 6.49%. IR (KBr): 1760, 1525, and 1350 cm^{-1}.

The acetate was reduced by catalytic hydrogenation to yield 3-acetoxy-4-chloroaniline which was recrystallized from hexane–benzene, mp 98—99 °C.

A solution of the amine (0.32 g) and *p*-chloronitrosobenzene (0.24 g) in acetic acid was allowed to stand for 24 h at room temperature. The reaction mixture was poured into cold water. The precipitate was filtered off and purified by chromatography on silica gel, and then recrystallized from hexane (yield 42%), mp 117—118.5 °C. Found: C, 54.25; H, 3.09; N, 9.14%. Calcd for $C_{14}H_{10}Cl_2N_2O_2$: C, 54.39; H, 3.26; N, 9.06%. IR (KBr): 1780 and 1480 cm^{-1}.

Acetate of **3c** was obtained by a similar method, mp 139—141 °C. Found: C, 42.05; H, 2.37; N, 7.27%. Calcd for $C_{14}H_{10}Br_2N_2O_2$: C, 42.24; H, 2.54; N, 7.04%. IR (KBr): 1770 cm^{-1}. The acetate was hydrolyzed by the chromatography on alumina to yield **3c**, mp 212—212.5 °C. Found: C, 40.66; H, 2.32; N, 7.92%. Calcd for $C_{12}H_8Br_2N_2O$: C, 40.48; H, 2.27; N, 7.87%. IR (KBr): 3480 and 1480 cm^{-1}.

References

1) P. H. Gore and G. K. Hughes, *Aust. J. Sci. Res.*, **4A**, 185 (1951).

2) R. A. Cox and E. Buncel, "The Chemistry of the Hydrazo, Azo and Azoxy Groups," ed by S. Patai, John Wiley and Sons, New York (1975), p. 808.

3) I. Shimao and S. Matsumura, *Bull. Chem. Soc. Jpn.*, **49**, 2294 (1976).

4) A. Lachman, *J. Am. Chem. Soc.*, **24**, 1178 (1902).

5) S. Oae, T. Maeda, and S. Kozuka, *Bull. Chem. Soc. Jpn.*, **44**, 442 (1971).

6) S. Oae and N. Kunieda, *Bull. Chem. Soc. Jpn.*, **41**, 696 (1968).

7) Concentrated sulfuric acid containing any one of 4,4'-dihaloazoxybenes gives complex but distinct ESR signals, a part of which may be ascribed to those of the cation radicals **7**, but further study is necessary to understand the nature of the ESR signals.

8) H. J. Shine and L. Piette, *J. Am. Chem. Soc.*, **84**, 4798 (1962).

9) C. C. Price and S. Oae, "Sulfur Bonding, "Ronald Press, N. Y. (1962), pp. 26—28.

10) M. M. Shemyakin, T. E. Agadzhanyan, V. M. Mainind, and R. V. Kudryantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 1339; *Chem. Abstr.*, **59**, 12619b (1963).

11) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Jpn.*, **36**, 601 (1963).

12) I. Shimao and S. Matsumura, *Bull. Chem. Soc. Jpn.*, **51**, 926 (1978).

13) C. Hahn and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 946 (1962).

14) D. Duffey and E. C. Hendley, *J. Org. Chem.*, **33**, 1918 (1968).

15) B. T. Newbold, *J. Org. Chem.*, **27**, 3919 (1962).

16) H. W. Galbraith, F. Degering, and E. F. Hitch, *J. Am. Chem. Soc.*, **73**, 1323 (1951).

17) L. C. Behr, *J. Am. Chem. Soc.*, **76**, 3672 (1954).

18) T. E. Stevens, *J. Org. Chem.*, **29**, 311 (1964); *ibid.*, **32**, 1641 (1967).

19) R. Tanikaga, *Bull. Chem. Soc. Jpn.*, **41**, 2151 (1968).

20) J. T. Hewitt, *Ber.*, **26**, 2978 (1893).

21) J. J. Fox and J. T. Hewitt, *J. Chem. Soc.*, **93**, 340 (1908).

22) F. D. Chattaway and A. B. Constable, *J. Chem. Soc.*, **105**, 128 (1914).

23) The yield of reduction product **6a** was low under this conditions, because monoprotonated azoxy compound (**10**) may preferentially undergo the nucleophilic attack and hence the formation of radical cation **7** may be depressed.

24) Y. Nomura and S. Tomoda, "Shin-jikken-kagaku-koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1978), **14**/III, pp. 1516—1534.

25) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, **1954**, 2243.