Summary

1. The preparation of diphenyl, di-*p*-tolyl, di-*p*-anisyl and di-α-naphthyl mercury from the interaction of an arylmagnesium halide and mercuric chloride has been described.

2. Phenyl-, *p*-tolyl-, *p*-anisyl- and α-naphthylarsine oxide have been prepared. Two methods of preparation were used: (a) the diaryl mercury compound was heated with arsenic trichloride and the aryldichloroarsine formed was hydrolyzed; (b) the arylarsonic acid was reduced with sulfur dioxide in the presence of hydrochloric acid and the aryldichloroarsine was hydrolyzed.

3. A number of tetra-arylarsyl oxides of the type RR'As—O—AsR'R were prepared from the interaction of an arylarsine oxide and an arylmagnesium halide. In addition several mixed diarylarsinic acids and mixed diarylarsyl chlorides have been described.

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[Contribution from the Chemical Laboratory, The Pennsylvania State College]

CLEAVAGE OF AZO DYES BY MEANS OF SULFITES. THE CLEAVAGE OF 4-HYDROXY-AZOBENZENE-5-CARBOXYLIC ACID AND OF 3-METHYL-4-HYDROXY-AZOBENZENE-5-CARBOXYLIC ACID

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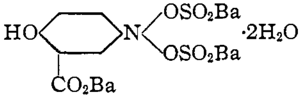
It has been reported in This Journal[1] that azo dyes suffer a distinctive cleavage when heated with aqueous sulfite solutions. In a further study of this reaction, the behavior of the above-mentioned dyes has been investigated. The cleavage of these dyes followed closely the reaction course of 4-hydroxy-azobenzene: the primary dye component yielded aniline and an N-sulfonic acid of aniline, the secondary components N-mono- and N-disulfonic acid derivatives of salicylic and of *o*-cresotinic acids, respectively.

4-Hydroxy-azobenzene-5-carboxylic acid yielded an interesting N-disulfonic acid which could be isolated in pure form, as its tribarium salt, represented, presumably, by the formula



This compound was rather difficultly soluble and perfectly stable in neutral or alkaline solution. It rearranged, in the presence of mineral acids, in a

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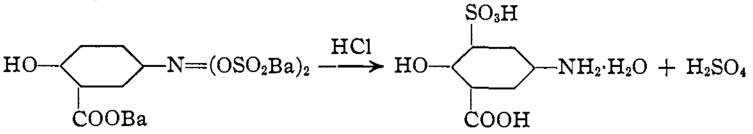
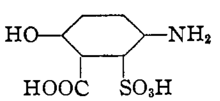
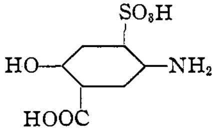
[1] Engel, This Journal, **51**, 2986 (1929).

definite and clear cut way, yielding, quantitatively, the difficultly soluble aminosulfosalicylic acid, which may also be obtained by direct sulfonation of aminosalicylic acid.

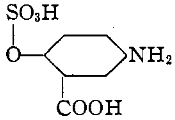


The N-monosulfonic acid, which was obtained in a smaller yield, differed strikingly from the N-disulfonic acid. It was extraordinarily soluble, sensitive to light and to air oxidation. Its free acid rearranged into an extremely soluble sulfonic acid derivative of aminosalicylic acid which could be diazotized and coupled with secondary azo components. It could possess one of the following structures





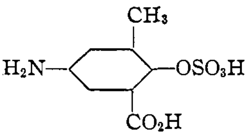
or

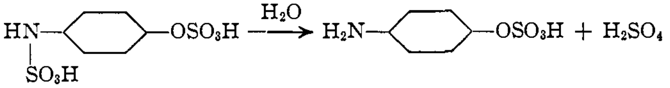


The first two formulas appeared highly improbable (especially the first), in view of the generally observed resistance of *p*-aminophenols to sulfonation in the *m*-position to the hydroxyl group. Since the reduction products of 4-hydroxy-azobenzene yielded the extremely soluble sulfonic ester of 1-amino-4-phenol and no trace of the isomeric 1-amino-4-phenol-6-sulfonic acid, it might be concluded that the dye under investigation yielded a similar product, represented by the third formula.

The decided difference between the N-sulfonic acids, their strikingly reversed solubility relations, may be cited in support of a previously developed view that the N-disulfonic acids encountered in cleavage experiments should be looked upon as sulfurous esters of a substituted *o*-nitrous acid, N-monosulfonic acids as derivatives of amines, or true "sulfaminic" acids.

The cleavage of 3-methyl-4-hydroxy-azobenzene-5-carboxylic acid was investigated for a theoretical and a practical end. It was hoped that this dye, like its simpler homolog, would yield an N-disulfonic acid amenable to isolation in the form of its barium or lead salt, a hope which was not fulfilled. It was furthermore reasoned that such a product, of which a fair yield could be expected, might hydrolyze instead of yielding a nuclear sulfonic acid, the usual rearrangement, sulfonation in *o*-position to the hydroxyl group being prevented by the presence of substituents. The expected product, aminocresotinic acid, economically made, would be a useful dye intermediate. These premises proved correct to some extent; 18% of the theoretically possible yield of the desired substance was actually obtained. Unfortunately, for the economic aspects, the larger part of the N-disulfonic acid reacted in a third, and not completely unexpected, way, yielding the stable and extremely soluble sulfonic ester of aminocresotinic acid: a dye intermediate of much smaller value. The N-disulfonic acid derived through cleavage of 4-hydroxy-azobenzene[1] furnished a parallel to this behavior. It yielded 1-amino-4-phenol-5-sulfonic acid and, to a smaller extent, a compound which retained both sulfonic acid groups at a lower temperature, but lost one of these on further heating (or on diazotization in the cold), yielding aminophenol sulfonic ester, the reaction presumably proceeding in the following way





Sulfate Formation During Cleavage.—The cleavage of 3-methyl-4-hydroxy-azobenzene-5-carboxylic acid resulted in the formation of a considerable amount of mineral sulfate, corresponding to 12.1% of the sulfite consumed, as compared with 3.4% in the case of the salicylic acid derivative, and with 1.2% in the cleavage of 4-hydroxy-azobenzene. It was observed, as a general rule, applying to hydroxy as well as to amino azo dyes, that compounds which contained highly reactive secondary components (capable of coupling in the presence of a considerable hydrogen-ion concentration) yielded negligible amounts of sulfate, about 1%. On the other hand, dyes with weak secondary components, which coupled only in alkaline solutions, invariably yielded higher percentages. Reaction temperatures above 100° caused a considerable increase in sulfate formation, particularly in the latter class of dyes.

Increased sulfate formation did not lead to a gain in totally unsulfonated products, but to a decrease of N-disulfonic acids of the secondary components, reflected in a decrease in yield of their typical acid rearrangement products. Since the N-disulfonic acids, once formed, appeared resistant to prolonged heating at the reaction temperatures employed, it could be concluded that sulfate formation was due to hydrolysis of the first-formed sulfonic acid of the hydrazo bodies.

Experimental

Preparation of the Pure Dyes.—The sodium salts of the crude dyes were prepared by the usual coupling reactions, and the free dye acids by addition of acetic acid to solutions of the recrystallized sodium salts. The dried products were insoluble in alcohol, acetone or benzene, but became readily soluble in these solvents after a single recrystallization from 90% acetic acid. They also possessed sharp melting points then, whereas they charred without softening before recrystallization. The dyes were repeatedly recrystallized from ethyl alcohol. 4-Hydroxy-azobenzene-5-carboxylic acid was found to melt at 220.5°, corr.

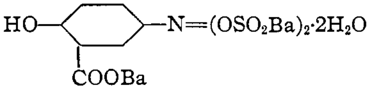
Anal. Calcd. for $C_{13}H_{10}O_3N_2$: N, 11.59. Found: N, 11.50.

3-Methyl-4-hydroxy-azobenzene-5-carboxylic acid melted at 202.0° corr.

Anal. Calcd. for $C_{14}H_{12}O_3N_2$: N, 10.96. Found: N, 10.92.

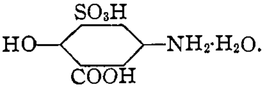
Cleavage of 4-Hydroxy-azobenzene-5-carboxylic Acid.—Twenty-four and twenty hundredths g. of the pure dye (0.1 mole) dissolved in water, the requisite amount of ammonia to form the ammonium salt, and ammonium sulfite equivalent to 420.2 cc. of 1 *N* solution (a total volume of 320 cc.) were heated in a nitrogen-filled pressure bottle at 90 to 93°. Decolorization was complete after six hours. This experiment, for quantitative determinations, was carried out in duplicate; the bottle contents were diluted accurately to 500 cc. Larger quantities of reagents (0.5 mole of the dye) were heated under identical conditions in a closed iron container. A qualitative separation of cleavage products from the resulting solution was attempted.

Isolation of Cleavage Products.—Aniline, which had formed as a result of the cleavage, was removed by benzene extractions. One equivalent of barium hydroxide, in solution, was then added for every sulfite equivalent originally present; precipitated barium sulfate and sulfite were removed by filtration of the hot suspension. The filtrate was evaporated to about 1200 cc. under a current of carbon dioxide, and additional precipitate again removed. On standing the clear filtrate yielded a heavy white precipitate of uniform composition. It was isolated and recrystallized from hot water. It was found to be the tribarium salt of an N-disulfonic acid derived from the secondary dye component, and may be assigned the formula



Anal. Calcd. for $C_7H_4O_9NS_2Ba_3 \cdot 2H_2O$: N, 2.55: S, 11.62; Ba, 37.25. Found: N, 2.43; S, 11.49; Ba, 37.05. Calcd. for $2H_2O$, 6.52; loss on drying, 6.76. (The material was dried under a current of nitrogen at 120°. It regained its original weight when exposed to the atmosphere.)

It tended to form clusters of microscopic crystals, short rods, apparently belonging to the rhombic system. The substance was capable of reducing ammoniacal silver solution but was quite resistant to air oxidation, even in solution. It produced, at great dilutions, a deep violet blue or prune coloration with ferric chloride and acetic acid. Addition of mineral acid caused rearrangement into aminosulfosalicylic acid,



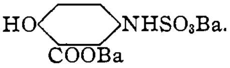
This compound was practically insoluble in cold but readily soluble in hot water. It was identical in composition and crystal habit and in its ferric chloride and diazo reactions, with the product obtained by direct sulfonation of 1-amino-4-hydroxybenzene-5-carboxylic acid.

Anal. Calcd. for $C_7H_7O_6NS \cdot H_2O$: N, 5.58; S, 12.77; H_2O, 7.17. Found: N, 5.53; S, 12.78; loss on drying (over P_2O_5), 7.37.

The yield of this product from 3.000-g. portions of the tribarium salt was quantitative, 1.347 g. (theoretically possible, 1.365 g.).

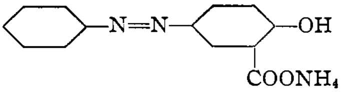
Phenylsulfaminic Acid, Barium Salt.—The mother liquor of the tribarium salt, described above, contained additional amounts of that product, which was precipitated by an equal volume of acetone. The filtered acetone solution was then evaporated to 200 cc.; to the remaining aqueous solution was added 500 cc. of methanol which precipitated the barium salt of phenylsulfaminic acid, $C_6H_5NHSO_3Ba$. This was isolated by filtration, washed with methanol and directly analyzed. It yielded aniline and sulfuric acid in the presence of hydrochloric acid. In solution, it was sensitive to air oxidation.

Anal. Calcd. for $C_6H_6O_3NSBa$: N, 5.83; S, 13.32; Ba, 28.47. Found: N, 5.62; S, 13.04; Ba, 28.61.

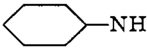
The alcoholic mother liquor, after concentration to a small volume, deposited mixtures of barium salts, which, on addition of acids, yielded both aniline and an extremely soluble salicylic acid derivative. Presumably the mixture contained the barium salt of the N-monosulfonic acid derived from the secondary dye component,  $HOC_6H_3(COOBa)NHSO_3Ba$. It was quite sensitive to air oxidation. Ferric chloride caused a claret-red coloration.

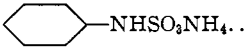
Quantitative examinations of the 500-cc. solutions, containing a tenth mole of dye, were made in the manner described for 4-hydroxy-azo benzene.[1] Aniline, recovered by benzene extractions, required 65.0 and 65.4 cc. of normal nitrite solution, a yield of 65.2% of the theoretical. An excess of 26.6 cc. of 1 *N* sulfite solution was found present after cleavage; 393.6 cc. of a normal, or 196.8 cc. of a molar solution of sulfite was therefore consumed, or 1.968 mole to one mole of dye. Sulfate formed during cleavage corresponded to 1.596 g. of barium sulfate, equivalent to 13.7 cc. of 1 *N* sulfite solution or to 3.4% of the consumed sulfite. No totally unsulfonated derivative of the secondary dye component could be detected.

Upon the preceding determinations the following tabulation of products and yields could be based.

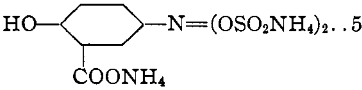
CLEAVAGE OF THE DYE 

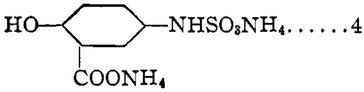
From primary component

Ia  65.2%

Ib  ..34.8%

From secondary component

IIa  ..58.4%

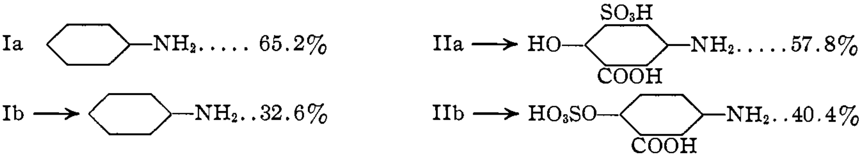
IIb  41.6%

Two hundred and fifty-cc. portions (0.05 mole of dye) were heated to 95° and acidified with 60 cc. of concd. hydrochloric acid, thus causing decomposition of phenylsulfaminic acid (Ib) into aniline and sulfuric acid, rearrangement of the N-disulfonic acid (IIa) into nuclear aminosulfosalicylic acid with incidental hydrolysis of one of its sulfonic acid groups, and rearrangement of the N-monosulfonic acid (IIb) into the extremely soluble sulfonic ester of aminosalicylic acid. The aniline liberated and isolated required 16.3 cc. of 1 *N* nitrite solution; 7.253 g. of aminosulfosalicylic acid ($1H_2O$) was isolated. Diazotization of the remaining soluble aminosalicylic acid derivative consumed 20.2 cc. of 1 *N* nitrite solution. The product itself could not be induced to crystallize from its solution. It was quite resistant toward hydrolytic action of strong acids. Prolonged heating at 100° in the presence of about 5 *M* hydrochloric acid solution caused some decomposition but no appreciable sulfuric acid formation. The diazonium derivative was coupled with 1-naphthylamine in the presence of acetate and acetic acid. The resulting brown dye was insoluble, in the form of its free acid, and permitted quantitative isolation. Nitrogen and sulfur determinations showed the presence of one sulfonic acid group in the dye molecule.

Anal. Calcd. for $C_{17}H_{13}O_6N_3S$: N, 10.87; S, 8.28. Found: N, 10.67; S, 8.03; sulfated ash, none.

Azo dyes differed very little in dyeing shades from corresponding azo derivatives of the nuclear aminosulfosalicylic acid. They did possess greater solubility.

ACTUAL YIELDS OF FINAL USEFUL PRODUCTS FROM REARRANGEMENT OF PRODUCTS TABULATED ABOVE

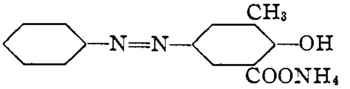


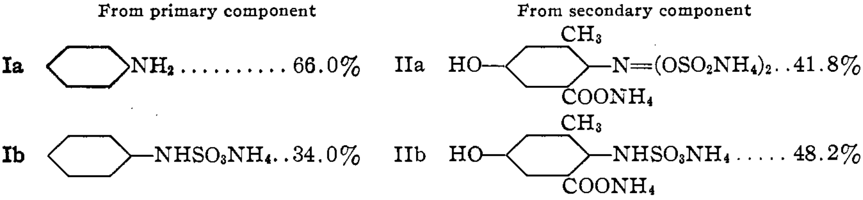
Cleavage of 3-Methyl-4-hydroxy-azobenzene-5-carboxylic Acid.—Portions of one tenth mole of dye, 25.622 g., an equivalent amount of ammonia for its solution and ammonium sulfite corresponding to 419.6 cc. of 1 *N* solution, contained in about 320 cc. of water, were heated in closed nitrogen-filled bottles at 90 to 93°. The dye was reduced with exceptional ease, three hours of heating being sufficient. The solutions were diluted to 500 cc., accurately, and analytical determinations made as described before.

Aniline, extracted with benzene, consumed 66.0 cc. of 1 *N* nitrite solution for diazotization. N-sulfonic acids remaining in solution could not be induced to crystallize from solution either as calcium, barium or lead salts. Their solution was quite sensitive to air oxidation. Dilute ferric chloride caused a transient reddish-blue coloration.

Determination of unconsumed sulfite showed the presence of 27.9 cc. of 1 *N* solution; 391.4 cc. of 1 *N* or 195.7 cc. of a molar solution was therefore used, or slightly less than two moles of sulfite to one of dye. Sulfate generated during cleavage was determined in 25-cc. portions of the ammoniacal solution. 0.2810 g. of barium sulfate was found, or 5.620 g. in 500 cc. of the original solution, corresponding to 48.2 cc. of 1 *N* solution, or to 12.1% of the sulfite consumed. Dilute acetic acid added to the cold solution of cleavage products did not cause a precipitate. Totally unsulfonated aminocresotinic acid, which is difficultly soluble, therefore, could not have been present. On these various determinations may be based the following tabulation of primary cleavage products and their approximate yields.

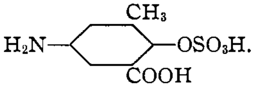
CLEAVAGE OF THE DYE



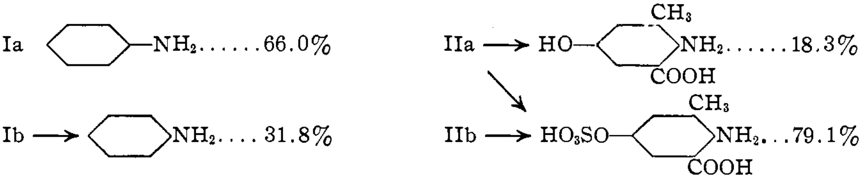


Decomposition and Rearrangement of N-sulfonic Acids.—Addition of an excess of mineral acid to the hot solution of cleavage products caused decomposition of the primarily formed phenylsulfaminic acid, aniline corresponding to 31.8 cc. of 1 *N* nitrite solution and sulfuric acid being formed. The secondary component yielded two products: aminocresotinic acid and an extremely soluble monosulfonic acid derivative of the same compound. One-tenth mole of dye yielded 3.052 g. of aminocresotinic acid, or 18.3% of the theoretically possible amount.

Anal. Calcd. for $C_8H_9O_3N$: N, 8.40; acidity, 1.0000 g. = 5.983 cc. of 1 *N* NaOH solution. Found: N, 8.26; acidity (electrometric titration with 0.1 *N* NaOH), 1.0000 g. = 5.830 cc. of 1 *N* NaOH.

The sulfonated aminocresotinic acid differed distinctly in solubility and crystal habit from the product obtained through direct sulfonation of aminocresotinic acid. It appeared highly probable, therefore, that the rearrangement product was not a nuclear sulfonic acid but a phenol ester  Diazotized and coupled with azo components, this compound yielded dyes which differed from corresponding azo derivatives of aminocresotinic acid and of its nuclear sulfonic acid by a visible shift toward absorption in regions of longer wave lengths. Diazotization of the sulfonic ester of aminocresotinic acid, originating from one-tenth mole of dye, required 79.1 cc. of 1 *N* nitrite solution.

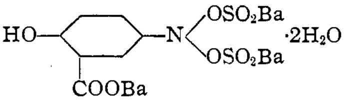
Rearrangement of N-Sulfonic Acids Tabulated Above (Actual Yields)

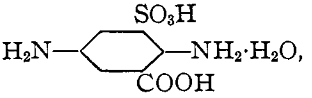
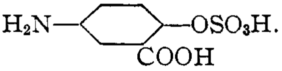
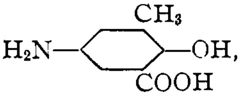
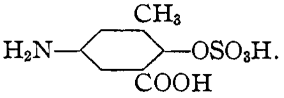


Summary

1. The sulfite cleavage of 4-hydroxy-azobenzene-5-carboxylic acid and of its 3-methyl homolog has been investigated.

2. A difficultly soluble barium salt of an N-disulfonic acid derived from 1-amino-4-hydroxybenzene-5-carboxylic acid could be isolated in pure form. Its distinctive reactions substantiated a newly proposed formulation for N-disulfonic acids as, for example



3. Hydrolysis and rearrangement of N-sulfonic acids resulted in complete re-formation of the primary dye component, aniline. The secondary component of the first dye yielded aminosulfosalicylic acid,  and the sulfonic ester,  The secondary component of the other dye yielded aminocresotinic acid,  and its sulfonic ester, 

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