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The Wallach Rearrangement of Some 4,4′-Disubstituted Azoxybenzenes

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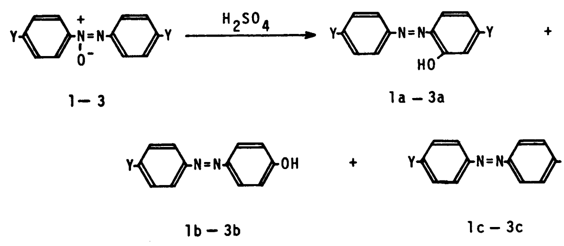
Synopsis. The treatment of azoxybenzenes bearing electron-withdrawing substituents at 4,4′-positions with sulfuric acid gave the corresponding 2-hydroxyazobenzenes, together with 4′-substituted 4-hydroxyazobenzenes. The treatment of 4,4′-dimethoxyazoxybenzene with *p*-toluenesulfonic acid and acetic anhydride afforded 4,4′-dimethoxy-3-acetoxyazobenzene and 4,4′-dimethoxy-2-tosyloxyazobenzene as the main rearrangement products.

In the Wallach rearrangement of 4,4′-dialkylazoxybenzenes with sulfuric acid, the main product was not the *o*-hydroxyazo compound, but an abnormal product formed by the ipso nucleophilic attack on the ring carbon atom bearing the alkyl group.[1] Another abnormal rearrangement was also observed in the reaction of 4,4′-dihaloazoxybenzenes with sulfuric acid; in this reaction, however, the major products were the reduction products, *i.e.*, 4,4′-dihaloazobenzenes.[2] The pattern of the reaction of azoxybenzenes with strong acids seems to be markedly affected by the *p*-substituents.

We have now found another example of the ipso substitution reaction of 4,4′-disubstituted azoxybenzenes. That is, when 4,4′-dinitroazoxybenzene (**1**), 4,4′-diacetylazoxybenzene (**2**), and azoxybenzene-4,4′-dicarboxylic acid (**3**) were treated with sulfuric acid, not only the normal rearrangement products (**1a**—**3a**), but also the ipso rearrangement products (**1b**—**3b**), were obtained. The results are shown in Table 1.



Compound **1** was found to rearrange in a normal fashion, giving preferentially 5-nitro-2-(*p*-nitrophenylazo)phenol (**1a**). This is a typical example of the Wallach rearrangement with sulfuric acid to give the ortho-rearranged azophenol.

The reaction of **2** gave 4-(*p*-acetylphenylazo)phenol (**2b**) as the main rearrangement product. When the aqueous solution was carefully concentrated in the work-up process, the characteristic odor of acetic acid was perceived. In the reaction of **3**, the evolution of carbon dioxide was observed when the reaction mixture was heated. These ipso substitution may be explained on the basis of the mechanistic scheme involving the initial formation of the dicationic inetermediate, $\mathrm{Ar{-}\overset{+}{N}{\equiv}\overset{+}{N}{-}Ar}$, proposed previously.[1,2]

Table 1. Reactions of 4,4′-disubstituted azoxybenzenes with sulfuric acid

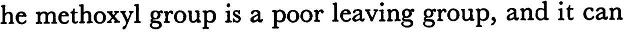
Azoxy-benzene Y	Temp °C	Time h	Yield/% a	b	c	Recovered material/%
1 NO_2	100	3	54	11	4	27
2 $COCH_3$	70	5	2.5	46		31
3 COOH	100	1/3	29	49	9	

Although an acetyl group of **2** was readily removed, the reaction of *p*-acetylazoxybenzene (a mixture of *α*- and *β*-isomers) with sulfuric acid afforded **2b** (yield, 93%), without removing acetyl group. In this case, the nucleophilic attack of the hydrogen-sulfate ion on the dicationic intermediate occurs preferentially at the para position of the unsubstituted phenyl ring. This is different from the reaction of 4-*t*-butylazoxybenzene, in which 4-(phenylazo)phenol was formed as the main product.[3]

Several azoxybenzenes were treated with concentrated sulfuric acid at 100 °C for 20 min, and the yields of the recovered azoxy compounds (determination by gas-chromatographic analysis) were the following: **1**, 92%; **2**, 42%; 3,3′-dinitroazoxybenzene, 33%; **3**, 0%. The reaction is obviously retarded by the electron withdrawing substituent, in keeping with the kinetic results reported by Duffey and Hendley.[4]

Contrary to Cox and Buncel's description,[5] 4,4′-dimethoxyazoxybenzene (**4**) was found to react readily with 80% sulfuric acid. A black tarry substance was mainly formed, and only a small amount of 4,4′-dimethoxyazobenzene (**4c**) (yield, 2%) was isolated. However, no rearrangement product was obtained. Similary, 4-methoxyazoxybenzene did not give hydroxymethoxyazobenzene, but 4-methoxyazobenzene (34%) and 4-hydroxyazobenzene (0.5%) were obtained.

Meanwhile, the reaction of **4** with a mixture of *p*-toluene-sulfonic acid (TsOH) and acetic anhydride gave 4,4′-dimethoxy-3-acetoxyazobenzene (42%), 4,4′-dimethoxy-2-tosyloxyazobenzene (3.5%), and **4c** (32%) as the main products.



Under the same conditions, azoxybenzene gave 2- and 4-(tosyloxy)azobenzene as the main rearrangement products, while 4,4′-diacetoxyazoxybenzene gave *p*-acetoxyphenyl tosylate and hydroquinone diacetate.[6] The methoxyl group is a poor leaving group, and it can stabilize the dicationic intermediate, Ar–$\overset{+}{N}\equiv\overset{+}{N}$–Ar. Hence, the rearrangement is believed to proceed very readily, without cleaving the azo linkage.

Thus, when 4-methoxyazoxybenzene was treated with TsOH and acetic anhydride, 4-methoxy-3-acetoxyazobenzene (38%), 4-methoxy-4′-tosyloxyazobenzene (5.6%), and 4-methoxyazobenzene (42%) were obtained as the main products.

Experimental

The reaction products were identified by a comparison of their properties with those of independently prepared samples.

The azoxy compounds, except **3**, were treated with sulfuric acid according to a procedure similar to those reported previously.[2] **1a**, mp 246—247 °C (from $CHCl_3$). Found: C, 49.85; H, 2.62; N, 19.29%. Calcd for $C_{12}H_8N_4O_5$: C, 50.00; H, 2.80; N, 19.44%. **2a**, mp 206—207 °C (from hexane–benzene). Found: C, 67.85; H, 5.08; N, 9.79%. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.08; H, 5.00; N, 9.92%.

*Reaction of **3** with Sulfuric Acid.* A solution of **3** (0.5 g) in concentrated sulfuric acid (50 ml) heated at 100 °C for 20 min. The solution was poured into a large amount of cold water. The precipitates were filtered and then extracted with acetone. The extract gave **3b** (0.18 g); mp 270 °C (decomp). The acetone-insoluble material was added to a solution of H_2SO_4 (1 ml) in MeOH (30 ml). The suspension was refluxed for 24 h with stirring and then poured into cold water. The methyl ester was collected by filtration and then treated further with acetic anhydride and pyridine, as usual, to afford the acetate. The resulting esters were chromatographed on silica gel (benzene). The first fraction gave methyl 4-(*p*-methoxyphenylazo)benzoate (0.035 g); mp 170—171 °C (from MeOH). Found: C, 66.83; H, 5.31; N, 10.48%. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.23; N, 10.37%. The second fraction gave dimethyl azobenzene-4,4′-dicarboxylate (0.05 g); mp 242—243 °C. The third fraction gave dimethyl 2-acetoxyazobenzene-4,4′-dicarboxylate (0.18 g); mp 151—153 °C (from MeOH). Found: C, 60.77; H, 4.25; N, 8.08%. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.66; H, 4.50; N, 7.87%.

*Reaction of **4** with TsOH and Ac_2O.* A solution of **4** (0.5 g) and $TsOH\cdot H_2O$ (5.0 g) (dehydrated by heating under reduced pressure) in Ac_2O (12.5 ml) was heated at 100 °C for 1 h. The reaction mixture was poured into a cold $NaHCO_3$ solution and then extracted with benzene. The extract was chromatographed on a silica-gel column (benzene). The first fraction gave **4c** (0.15 g); mp 168—169 °C. The second fraction gave 4,4′-dimethoxy-2-tosyloxyazobenzene (0.029 g); mp 100—101 °C. Found: C, 61.09; H, 4.87; N, 7.01%. Calcd for $C_{21}H_{20}N_2O_5S$: C, 61.15; H, 4.89; N, 6.79%. The tosylate was heated with a 30% NaOH solution at 100 °C for 3 h to give 4,4′-dimethoxy-2-hydroxyazobenzene (**4a**) (0.014 g); mp 137—138 °C. The third fraction was recrystallized from hexane–benzene to give 3-acetoxy-4,4′-dimethoxyazobenzene (0.20 g); mp 188—189 °C. The mother liquor was treated with 3% NaOH to give **4a** (0.008 g) and 3-hydroxy-4,4′-dimethoxyazobenzene; mp 177—178 °C (0.038 g). This azophenol was refluxed with dimethyl sulfate in acetone in the presence of K_2CO_3 for 6 h to yield 3,4,4′-trimethoxyazobenzene; mp 128—130 °C. Found: C, 66.36; H, 5.97; N, 10.29%. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.28%.

Reaction of 4-Methoxyazoxybenzene with TsOH and Ac_2O. This reaction was carried out according to a procedure similar to those described above. Products: 4-methoxy-4′-tosyloxyazobenzene; mp 131.5—133 °C (from MeOH), 3-acetoxy-4-methoxyazobenzene; mp 112—113 °C (from hexane), 3-hydroxy-4-methoxyazobenzene; mp 95—97 °C (from hexane).

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