[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

THE REACTION PRODUCT OF AZOXYBENZENE AND CHLOROSULFONIC ACID[1]

IRWIN A. PEARL AND ANTHONY R. RONZIO[2]

Received April 17, 1947

The preparation of azobenzene, azoxybenzene, and sodium *p*-azobenzenesulfonate by the reduction of nitrobenzene with sulfite waste liquor was described in recent papers (1, 2). Both azobenzene and sodium *p*-azobenzenesulfonate, upon treatment with chlorosulfonic acid, yielded *p*-azobenzenesulfonyl chloride which in turn was successfully used for the preparation of sulfanilamide derivatives (3). This latter study prompted the investigation of the chlorosulfonation of azoxybenzene (the chief product of the reduction of nitrobenzene by sulfite waste liquor at atmospheric pressure) and the possible use of azoxybenzenesulfonyl chloride for the preparation of sulfanilamide derivatives.

Azoxybenzene (I) reacted smoothly with chlorosulfonic acid at room temperature, at 100°, or in a solvent to yield a compound (II) as translucent orange platelets, insoluble in cold sodium hydroxide, melting sharply at 117–118° and corresponding to the empirical formula for azoxybenzenesulfonyl chloride (III), $C_{12}H_9ClN_2O_3S$. Reaction of (II) with aqueous ammonia did not give the desired azoxybenzenesulfonamide, but yielded only *p*-hydroxyazobenzene (IV). Further attempts to prepare azoxybenzenesulfonamides were equally fruitless.

The failure of (II) to condense with ammonia or other amines, indicating that (II) might not have the structure (III), prompted a more comprehensive study of the compound in order to account for its anomalous behavior.

The experiments described in this paper have enabled us to assign to compound (II) the structure—*p*-azobenzene chlorosulfonate[3].

A saturated alcoholic solution of (II) gave no precipitate with either alcoholic silver nitrate or alcoholic barium chloride. Refluxing with absolute ethanol in the presence of concentrated sulfuric acid yielded only the original (II). No reaction was obtained by warming with concentrated sulfuric acid at 60°. Boil-

---

[1] This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

Presented before the Division of Organic Chemistry at the 15th Midwest Regional Meeting of the American Chemical Society, Kansas City, Missouri, June 23–25, 1947.

[2] Present address, Colorado State College, Fort Collins, Colorado.

[3] Note added October 17, 1947. While this article was in press, *Chemical Abstracts* **41**, 5472 (Sept. 10, 1947) was received; this contains an abstract of an article by Lukashevich and Sokolova (*Compt. rend. acad. sci. U.R.S.S.* **54**, 693 (1946)), in which the authors describe *p*-azobenzene chlorosulfonate (which they designate as *p*-hydroxyazobenzene chlorosulfonate). They prepared the compound in 70% yield by treating azoxybenzene in a little carbon tetrachloride with a ten-fold excess of chlorosulfonic acid at a temperature below −8°. The melting point of their compound is identical with that of the compound described in this paper.

ing of (II) with sodium hydroxide solution gave (IV), sodium sulfate, and sodium chloride as the chief reaction products, together with small amounts of azobenzene and *p*-chloroazobenzene. Boiling (II) with concentrated ammonium hydroxide yielded the theoretical amount of (IV) but no azobenzene or *p*-chloroazobenzene.

Reduction of (II) with stannous chloride in alcoholic hydrochloric acid solution or with zinc in aqueous hydrochloric acid solution yielded hydrogen sulfide, *p*-aminophenol, and aniline. Reduction with zinc in sulfuric acid solution yielded chloride ions. Hydrogenation of (II) over Raney nickel in benzene at 50 lbs. yielded aniline, *p*-aminophenol, hydrogen sulfide, and hydrogen chloride.

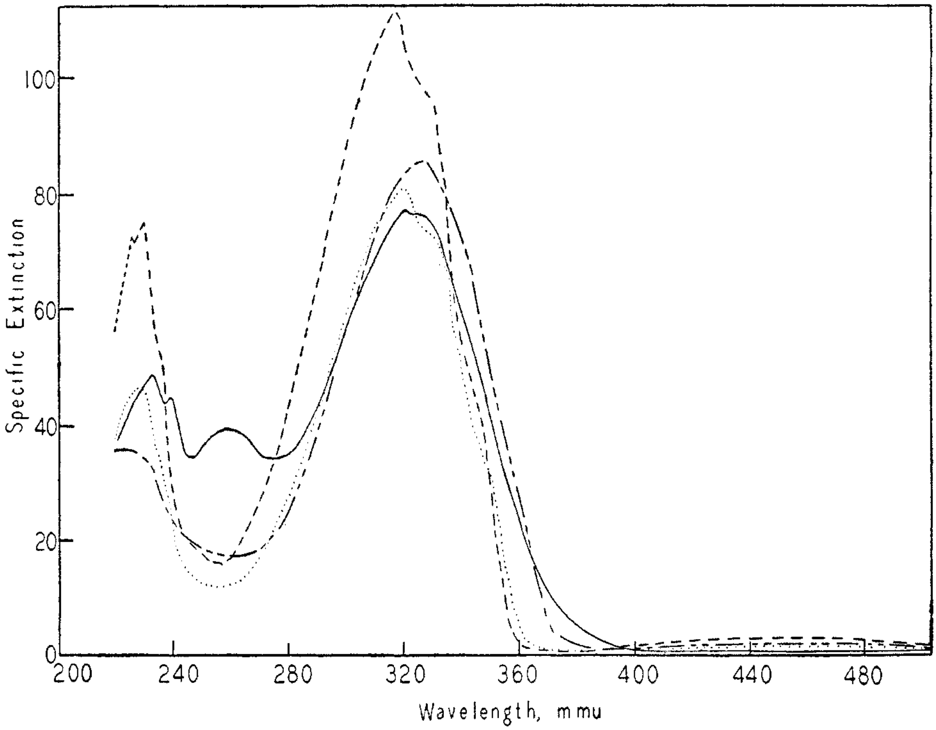


FIGURE 1. ULTRAVIOLET ABSORPTION SPECTRA FOR COMPOUNDS IN *n*-HEPTANE

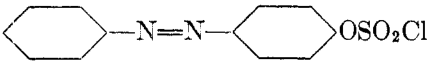
---------------- Azobenzene
———————— Azoxybenzene
—--—--—-- *p*-Azobenzenesulfonyl chloride
.... *p*-Azobenzene chlorosulfonate (Compound II)

The molecular weight of (II) was determined by the freezing point method in three different solvents. In benzene the molecular weight was found to be 295. However, in camphor and dioxane values of 149 and 557 were obtained, indicating dissociation and association, respectively, in these two solvents.

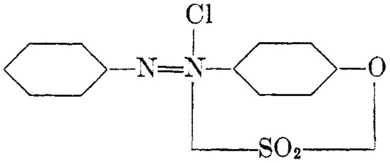
Ultraviolet absorption spectra were obtained and compared with those of azobenzene, azoxybenzene, and *p*-azobenzenesulfonyl chloride. These curves are shown in Figure 1.

DISCUSSION

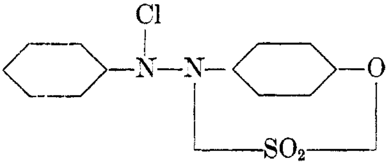
Of the many possible structures for compound (II) those possessing a sulfur atom para to the two nitrogen atoms are precluded by the hydrogenation and reduction experiments in which *p*-aminophenol is obtained as one of the reduction products. The many experiments in which (IV) is formed as a result of the alkaline treatment of (II) further support this conclusion. Thus, the following formulas remain as possibilities:



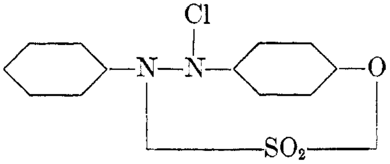
(IIa)



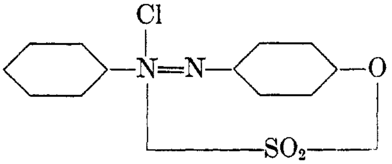
(IIb)



(IIc)



(IId)



(IIe)

Although the chemical data do not provide us with the required evidence to eliminate any of these structures, the ultraviolet absorption data and color of the compound enable us to choose (IIa) on the basis of the similarity of the spectra of compound (II), azobenzene, and *p*-azobenzenesulfonyl chloride. Only this structure possesses the unsubstituted chromophoric azo group.

The ultraviolet absorption spectrum of azobenzene in *n*-heptane determined with a Beckman spectrophotometer at minimum slit width is shown in Figure 1. The curve thus obtained indicates more detail than curves reported in the literature. The ultraviolet absorption of azobenzene has been studied by many investigators. On the basis of all work prior to 1929, Henri (4) has reported maxima at 230 mmu, 310 mmu, and 435 mmu, and minima at 210 mmu, 255 mmu, and 380 mmu for the absorption spectrum of azobenzene in hexane. Brode (5), working with an alcoholic solution, noted a break at 345 mmu. In addition we have found a maximum at 225 mmu, a minimum at 227 mmu, and breaks in the curve at about 237 mmu and about 325 mmu.

Similarly, the curve obtained for azoxybenzene under the same conditions contains more detail than those in the literature. Ramart-Lucas and Biquard (6) reported maxima at 260 mmu and 320 mmu and minima at 245 mmu and

275 mmu for azoxybenzene in hexane. Szegö (7) noted another maximum at 230 mmu and breaks in the curve at 300 mmu and 375 mmu. Our curve shows an additional maximum at 239 mmu, a minimum at 237 mmu, breaks in the curve at 228 mmu and 322 mmu, and a very weak and diffuse fundamental band at 430 mmu.

The curve for compound (II) contains all the essential characteristics of the azobenzene curve, in fact much more so than that of *p*-azobenzenesulfonyl chloride prepared from azobenzene and chlorosulfonic acid. The maxima at 230 mmu, 320 mmu, and 440 mmu and minima at 255 mmu and 380 mmu, and even the breaks in the curve at 325 and 345 mmu are retained. On the basis of this similarity with the azobenzene curve and the dissimilarity with the azoxybenzene curve, it appears that compound (II) contains the azobenzene nucleus.

In order to determine whether this anomalous reaction took place by way of the Wallach rearrangement of azoxybenzene to *p*-hydroxyazobenzene, the latter compound was treated with chlorosulfonic acid under a variety of conditions, but no *p*-azobenzene chlorosulfonate could be isolated. Attempts to prepare *p*-azobenzene chlorosulfonate by the reaction of sulfuryl chloride and *p*-hydroxyazobenzene were equally unsuccessful. Therefore, it appears that rearrangement and chlorosulfonation take place simultaneously or chlorosulfonation must take place on the oxygen of the azoxy group before rearrangement occurs.

Acknowledgment. The authors are indebted to the Analytical Department of The Institute of Paper Chemistry under the direction of Dr. B. L. Browning for the microanalyses and ultraviolet spectral data reported in this paper.

EXPERIMENTAL

All melting points given are uncorrected.

The preparation of compound (II) (p-azobenzene chlorosulfonate). A. Room temperature. In a 2-liter flask surrounded by a cooling bath was placed 580 g. of chlorosulfonic acid. With vigorous stirring 198 g. of azoxybenzene was gradually added over a period of 30 minutes, with the temperature maintained at 30°. After all the azoxybenzene had been added, the black mixture was stirred for 2 hours at room temperature, and then poured with stirring into 3 liters of crushed ice and water. The mixture was allowed to stand overnight. The light brown, powdery precipitate was filtered, washed with water, and dried as thoroughly as possible by suction. The semidry precipitate was then vigorously agitated with an ice-cold dilute sodium hydroxide solution to remove any *p*-hydroxyazo material. Very little dissolved. After 2 hours, the precipitate was filtered, washed with water, and then dried in a vacuum desiccator. The yield was 275 g. The crude product was dissolved in boiling ether, filtered, concentrated to incipient crystallization, and cooled. The orange crystals which separated were filtered and recrystallized from petroleum ether (65–110°) to give translucent orange platelets melting at 117–118°.

Anal. Calc'd for $C_{12}H_9ClN_2O_3S$: C, 48.69; H, 3.03; Cl, 11.96; N, 9.45; S, 10.81.
Found: C, 48.82; H, 3.19; Cl, 11.91; N, 9.88; S, 10.74.

B. High temperature. Into a 1-liter 3-neck flask, equipped with a mechanical stirrer and a thermometer reaching below the level of the reaction mixture, was placed 290 g. of chlorosulfonic acid. With vigorous stirring 100 g. of azoxybenzene was added gradually over a period of 30 minutes. A violent reaction, with the evolution of yellow fumes, took place. No external cooling was applied and the temperature rose to 110°. Stirring was continued for one hour and then the mixture was heated on the steam-bath with stirring for an additional hour to complete the reaction. After cooling, the mixture was slowly poured into 2 liters of crushed ice and water with vigorous stirring. The granular golden precipitate which separated was purified as above to yield orange platelets melting at 117–118° and not depressing the melting point in mixture with the compound prepared at room temperature.

C. In a solvent. To a solution of 18.8 g. of azoxybenzene in 250 ml. of carbon tetrachloride was added dropwise with vigorous stirring, 11.6 g. of chlorosulfonic acid. After approximately one-half of the acid was added, reaction set in and an oily precipitate separated. After all the acid was added, stirring was continued for a short while and the solvent was then decanted from the precipitate. The solvent layer was washed with water, dried with anhydrous sodium sulfate, and evaporated to give 8.9 g. of azoxybenzene. The oily precipitate was treated with water which caused it to solidify. After filtering, washing with water, and drying in a vacuum desiccator, it was recrystallized from methanol and petroleum ether to give 14.6 g. of orange platelets melting at 117–118° and not depressing the melting point in mixture with the compound prepared at room temperature.

Reaction of compound (II) with ammonia. A. A mixture of 5 g. of compound (II) and 50 cc. of concentrated ammonium hydroxide was allowed to stand for 24 hours at room temperature. The clear solution which resulted was acidified with dilute hydrochloric acid, giving an orange precipitate. This was filtered, washed, air dried, and recrystallized from benzene to give 3 g. of *p*-hydroxyazobenzene melting at 150–151°. A mixed melting point with authentic *p*-hydroxyazobenzene prepared from azoxybenzene and sulfuric acid (8) was not depressed.

Anal. Calc'd for $C_{12}H_{10}N_2O$: C, 72.8; H, 5.05; N, 14.14.
Found: C, 73.0; H, 5.13; N, 14.31.

B. A solution of 5 g. of compound (II) in 250 cc. of ordinary U.S.P. ether was saturated with gaseous ammonia below 20°. The precipitate which formed was filtered and recrystallized from ethanol and decolorizing carbon. Colorless platelets of ammonium sulfamate melting at 130–131° were obtained. A mixed melting point with authentic ammonium sulfamate was not depressed.

Anal. Calc'd for $H_6N_2O_3S$: N, 24.56; S, 28.07.
Found: N, 24.59; S, 28.81.

The ether was evaporated and the residue was taken up in water and acidified with dilute hydrochloric acid. Recrystallization of the precipitate from benzene yielded *p*-hydroxyazobenzene.

Similar experiments in both warm and cool anhydrous ether yielded only the original compound (II).

C. A solution of 5 g. of (II) in 100 ml. of pyridine was saturated with gaseous ammonia below 25° and stirred into a mixture of 150 ml. of concentrated hydrochloric acid, 500 ml. of water, and 500 g. of cracked ice. The dark precipitate which separated was filtered and recrystallized from dilute methanol to yield 3.3 g. of *p*-hydroxyazobenzene as orange-red crystals.

Reaction of compound (II) with 2-aminopyridine. A. In pyridine. To a solution of 22.6 g. of 2-aminopyridine dissolved in 125 ml. of pyridine maintained below 30° was added 68.5 g. of (II) over a period of 10 minutes. A portion of (II) did not dissolve. The mixture was warmed in a water-bath and at approximately 40° all (II) went into solution. The mixture was heated under reflux for 2 hours and allowed to cool. Approximately one-half of the pyridine was distilled under reduced pressure and the residue was triturated with 450 ml. of 1:2 hydrochloric acid and stirred into 1200 ml. of cracked ice and water. The semisolid which separated was allowed to settle overnight, filtered, dissolved in dilute sodium hydroxide, and reprecipitated with carbon dioxide. Recrystallization from dilute methanol gave pure *p*-hydroxyazobenzene.

B. In acetone-pyridine. A solution of 14.8 g. of (II) in 200 ml. of dry acetone was treated successively with 15 ml. of pyridine, 4.7 g. of 2-aminopyridine, and 50 ml. of dry acetone. The mixture was shaken and allowed to stand at room temperature. An immediate precipitation of a yellow crystalline solid took place. After standing overnight the precipitate was filtered and washed with dry acetone. The yield was 8.1 g. The product was repeatedly recrystallized from ethanol to give colorless crystals of 2-aminopyridine sulfate melting at 208–210° and not depressing the melting point in mixture with authentic 2-aminopyridine sulfate prepared from 2-aminopyridine and sulfuric acid. The picrate melted at 216–217° and a mixed melting point with the known picrate was not depressed.

The filtrate and washings were distilled under diminished pressure to a small volume and diluted with an excess of water. The dark oil which separated solidified under vigorous agitation. The solid was filtered, washed with water, dissolved in dilute sodium hydroxide, precipitated with hydrochloric acid, and recrystallized from methanol, giving 9.8 g. of *p*-hydroxyazobenzene melting at 150–151°.

Reaction of compound (II) with alkali. A. Ten grams of (II) was placed in a 500-ml 2-neck flask set up for distillation. A solution of 20 g. of sodium hydroxide in 250 ml. of water was added and the mixture was boiled. Water was gradually added from a dropping-funnel to keep the volume constant. The reaction mixture became clear and orange-red in color. A bright orange oil which solidified on cooling distilled with the steam. A yield of 0.8 g. of orange crystals melting at 50–52° was obtained. The clear alkaline solution in the distilling flask was acidified with hydrochloric acid and filtered. The precipitate was recrystallized from methanol to yield 6.0 g. of *p*-hydroxyazobenzene. Treatment of the aqueous filtrate gave a heavy precipitate of barium sulfate, indicating the presence of sodium sulfate in the original alkaline solution. The presence of sodium chloride in the alkaline solution was proved by another identical experiment in which some of the alkaline solution was acidified with nitric acid and treated with silver nitrate. A heavy precipitate of silver chloride formed.

The steam-distillable orange crystals melting at 50–52° were recrystallized repeatedly from 90% ethanol to yield orange chlorine-containing crystals melting at 86–87°. Bamberger (9) reports the melting point 87° for *p*-chloroazobenzene. A sample was dissolved in concentrated sulfuric acid, allowed to stand overnight, and diluted with water. The yellow precipitate which separated was recrystallized from ethanol to give crystals melting at 146–147°, which is the melting point of *p*-chloroazobenzenesulfonic acid prepared by Mentha and Heumann (10).

The mother liquors from the above recrystallization were evaporated to dryness and the residue was recrystallized from petroleum ether to give orange plates of azobenzene melting at 65–66° and not depressing a mixed melting point with authentic azobenzene. Reduction with stannous chloride in acid solution or with zinc in alkaline solution and subsequent acid treatment yielded benzidine melting at 124–125°.

B. The above experiment was repeated with concentrated ammonium hydroxide in place of the sodium hydroxide solution. No red oil distilled with the steam. The aqueous solution yielded 6.6 grams of *p*-hydroxyazobenzene. Both chloride ions and sulfate ions were identified in the solution.

Reduction of compound (II). A solution of 6.5 g. of compound (II) in 150 ml. of purified benzene was treated with 20 g. of alcohol-washed Raney nickel catalyst and shaken with hydrogen at 50 lbs./sq. in. at room temperature. The solution became colorless and hydrogen absorption was complete in 2 hours. The catalyst was removed, and the clear solution was concentrated to a small volume. The residual solution gradually deposited colorless crystals. These were filtered and dried to give *p*-aminophenol melting at 184–185°, no depression in mixture with authentic *p*-aminophenol. Acetylation of the crystals with acetic anhydride gave *p*-aminophenol diacetate melting at 151–152°.

The benzene filtrate from the *p*-aminophenol crystals was refluxed a short time with acetic anhydride in anhydrous pyridine and then concentrated to dryness under reduced pressure on the steam-bath. The product was recrystallized from water to give acetanilide melting at 113–114° and not depressing the melting point of a mixture with authentic acetanilide. This proves that aniline was present in the original hydrogenation solution. The amounts of aniline and *p*-aminophenol were approximately equal.

One-half of the catalyst was washed well with alcohol, to remove any benzene, and the resulting black powder was suspended in water and acidified with dilute hydrochloric acid.

Hydrogen sulfide was liberated in considerable quantity. This indicated that the sulfur in compound (II) was reduced to hydrogen sulfide.

The other half of the catalyst was boiled with benzene and filtered hot. The cooled benzene was shaken with dilute, acidified silver nitrate solution. A precipitate of silver chloride separated, indicating that the chlorine present in the original (II) was reduced to hydrogen chloride.

Ultraviolet absorption. The ultraviolet absorption spectra were measured with a Beckman model DU quartz spectrophotometer employing 1.0-cm. quartz cells and minimum slit widths. Measurements were made on freshly and accurately prepared solutions containing 0.01 g. of compound per liter in purified *n*-heptane. Azobenzene and azoxybenzene were prepared by the reduction of nitrobenzene with sulfite waste liquor and alkali at superatmospheric and atmospheric pressure, respectively (1). Azobenzenesulfonyl chloride was prepared from azobenzene and chlorosulfonic acid (3). All products were repeatedly recrystallized from reagent grade petroleum ether.

SUMMARY

Reaction of azoxybenzene with chlorosulfonic acid yields an anomalous reaction product. On the basis of chemical reactions and ultraviolet absorption spectra, the structure *p*-azobenzene chlorosulfonate has been proposed.

APPLETON, WISCONSIN

REFERENCES

(1) PEARL AND LEWIS, *Ind. Eng. Chem.*, **36**, 664 (1944).
(2) PEARL, *J. Org. Chem.*, **9**, 424 (1944).
(3) PEARL, *J. Org. Chem.*, **10**, 205 (1945).
(4) HENRI, "International Critical Tables," McGraw-Hill, New York, N. Y., 1929, Vol. V, page 375.
(5) BRODE, *J. Am. Chem. Soc.*, **48**, 1984 (1926).
(6) RAMART-LUCAS AND BIQUARD, *Bull. soc. chim.*, (5) **3**, 430 (1936).
(7) SZEGÖ, *Ber.*, **62**, 736 (1929).
(8) WALLACH AND BELLI, *Ber.*, **13**, 525 (1880).
(9) BAMBERGER, *Ber.*, **29**, 2972 (1896).
(10) MENTHA AND HEUMANN, *Ber.*, **19**, 2972 (1886).