on a 100 × 2.2 cm Florisil column slurry packed in 1:9 ether–hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane; 0.5 l. of 1:99 ether–hexane; 0.5 l. of 1:49 ether–hexane; 1.0 l. of 1:24 ether–hexane; 0.5 l. of 1:12 ether–hexane; and 0.5 l. of 1:6 ether–hexane.

Fractions 82–119 yielded 117 mg of benzalazine as yellow crystals, mp 91–94°. Fractions 121–131 gave 13.8 mg of a clear oil identified as benzaldehyde by comparison of ir and uv spectra with those of a known sample. Fractions 134–168 afforded 39.4 mg of a clear liquid identified as benzonitrile also by comparison of the ir and uv spectra of the photoproduct with those of a known sample of benzonitrile.

Registry No.—Benzophenone, 119-61-9; benzalazine, 588-68-1.

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Deoxygenation and Chlorination of Azoxybenzene by Acidic Halides[1]

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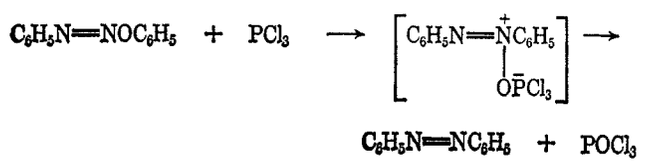
Recent investigations[2-4] of the mechanism of the Wallach rearrangement[5] of azoxybenzene to *p*-hydroxyazobenzene induced by chlorosulfonic acid led to the identification of small amounts of azobenzene and *p*-chloroazobenzene as additional products of this reaction.[6] This suggested the possibility of the initial formation of an intermediate product through chlorosulfonation of the oxygen of azoxybenzene followed either by rearrangement and decomposition to *p*-chloroazobenzene or by direct decomposition to azobenzene. This also indicated the possibility of a much simpler general method for preparing halogenated azo compounds than those that are now available.

Deoxygenation of Azoxybenzene.—Azoxybenzene is deoxygenated to azobenzene by certain acidic halides which can undergo oxidation. Scheme I, which suggests a possible way in which this transformation may occur in the deep red reaction mixture, shows phosphorus trichloride being oxidized to phosphorus oxychloride as azoxybenzene is reduced to azobenzene practically quantitatively. Other observations which appear in the Experimental Section show similar results that were obtained with several other inorganic acidic halides. Acetyl bromide and acetyl iodide also yield azobenzene in this reaction below 20°. At higher temperatures, these halides lead to the formation of some aniline and benzidine in addition to azobenzene.

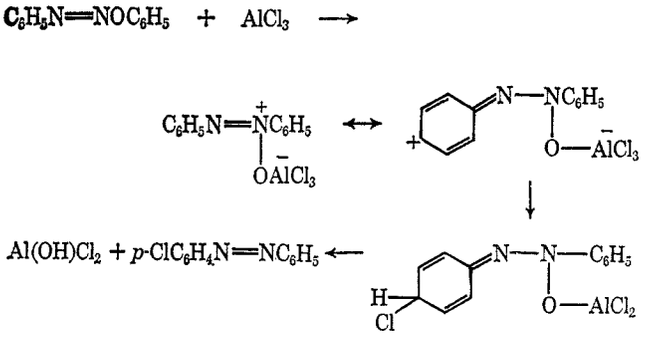
SCHEME I



Deoxygenation of Azoxybenzene with Chlorination.—The unusual deoxygenation and chlorination of azoxybenzene by aluminum chloride was observed under various conditions. A solid mixture of aluminum chloride and azoxybenzene reacts spontaneously and highly exothermically after a brief induction period. This reaction is violent at 40° in molten azoxybenzene. However, in refluxing carbon disulfide the red reaction mixture yields *p*-chloroazobenzene in 83% yield *via* a smooth reaction. Similar results are obtained in a refluxing acetyl chloride solution of molar equivalent amounts of azoxybenzene and aluminum chloride. Both of these procedures are recommended for the preparation of *p*-chloroazobenzene over the Curtin and Ursprung[7] method because of their simplicity and high yield of product.

Ferric chloride may replace aluminum chloride in this reaction, but the yield of *p*-chloroazobenzene is usually smaller. However, aluminum bromide and aluminum iodide reduce azoxybenzene to azobenzene even under mild conditions (0°). It was also noted that aluminum chloride fails to convert azoxybenzene to *p*-chloroazobenzene if any halide that deoxygenates azoxybenzene is present in the reaction mixture. This suggests that preferential deoxygenation of azoxybenzene by reducing halides prevents the aluminum chloride from reacting as proposed in Scheme II, which attempts to present a possible rationalization of the manner in which this reaction occurs under mild conditions.

SCHEME II



The reaction of azoxybenzene in benzenesulfonyl chloride in the presence of ferric chloride is more complex. A small amount of *p*-chloroazobenzene and a product which was characterized as a sulfone are formed in this reaction. As ferric chloride appears to function as a Friedel–Crafts catalyst in this reaction as well as the chlorinating agent, the yield of *p*-chloroazobenzene is improved by increasing the concentration of ferric chloride in the reaction mixture. Aluminum chloride is much less effective than ferric chloride in this reaction.

Azoxybenzene, aluminum chloride, and sulfuryl chloride react to form *p*-chloroazobenzene and *p,p'*-dichloroazobenzene. An increase in the molar ratio of alu-

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minum chloride to azoxybenzene favors the formation of the dichloro compound. This simple preparative procedure, coupled with the ease of separating the monochloro compound from the dichloro compound with 95% ethanol in which the latter is much less soluble, makes *p,p'*-dichloroazobenzene much more easily available than by methods recorded in the literature.[8,9]

Azoxybenzene and aluminum chloride react in benzene to form *p*-phenylazobenzene in 84% yield. Apparently, in this reaction the electron-rich benzene ring replaces the chloride ion as the nucleophile, if the reaction proceeds in the manner suggested in Scheme II. The appearance of a deep red color in this reaction mixture was once suggested as a qualitative test for aromatic hydrocarbons.[10] Attempts to extend this reaction to biphenyl and fused aromatic ring systems failed to produce the expected azo compounds. Rather, certain amines were formed which were similar to those identified in reaction mixtures consisting of these hydrocarbons, aluminum chloride, and azobenzene.[11,12]

Fluoroazo compounds cannot be prepared by reactions of the type that have been described. Most inorganic fluorides, including aluminum fluoride and boron trifluoride, as well as organic fluorides do not react with azoxybenzene. Only those fluorides, such as antimony trifluoride, which can deoxygenate azoxybenzene, react to form azobenzene.

Experimental Section

The identity of every compound that was isolated in the following experiments was established by means of elemental analysis and by comparison of its ir spectrum and melting point with those of an authentic sample.

Deoxygenation and Chlorination of Azoxybenzene by Aluminum Chloride. A. *p*-Chloroazobenzene.—To a mixture of 4.0 g (0.03 mol) of $AlCl_3$ or 4.9 g (0.03 mol) of $FeCl_3$ in 50 ml of CS_2 or 30 ml of CH_3COCl in a three-neck flask equipped with a dropping funnel, mechanical stirrer, and a condenser protected by a $CaCl_2$ tube, a solution of 6.0 g (0.03 mol) of azoxybenzene in 50 ml of CS_2 or 20 ml of CH_3COCl was added slowly. The dark red mixture was stirred for 5 hr at reflux temperature and then distilled to dryness at reduced pressure. The dark residue was treated with 40 ml of 0.1 *N* HCl solution and then extracted with three 35-ml portions of ether. The ether solution was washed twice with water, 5.0% $NaHCO_3$ solution, and water and then dried over anhydrous $CaCl_2$. The crude product which was recovered from the ether solution was recrystallized from petroleum ether (bp 30–75°), yielding 5.4 g (83% with $AlCl_3$) or 4.1 g (63% with $FeCl_3$) of *p*-chloroazobenzene, mp 87–88° (lit.[13] 87–88°).

B. *p,p'*-Dichloroazobenzene.—To a mixture of 16.0 g (0.12 mol) of $AlCl_3$ in 35 ml of SO_2Cl_2, a solution of 6.0 g (0.03 mol) of azoxybenzene in 20 ml of SO_2Cl_2 was added. The mixture was refluxed for 5 hr and then worked up according to the procedure described in part A. The product obtained from the ether solution was treated with 25 ml of hot 95% ethanol. The undissolved material was filtered and dissolved in a hot mixture of 15 ml of acetone and 15 ml of 95% ethanol. From the concentrated, cold ethanol–acetone solution, 5.3 g (70%) *p,p'*-dichloroazobenzene, mp 186° (lit.[14] 187°), was obtained. From the concentrated, cold ethanol solution, 0.9 g (13%) *p*-chloroazobenzene was recovered.

C. Reaction in Benzenesulfonyl Chloride.—To a mixture of 4.9 g (0.03 mol) of $FeCl_3$ in 30 ml of benzenesulfonyl chloride, a solution of 6.0 g (0.03 mol) of azoxybenzene in 20 ml of benzenesulfonyl chloride was added and the mixture was stirred at 100° for 5 hr and then worked up according to the procedure described in part A. The product obtained from the ether solution was treated with 30 ml of petroleum ether and the residue was dissolved in 25 ml of 95% ethanol. From the concentrated, cold petroleum ether solution 0.7 g (10.7%) of *p*-chloroazobenzene was obtained. The cold, concentrated 95% ethanol solution yielded 1.1 g (10.0%) of a sulfone, mp 106°, ir ($CHCl_3$) 1160 cm^{-1} (O=S=O).

Anal. Calcd for $C_{18}H_{14}N_2O_3S$: C, 63.91; H, 4.14; S, 9.46. Found: C, 63.86; H, 4.05; S, 9.39.

With 9.8 g (0.06 mol) of $FeCl_3$ in the reaction mixture, 2.0 g (30.7%) of *p*-chloroazobenzene and 0.55 g (5.0%) of sulfone were obtained.

***p*-Phenylazobenzene.**—To a mixture of 4.0 g (0.03 mol) of $AlCl_3$ in 40 ml of dry benzene, 6.0 g (0.03 mol) of azoxybenzene in 25 ml of benzene was added and the mixture was refluxed for 5 hr and then worked up according to the procedure described in part A. The ether solution yielded 6.1 g (84%) of *p*-phenylazobenzene (from ethanol), mp 150–151° (lit.[15] 150°).

Note: Addition of 0.03 mol of any of the halides listed below in the procedure entitled Deoxygenation of Azoxybenzene to any of the reaction mixtures described in the above procedures prevents the formation of the two chloroazo compounds or the *p*-phenylazobenzene. Instead, the reduction products described below (azobenzene, aniline, and benzidine) are formed.

Deoxygenation of Azoxybenzene. A. By Liquid Acidic Halides (PCl_3, $POCl_3$, $SOCl_2$, S_2Cl_2, CH_3COBr, and CH_3COI).—A solution of 6.0 g (0.03 mol) of azoxybenzene in 30 ml of each halide was refluxed for 3 hr except for the mixtures containing CH_3COBr and CH_3COI which were stirred at 20°. All mixtures were then worked up according to the procedure described earlier. The products obtained from the ether solutions in each case yielded azobenzene, mp 67–68° (lit.[16] 68°, *trans*), from petroleum ether in amounts ranging from 72% with S_2Cl_2 to 95% of the theoretical with PCl_3. From the $SOCl_2$ reaction product, *p*-chloroazobenzene (3.1%) and *p,p'*-dichloroazobenzene (5.2%) were obtained in addition to 75.3% azobenzene (see reaction with SO_2Cl_2 described earlier).

With CH_3COBr and CH_3COI azobenzene was obtained from the reaction mixtures which were stirred at 20° for 5 hr. At reflux temperatures these mixtures yielded aniline and benzidine.

B. By Solid Acidic Halides (AlI_3, $AlBr_3$, $ZnBr_2$, ZnI_2, and SbF_3) in CH_3COCl Solutions.—Following the procedure outlined in part A, a solution of 0.03 mol of azoxybenzene in 20 ml of CH_3COCl was added to a mixture of 0.03 mol of each halide in 30 ml of CH_3COCl and refluxed for 3 hr except for the mixtures containing AlI_3 and $AlBr_3$ which were stirred at 20°. The ether solutions obtained after working up the reaction mixtures according to the procedure described earlier yielded azobenzene in every case in amounts ranging from 55% with SbF_3 to 92% of the theoretical with ZnI_2.

In the aqueous acid solutions obtained from the hydrolysis of the reaction products in each experiment in part A the expected oxidation product of each halide was identified by the usual qualitative tests. PCl_3 and $POCl_3$ yielded phosphate ion; $SOCl_2$ yielded sulfate ion; S_2Cl_2 yielded S, SO_2, and some sulfate ion; CH_3COBr and CH_3COI yielded the free halogens. The solid iodides and bromides in part B yielded the free halogens, and SbF_3 yielded antimonate ion.

Registry No.—Azoxybenzene, 495-48-7.

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