5-31-1952

Preparation and reduction of azo dyes from 2-amino phenol-4-sulfonic acid

Guy J. Walker
New Jersey Institute of Technology

Recommended Citation

Walker, Guy J., "Preparation and reduction of azo dyes from 2-amino phenol-4-sulfonic acid" (1952). *Theses*. 2174.
https://digitalcommons.njit.edu/theses/2174

PREPARATION AND REDUCTION OF AZO DYES FROM 2-AMINO PHENOL-4-SULFONIC ACID

BY

GUY J. WALKER

Submitted in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

in Chemical Engineering

in the

Graduate Division

at the

Newark College of Engineering

May 6, 1952

ACKNOWLEDGEMENT

The author wished to express his gratitude to Professor James A. Bradley, of the Newark College of Engineering, for his counsel and guidance throughout the investigation.

TABLE OF CONTENTS

TABLE OF CONTENTS

ABSTRACT

Reduction of azo dyes is presented as a method for the synthesis of 2-amino phenol-4-sulfonic acid.

The synthesis and reduction of some azo derivatives of 2-amino phenol-4-sulfonic acid are described.

Preparation of the diazonium compounds of aniline, p-nitro aniline, 1-amino-2-naphthol, 1-amino-2-naphthol-4-sulfonic acid, 2-amino phenol-4-sulfonic acid, 1-naphthylamine, and 2-naphthylamine is discussed and their ability to couple with phenol-4-sulfonic acid evaluated.

Reduction of the resultant azo dyes is discussed with reference to fission and the benzidine rearrangement.

An over-all presentation of results is given in Tables I, II, and III on pages 27 - 29.

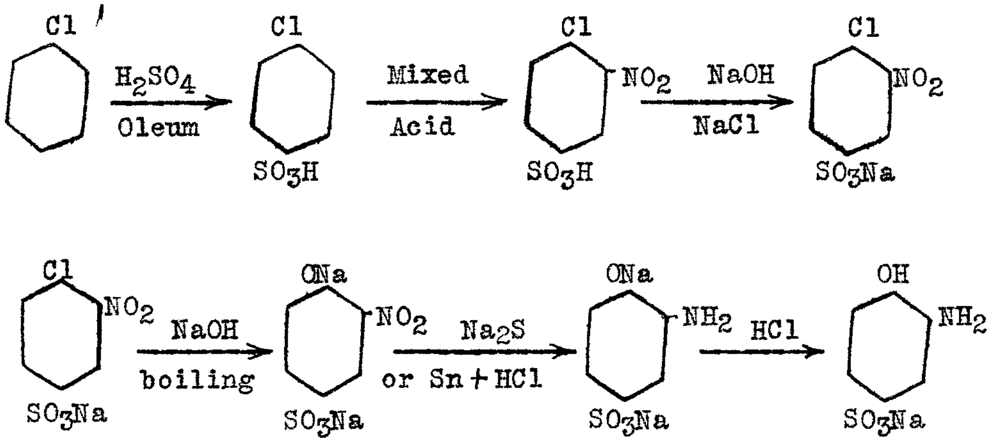
STATEMENT OF PROBLEM

The main purpose of this study was the development of a synthesis for 2-amino phenol-4-sulfonic acid, using diazonium compounds and phenol-4-sulfonic acid.

INTRODUCTION

2-Amino phenol-4-sulfonic acid is one of the important intermediates used in the manufacture of the mono azo and dihydroxy dyestuffs. From it such dyes (27) as Acid Alizarin Brown B, Palatine Chrome Brown W, Acid Alizarin Garnet B, Acid Alizarin Violet N, and Diamond Black PV are produced.

The industrial process (27) for production of 2-amino phenol-4-sulfonic acid stems from chlorobenzene as follows:



A method using the sulfonation of 2-amino-4-phenol is also reported (2).

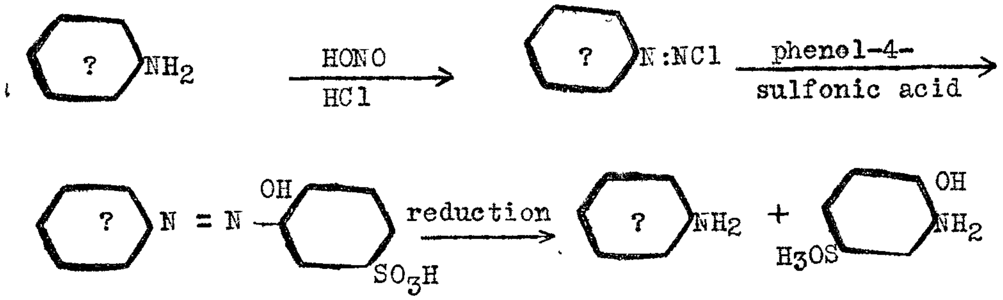
In addition to reduction of nitro compounds, amines are also prepared by the reduction of azo compounds. A search of the literature indicated that this latter procedure has not been successfully applied to the production of 2-amino phenol-4-sulfonic acid. This lack might be ascribed to problems associated with:

1. Formation of the diazonium salt.
2. Coupling.
3. Reduction of the azo link to give fission without benzidine rearrangement.
4. Isolation of amines from the reduction mixture.

Conditions for diazotization and coupling vary with the compound and no attempt will be made to predict procedure. An excellent treatise on the aromatic diazo-compounds, their preparation and reactions, has been prepared by Saunders (21).

Reduction of aromatic azo compounds has been the subject of much research. Amines, hydrazo compounds, benzidines, or semidines can be formed, depending upon the reduction procedure and the compound to be reduced. Robinson (19) indicates that except for o-amino-azo-benzene, aromatic azo compounds with the para position free reduce to hydrazo compounds and rearrange to benzidines in strong acid. Jacobson (16) found that methyl, bromo, iodo, acetoxy, or ethoxy groups in the para position do not hinder hydrazo formation and acidification gives semidines (diphenyl amines) instead of benzidines. In 1937 Whitmore and Revukas (28) presented a new method for reduction of aromatic azo compounds -- raney nickel catalyst and hydrogen under pressure -- and were able to reduce azo benzene to aniline with a 96% yield.

Formation and reduction of the azo compound, from which 2-amino phenol-4-sulfonic acid would be produced, might be illustrated thus:



It is evident that the main problems involved are the selection of "amine-?" and the reduction of its azo dye. This investigation deals with the diazonium compounds of aniline, p-nitro aniline, 1-amino-2-naphthol, 1-amino-2-naphthol-4-sulfonic acid, 2-amino phenol-4-sulfonic acid, 1-naphthylamine, and 2-naphthylamine as possibilities.

Phenol-4-sulfonic acid was selected as the acceptor in the coupling reaction with the diazonium salt because:

1. Two of the three required functional groups are present and in position.
2. Coupling is limited to the ortho position. There are no isomers.
3. Fission, by reduction, will yield the desired amine.

APPARATUS

Except for the Burgess-Parr apparatus (12) used for reductions with raney nickel catalyst, all beakers, flasks, and glass were were of the type that can be purchased in any laboratory supply house.

REAGENTS

Grade of reagent is indicated in the procedure for each compound. Distilled water was used whenever the use of alkali was required.

Since phenol-4-sulfonic acid was used as the acceptor in all but two of the coupling reactions, it might be considered a reagent. To avoid repetition, its preparation from sulfanilic acid by a modified Reumuth (22) procedure is given here, and this preparation applies wherever phenol-4-sulfonic acid was used:

Sulfanilic acid monohydrate, analytical grade, 9.1 gm. (0.0477 mole), was dissolved in a solution of 2.6 gm. anhydrous sodium carbonate (0.024 mole) in 49 cc. of distilled water, by heating. U.S.P. sodium nitrite, 3.5 gm., was dissolved in 9.5 cc. distilled water. A.C.S. grade hydrochloric acid, 10.3 cc., was mixed into 57 gm. of ice. The sodium sulfanilate solution was chilled to 15°C., mixed with the sodium nitrite solution, and the whole poured slowly into the rapidly stirred, iced acid. The white, sulfanilic acid diazonium salt precipitated almost at the start of addition. Care was taken to control addition so that hydrolysis did not take place, as indicated by a red color appearing at the mixing point of the two solutions. A positive test for nitrous acid was obtained on the solution with potassium iodide starch paper at the end of addition.

H2O
49
9.5
8
53
119.5

(Sulfanilic acid diazonium salt gave a bright orange color when spot tested with alcoholic, alkaline 2-naphthol).

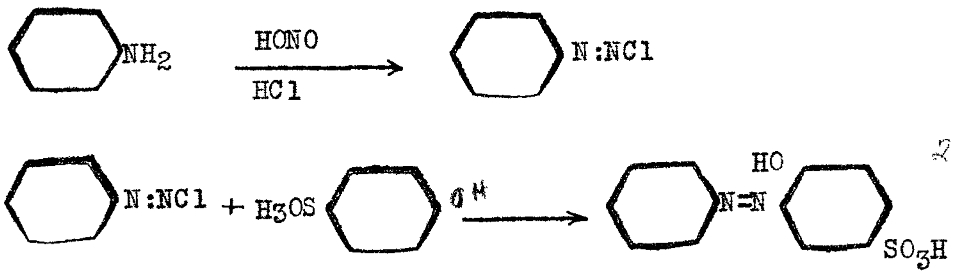
Molality = about $0.0477 \times \frac{1000}{120}$

= about 0.40

With vigorous stirring, the solution was quickly heated to boiling on an electric hot plate. The total heating time was 8 to 10 minutes. As the temperature rose the diazonium salt dissolved, the solution turned straw yellow, then orange, foamed at 65 - 70°C., and continued to foam until hydrolysis was complete after heating at 100°C. for 2 to 3 minutes. The wine-red solution of phenol-4-sulfonic acid was spot tested for absence of diazonium salt with alkaline 2-naphthol, as noted above, and cooled to 15°C. When used for coupling reactions, this solution was presumed to contain 0.0477 mole of phenol-4-sulfonic acid.

EXPERIMENTAL PROCEDURE

PREPARATION of 2-PHENYL-AZO-PHENOL-4-SULFONIC ACID



C.P. Aniline, 4.5 gm. (0.048 mole), was diazotized by the method of Schwalbe (23) for p-nitro aniline. After mixing, the solution gave a positive test for nitrous acid with potassium iodide starch paper, and diazonium salt with alcoholic, alkaline 2-naphthol.

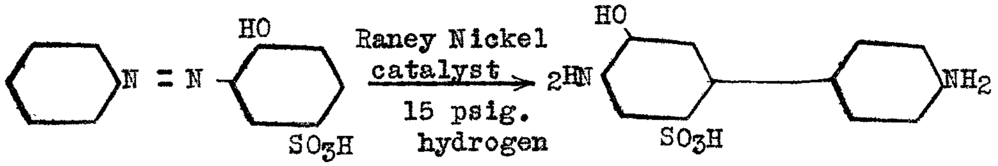
Sodium carbonate monohydrate was added to a 0.0477 mole solution of phenol-4-sulfonic acid (Page 6) until alkalinity to blue litmus was obtained. Iced (0 to 5°C.), diazotized aniline, prepared above, and sodium carbonate monohydrate, 7.5 gm., were added slowly and alternately to the rapidly stirred, chilled (0 to 5°C.), alkaline phenol-4-sulfonic acid over a 1-1/2 to 2 hour interval. The phenol-4-sulfonic acid was kept below 5°C. and alkalinity to litmus was held during the addition. Diazonium salt addition was controlled, to avoid self coupling, by spot testing the phenol-4-sulfonic acid with alcoholic, alkaline 2-naphthol. A light colored test was maintained.

The mixture was held at 0 to 5°C. for 8 hours, with occasional stirring, filtered, and washed with 15 to 20 cc. of saturated sodium chloride solution. The red-brown cake, 15.5 gm., was dissolved in 400 cc. of boiling methanol and filtered. The methanol was replaced with acetone and the solution was concentrated to heavy crystals, chilled to 5°C., and filtered. 12.1 gm. of orange, sodium 2-phenyl-azo-phenol-4-sulfonate was obtained.

The cake filtrate was acidified to Congo Red with A.C.S. grade hydrochloric acid, saturated with sodium chloride, chilled to 5°C., and filtered. The filtrate was extracted twice with ethyl ether and the cake was extracted with methanol. The combined ether and methanol extracts, taken to dryness, yielded 1.6 gm. of olive green, 2-phenyl-azo-phenol-4-sulfonic acid.

Total yield calculated as 2-phenyl-azo-phenol-4-sulfonic acid was 12.8 gm., 96.7% of theoretical based on sulfanilic acid. Identification tests on the product agreed with those in Beilstein (4).

PREPARATION OF 4,4'-DIAMINO-3-HYDROXY-DIPHENYL-6-SULFONIC ACID



The method of Whitmore and Revukas (28) was used, in the reduction of 2-phenyl-aso-phenol-4-sulfonic acid, as follows: Sodium 2-phenyl-aso-phenol-4-sulfonate, 5.0 gm. (0.0167 mole), see above, was dissolved in a mixture of 30 cc. distilled water and 80 cc. methanol in a Burgess-Parr hydrogenator (12). Raney nickel catalyst, Raney Catalyst Co., Chattanooga, Tenn., was activated by the method of Covert and Adkins (8) using methanol instead of ethanol. 9.0 gm. of the wet, activated catalyst in 20 cc. of methanol were added to the solution in the hydrogenator. 15 psig. hydrogen was introduced, through a 1.770 liter storage tank connected to a pressure gauge, and agitation was started.

In 20 minutes reduction was completed, as evidenced by no further drop in storage tank pressure. The bright red solution in the hydrogenator turned a pale yellow during reduction. The solution was transferred from the hydrogenator with methanol and the catalyst filtered off and washed well with methanol.

The filtrate turned a dark green, after standing 2 to 3 minutes. The cake was then extracted with 2% aqueous, sodium hydroxide until a sample of the wash gave no precipitate when acidified, to litmus, with hydrochloric acid. Great care was taken to keep the catalyst wet with solvent, at all times, to prevent a fire, and it was dumped immediately into water after extraction.

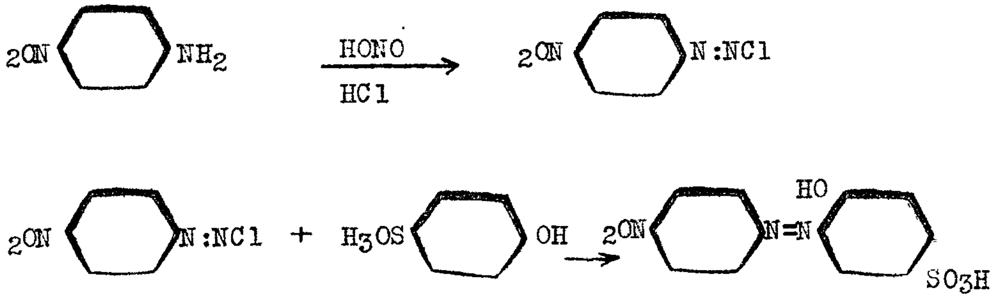
The methanol and sodium hydroxide filtrates were combined and extracted with ethyl ether. These ether extracts, when dried over anhydrous calcium sulfate and concentrated to dryness, yielded a trace of brown tar. This tar showed no evidence of aniline and was not investigated further.

The extracted filtrate yielded 1.2 gm. of pink 4,4'-diamino-3-hydroxy-diphenyl-6-sulfonic acid, after acidification to litmus with A.C.S. grade hydrochloric acid and chilling (0 to 5°C.) for 8 hours. More product, 2.0 gms., was isolated by concentrating the mother liquor, chilling (0 to 5°C.), and adding ethyl ether.

Total yield of 4,4'-diamino-3-hydroxy-diphenyl-6-sulfonic acid was 3.2 gms. 68.7% of theoretical. Identity was confirmed by microscopic comparison with 4,4'-diamino-3-hydroxy-diphenyl-6-sulfonic acid prepared from sodium 2-phenyl-azo-phenol-4-sulfonate using stannous chloride and hydrochloric acid (3).

A repeat reduction using a larger amount of raney nickel catalyst, 20.0 gm., on 5.0 gm. (0.0167 mole) of sodium 2-phenyl-azo-phenol-4-sulfonate, dissolved in 200 cc. of methanol only, gave the same result: benzidine rearrangement and the production of 4,4' diamino-3-hydroxy-diphenyl-6-sulfonic acid, 2.7 gm., 57.8% of theoretical. The same reduction filtrate color change was noted. The ether extraction procedure was not used. Additional evidence for benzidine rearrangement was hydrogen consumption, measured by storage tank pressure drop, 1.2 moles per mole of azo compound.

PREPARATION OF 4-NITRO PHENYL-(1 AZO 6)-PHENOL-4-SULFONIC ACID



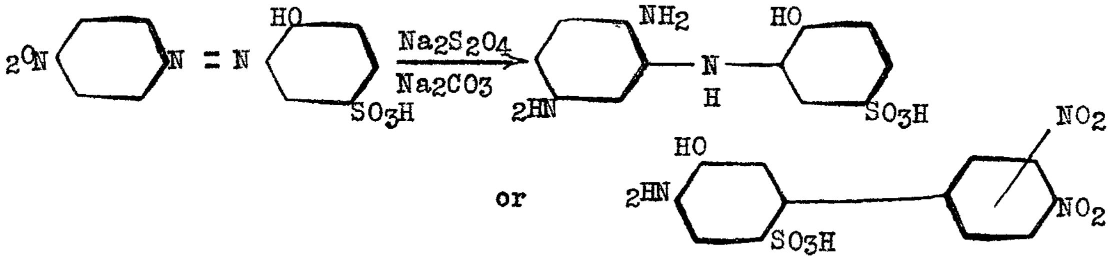
C.P. p-nitro aniline, 5.6 gm. (0.0406 mole), was diazotized by the method of Sunder (22), using hydrochloric acid.

Sodium carbonate monohydrate was added to a 0.0477 mole solution of phenol-4-sulfonic acid (Page 6) until alkalinity to blue litmus was obtained. The iced (0 to 5°C.), diazotized p-nitro aniline and sodium carbonate monohydrate, 21.0 gm., were added slowly and alternately to the rapidly stirred, chilled (0 to 5°C.), alkaline phenol-4-sulfonic acid over a 1-1/2 to 2 hour period. The phenol-4-sulfonic acid was kept below 5°C. and alkaline to blue litmus during the addition. Self coupling of the diazonium salt was kept to a minimum by controlling addition so that a light colored test was maintained when the phenol-4-sulfonic acid was spot tested on alcoholic, alkaline 2-naphthol.

The mixture was held below 5°C. for [illegible] hours, with occasional stirring, carefully acidified with A.C.S. grade hydrochloric acid to Congo Red, chilled to 5°C., and filtered. The dried orange cake yielded 15.4 gm. of impure 4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid. It was dissolved in boiling methanol and filtered. The methanol was replaced with ether and the solution was concentrated to heavy crystals, chilled to 5°C., filtered, and dried. 12.2 gm. of yellow-orange, 4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid was obtained, 97.1% of the theoretical based on p-nitro aniline.

Identity: Calculated nitrogen, 13.0%. Found nitrogen, 12.9%. No reaction when titrated with sodium nitrite.

REDUCTION OF 4-NITRO PHENYL-(1 AZO 6)- PHENOL-4-SULFONIC ACID



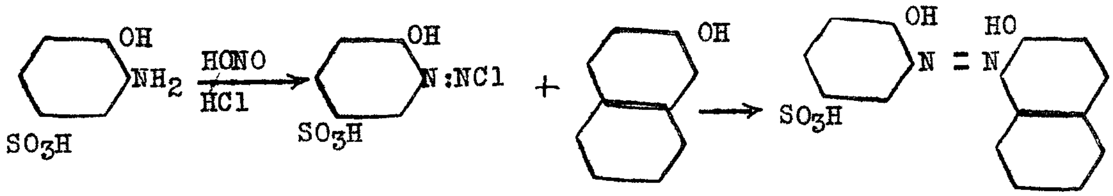
4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid, 5.0 gm. (0.0155 mole), was dissolved in a solution of 1.85 gm. (0.0462 mole) A.C.S. grade sodium hydroxide pellets in 50 cc. distilled water, heated to 40°C. C.P. sodium hyposulfite, 6.3 gm. (0.0362 mole), was added, with stirring, and the solution color changed from a deep red to a yellow. No crystals appeared after chilling the alkaline solution — evidence that little or no p-nitro aniline or para phenylenediamine was formed in the reduction. After acidification to Congo Red, with A.C.S. grade hydrochloric acid, the solution was carefully concentrated to crystals, chilled, and filtered. The dry, pink cake, 3.5 gms., was identified as either 2'-nitro-5-hydroxy-benzidine-6-sulfonic acid or 2,5-diamino-2'-hydroxy-diphenylamine-5'-sulfonic acid by nitrogen assay and sodium nitrite titration for amine groups. The calculated nitrogen agreed with the assay nitrogen for both compounds and no attempt was made to further establish identity.

Compound	Calc. N	Found N	Gm.	Yield % Theory
benzidine	12.9%	13.0%	0.94	18.7
diphenylamine	14.2	14.3	0.86	18.8

Instability of nitro groups, in reducing media, suggests that 2,5-diamino-2'-hydroxy-diphenylamine-5'-sulfonic acid is the more probable compound.

Because of this evidence that blocking the para position with a nitro group does not hinder rearrangement, the filtrate was not investigated further.

PREPARATION OF NAPHTHOL-2-(1 AZO 6)-PHENOL-4-SULFONIC ACID



A method similar to that used for Orange II (5) was used for the preparation of naphthol-2-(1 azo 6)-phenol-4-sulfonic acid.

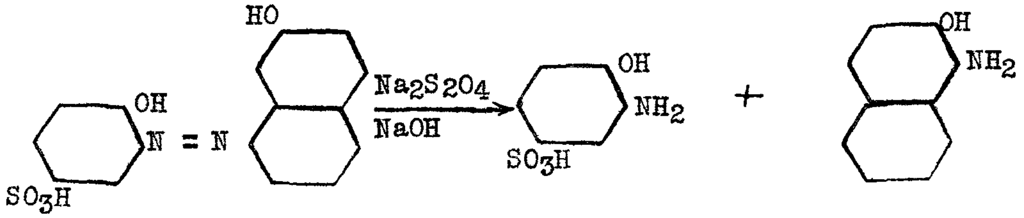
2-Amino phenol-4-sulfonic acid, 98.9% pure, 9.9 gm. (0.052 mole), was dissolved in a solution of 2.7 gm. (0.025 mole) anhydrous sodium carbonate in 50 cc. distilled water and chilled to 15°C.

U.S.P. sodium nitrite, 3.7 gm. (0.054 mole), was dissolved in 10 cc. distilled water and combined with the sulfonic acid solution. The whole was poured slowly into a rapidly stirred mixture of 10.6 cc. (0.128 mole) A.C.S. grade hydrochloric acid and 60 gm. ice. The mixture gave a positive test for excess nitrite with potassium iodide starch paper. Diazonium salt formation was confirmed by spot test with alcoholic, alkaline 2-naphthol. A red-brown color was obtained.

C.P., alpha free, 2-naphthol, 7.2 gm. (0.050 mole), was dissolved in a warm solution of 7.5 gm. (0.188 mole) A.C.S. grade sodium hydroxide pellets in 60 cc. distilled water. The whole was then iced to 0°C., and 40 gm. ice was added. The rapidly stirred 2-naphthol solution was kept at 0 to 10°C. while the sulfonic acid diazonium salt was added over a 1-1/2 to 2 hour period. The 2-naphthol solution was kept alkaline to litmus during the addition. After 2 hours, coupling was complete and the red-brown mixture was carefully acidified to Congo Red with A.C.S. grade hydrochloric acid. The thick slurry was heated on a hot plate, with stirring, to 40 to 60°C. At this point the foam disappeared and the solids settled to the bottom of the beaker. After chilling to 0 to 5°C., the mixture was filtered and the red-brown cake was washed once with a small portion of chilled, saturated sodium chloride solution and dried.

The yield of red-brown, naphthol-2-(1 azo 6)-phenol-4-sulfonic acid was 16.9 gm., 98.2% of theoretical based on 2-naphthol. This material was reduced without further purification. Identity was established by the reduction products: 1-amino-2-naphthol and 2-amino phenol-4-sulfonic acid.

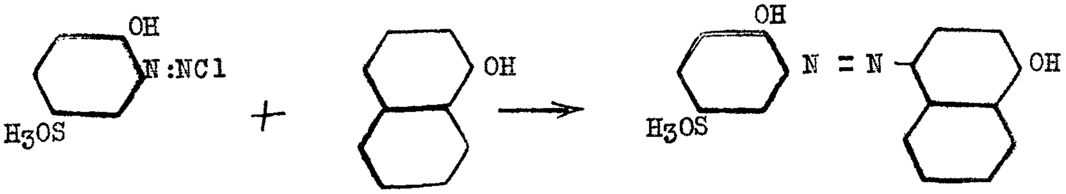
PREPARATION OF 1-AMINO-2-NAPHTHOL HYDROCHLORIDE AND 2-AMINO PHENOL-4-SULFONIC ACID



Naphthol-2-(1 azo 6)-phenol-4-sulfonic acid, 5.0 gm. (0.0145 mole), was dissolved in a 40 to 50°C. solution of 3.2 gm. (0.080 mole) A.C.S. grade sodium hydroxide pellets in 28.8 cc. distilled water. C.P. sodium hyposulfite, 6.0 gm. (0.0285 mole), was added cautiously and the solution was quickly heated to 70°C., with stirring. Heating was continued until frothing subsided. The red solution turned white and material precipitated. After cooling to 20 to 25°C. and filtering, the cake was dissolved in a warm solution of 0.05 gm. C.P. stannous chloride in 23 cc. distilled water containing 1.8 cc. A.C.S. grade hydrochloric acid. The whole was stirred and heated until solution was complete. 2.9 cc. A.C.S. grade hydrochloric acid was added and the solution was chilled to 0°C. and filtered. The white cake was air dried, below 35°C., on filter paper. 2.0 gm., 70.5% theoretical yield, of 1-amino-2-naphthol hydrochloride was obtained. Identity was confirmed by oxidising a sample to 1-2 naphthoquinone (decomposition melting point = 116°C.) with ferric chloride (6).

The filtrate after acidification to Congo Red with A.C.S. grade hydrochloric acid, chilled (0 to 5°C.) for 48 hours and filtered, yielded 1.9 gm., 69.3% theoretical yield of pale pink 2-amino phenol-4-sulfonic acid. Identity tests agreed with those in Beilstein (2) and microscopic comparison with 2-amino phenol-4-sulfonic acid substantiated composition.

PREPARATION OF NAPHTHOL-1-(4 AZO 6)-PHENOL-4-SULFONIC ACID



Naphthol-1-(4 azo 6)-phenol-4-sulfonic acid was prepared by coupling 9.4 gm. (0.050 mole) diazotized 2-amino phenol-4-sulfonic acid, (Page 15), with 6.9 gm. (0.048 mole) C.P. 1-naphthol. The same procedure (Page 13) as for 2-naphthol was used for coupling and isolation of the product.

The 1-naphthol solution, at the start of diazonium salt addition, became a bright orange. This color turned a deep red toward the end of the addition. Acidification produced a heavy, creamy precipitate which coagulated when heated.

Yield of green-brown, naphthol-1-(4 azo 6)-phenol-4-sulfonic acid was 9.1 gm., 52.8% of theoretical, based on 1-naphthol. This product was used directly in a reduction without further purification.

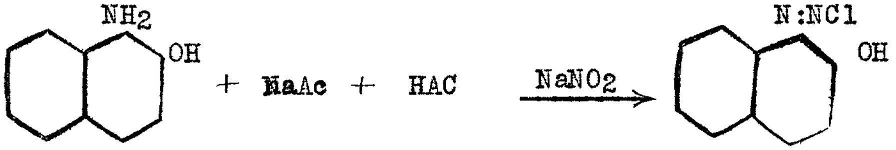
REDUCTION OF NAPHTHOL-1-(4 AZO 6)-PHENOL-4-SULFONIC ACID

5.0 gm. (0.0145 mole) of Naphthol-1-(4 azo 6)-phenol-4-sulfonic acid was dissolved in a 40 to 50°C. solution of 3.2 gm. (0.080 mole) A.C.S. grade sodium hydroxide pellets in 28.8 cc. distilled water. C.P. sodium hyposulfite, 6.0 gm. (0.0285 mole), was added cautiously and the dark red solution was quickly heated to 70°C. and stirred until frothing subsided. The color changed to an orange. The solution became too thick to stir and 5 cc. distilled water was added as diluent. After cooling to 20 to 25°C., the solution was filtered. During filtration the cake turned from a tan to pink. It was quickly transferred to a warm solution of 0.05 gm. C.P. stannous chloride in 23 cc. distilled water containing 1.8 cc. A.C.S. grade hydrochloric acid and heated to dissolve. The solution color was similar to that for 1-amino-4-naphthol hydrochloride (7), but the material did not completely dissolve. 5.8 cc. more A.C.S. grade hydrochloric acid was added, the solution was chilled to 0°C. and filtered. Again the cake color changed during filtration, from a tan to a pink. This color change may be observed when 1-amino-4-naphthol is prepared from Orange I (7). The yield, after drying below 35°C. on filter paper, was 0.5 gm. or 17.6% theoretical, presuming the material to be 1-amino-4-naphthol hydrochloride. Positive identification was not made because of the low yield.

Acidification of the filtrate to Congo Red with hydrochloric acid and chilling (0 to 5°C) overnight yielded no material.

After consideration of the low coupling yield and the extremely small reduction yield, investigation of the 4-azo-1-naphthol was terminated.

DIAZOTIZATION OF 1-AMINO-2-NAPHTHOL



When applied to 1-amino-2-naphthol, the method using sodium acetate (15) proved to be most convenient and easily managed.

An attempt to acetylate, using the method of Kroeber and Jagerspacher (16) was unsuccessful.

Diazotization in aqueous copper sulfate, recommended by Sandmeyer (20) and Hodgson and Birtwell (14), yielded a gum which was useful only when dissolved in acetic acid.

The sodium acetate procedure was used as follows: Analytical grade 1-amino-2-naphthol hydrochloride (5), 2.0 gm. (0.0102 mole), was dissolved, by warming in a solution of 1.02 gm. (0.0124 mole) anhydrous sodium acetate in 10.2 cc. (0.1772 mole) acetic acid. After cooling to 20 to 25°C., 0.85 gm. (0.0123 mole) U.S.P. sodium nitrite was slowly added. A dark red-violet solution of diazo-oxide formed. This solution coupled slowly with alcoholic, alkaline 2-naphthol, on a spot test, to give a blue-black color.

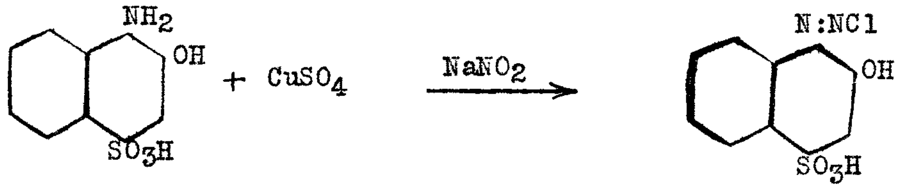
COUPLING OF 1-AMINO-2-NAPHTHOL DIAZO-OXIDE WITH PHENOL-4-SULFONIC ACID

All attempts to couple 1-amino-2-naphthol diazo-oxide with phenol-4-sulfonic acid failed. Solutions of phenol-4-sulfonic acid in dilute acetic acid and aqueous, alcoholic, potassium hydroxide (alkaline to brilliant yellow) were tried. Solutions were allowed to stand for as long as 3 days. There was no visible color change in the solution and positive coupling tests to 2-naphthol were obtained.

Acidification of all solutions, at the end of 3 days, with A.C.S. grade hydrochloric acid produced a small amount (0.5 to 1.0 gm.) of red-violet material. This material was not soluble in sodium hydroxide and could not be reduced with sodium hyposulfite. This proved that it was not the desired production, naphthol-2-(1 azo 6)-phenol-4-sulfonic acid (Page 13 and 14) which easily reduced. No further identification was made.

De Jonge and Dijkstra (10) investigated irradiation decomposition of o-hydroxy diazonium compounds, in acid solution. Red dyes were isolated which were proved to be the diazonium salt coupled to its decomposition product, indene and indene dicarboxylic acid. The red dye isolated here might be that mentioned by De Jonge and Dijkstra.

DIAZOTIZATION AND COUPLING OF 1-AMINO-2-NAPHTHOL-4-SULFONIC ACID



1-amino-2-naphthol-4-sulfonic acid (9), 2.45 gm. (0.0102 mole), was diazotized in the presence of copper sulfate (25). The yellow-grade diazonium compound was added to a solution of 0.0133 mole phenol-4-sulfonic acid (Page 6) containing enough sodium carbonate to make it just alkaline to brilliant yellow.

The solution, after standing at 10°C. for 3 days, was filtered; and 2.45 gm. material was isolated and identified as the original diazo-oxide, by appearance and color when coupled to alkaline 2-naphthol.

Another reaction tried with an alkaline, methanol solution of phenol-4-sulfonic acid gave the same result, no coupling.

COUPLING OF 2-AMINO PHENOL-4-SULFONIC ACID -- 2-amino phenol-4-sulfonic acid, 98.9% pure, 9.9 gm. (0.052 mole), was diazotized as previously described (Page 15).

A 0.052 mole solution of phenol-4-sulfonic acid (Page 6) was alkalized with 6.0 gm. A.C.S. grade sodium hydroxide pellets, and chilled to 0 to 5°C. The solution of diazotized 2-amino phenol-4-sulfonic acid was added. During addition, alkalinity to litmus was maintained and the temperature of the combined solution was kept below 5°C. Very little color change was noted after combination.

At this point the solution was split into two parts and methanol equal to twice the volume was added to one half. Both parts were then allowed to stand at 0 to 5°C. for 4 days.

A coupling test on the undiluted half, with alkaline 2-naphthol, indicated that the original amount of diazonium salt was still present and the solution was stored as before for 3 days more. After this second period, a test showed that diazonium salt was still present and coupling had not taken place. This method for coupling was not investigated further.

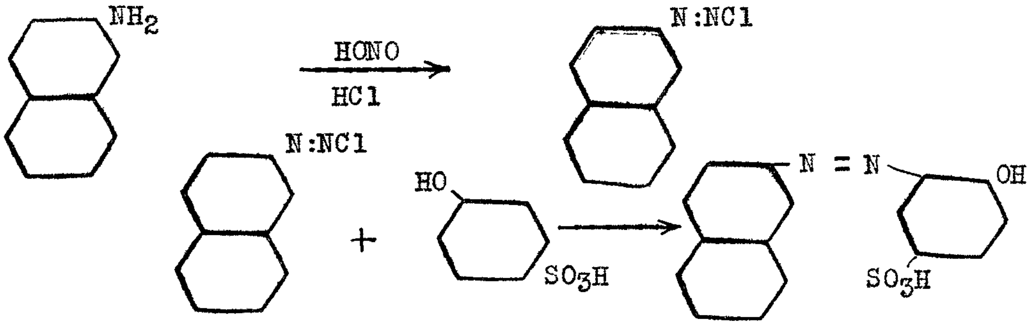
After 4 days, the methanol diluted half showed no signs of diazonium salt, even though the color was the same as before standing. No crystals appeared when the solution was acidified to Congo Red, with A.C.S. grade hydrochloric acid, heated until all methanol was removed, and chilled to 0 to 5°C.

A reduction on the amber solution without isolating the azo dye, if formed, was tried. A.C.S grade sodium hydroxide pellets were added until alkalinity to litmus was obtained. Then 6.0 gm. more (0.150 mole) alkali was added; the solution was heated to 50 to 60°C. 12.0 gm. (0.057 mole) C.P. sodium hyposulfite was added. The solution was stirred until no more color change was noted, filtered, acidified to Congo Red with A.C.S. grade hydrochloric acid, chilled to 0 to 5°C. overnight, and filtered.

Material, 5.4 gm., isolated was identified as a compound containing no amine groups, by titration with nitrous acid. Amines were not found in the acid filtrate.

Coupling of 2-amino phenol-4-sulfonic acid diazonium salt with phenol-4-sulfonic acid was therefore considered negligible.

PREPARATION OF NAPHTHYL-(2 AZO 6)-PHENOL-4-SULFONIC ACID



2-naphthylamine, 5.85 gm. (0.0408 mole), was diazotized according to Scheid's (26) procedure. The solution gave a brilliant red coloration when spot tested with alkaline 2-naphthol.

This diazonium salt was added to a chilled (0 to 5°C.), stirred, solution of 0.0408 mole phenol-4-sulfonic acid (Page 6) containing 50.7 gm. (0.0408 mole) sodium carbonate monohydrate. After standing 48 hours at 0 to 5°C., coupling was complete as determined by spot testing with alkaline 2-naphthol. The solution was acidified to Congo Red with A.C.S. grade hydrochloric acid, chilled to 0 to 5°C., and filtered.

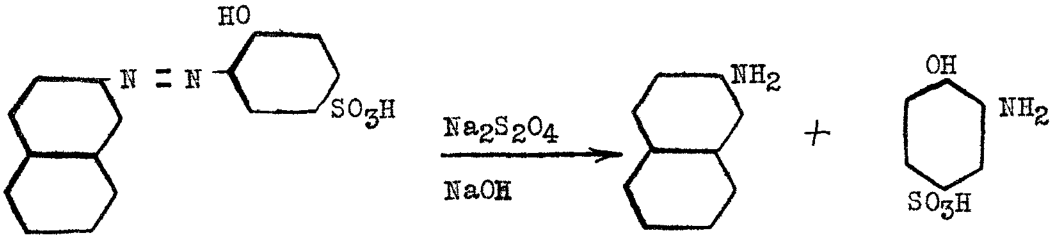
Green-brown Naphthyl-(2 azo 6)-phenol-4-sulfonic acid, 12.8 gm., 95.5% of theoretical, was obtained. The almost colorless filtrate was discarded.

Identity was established, see below, by reduction to 2-naphthylamine and 2-amino phenol-4-sulfonic acid. Purity was estimated at 79%.

Crystallisation from methanol can be affected by dissolving, filtering, concentrating to heavy crystals, diluting with ethyl ether, and chilling. A 78% yield of purified, yellow-green Naphthyl-(2 azo 6)-phenol-4-sulfonic acid was obtained by such a procedure.

For reduction purposes, a better yield was obtained by working directly with the crude dye.

REDUCTION OF NAPHTHYL-(2 AZO 6)-PHENOL-4-SULFONIC ACID



Crude Naphthyl-(2 azo 6)-phenol-4-sulfonic acid, prepared above, 10.0 gm. (0.0305 mole), was dissolved in a mixture of 5.3 gm. (0.1332 mole) A.C.S. grade sodium hydroxide pellets in 120 cc. distilled water by heating to 35 to 50°C. The red solution was filtered and 20 to 30 cc. distilled water was used to wash the cake and transfer the filtrate to a clean beaker. The dried cake weighed 2.1 gm. (melting point = 184 - 185°C.) indicating that the crude dye was approximately 79% pure and the charge was actually 7.9 gm. (0.024 mole).

C.P. sodium hyposulfite, 14.1 gm. (0.067 mole), was added, with stirring, to the warm filtrate, 35 to 45°C. The solution thickened and turned gray. When foaming subsided, the solution was chilled, 0 to 5°C., and filtered. The insoluble, 2-naphthylamine, oxidized when allowed to stand in the air and was converted to the more stable hydrochloride.

The light pink cake was quickly dissolved in a hot, 40 to 60°C., mixture of 5.2 cc. A.C.S. grade hydrochloric acid in 80 cc. distilled water. An equal volume of aqueous, saturated sodium sulfate solution was added and the whole was chilled, 0 to 5°C., and filtered.

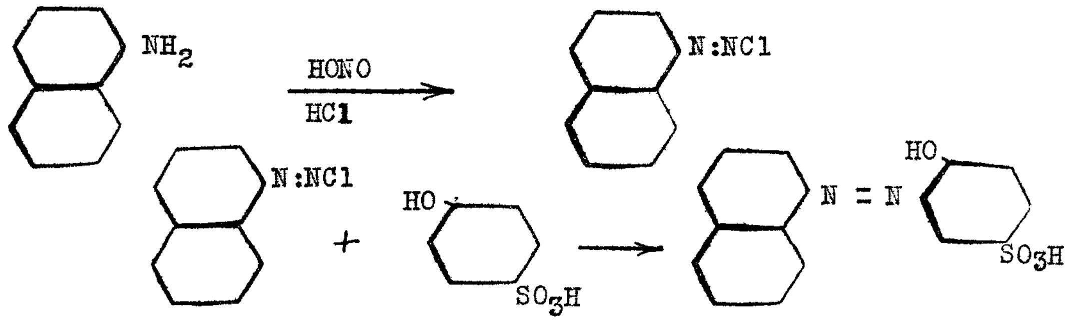
2.8 gm. of 2-naphthylamine hydrochloride, 64.8% of theoretical based on the corrected 0.024 mole charge of azo dye, was obtained. Identity was established by acetylation to form N-acetyl-2-naphthylamine, (melting point = 131 - 132°C.) There was no melting point change when a mixed melting point was run with known N-acetyl-2-naphthylamine. Conversion of the 2-naphthylamine hydrochloride to 2-naphthylamine by sludging in water and alkalizing to phenolphthalein, yielded material that had a melting point of 110-111°C. No melting point depression was exhibited when a mixed melting point was run with known 2-naphthylamine.

The reduction filtrate, when acidified to Congo Red with A.C.S. grade hydrochloric acid, concentrated to 75 cc., chilled (0 to 5°C.)

for 48 hours, and filtered, yielded 2.1 gm. of pale pink, 2-amino phenol-4-sulfonic acid, 46.1% of theoretical. Identity tests agreed with those in Beilstein (2) and microscopic comparison with 2-amino phenol-4-sulfonic acid substantiated composition.

Reduction of 10.0 gm. (0.0305 mole) Naphthyl-(2 azo 6)-phenol-4-sulfonic acid, purified by methanol crystallization, (Page 22), gave 3.0 gm., 68.8% theoretical, 2-naphthylamine and 3.0 gm., 52.2% theoretical, 2-amino phenol-4-sulfonic acid.

PREPARATION OF NAPHTHYL-(1 azo 6)-PHENOL-4-SULFONIC ACID



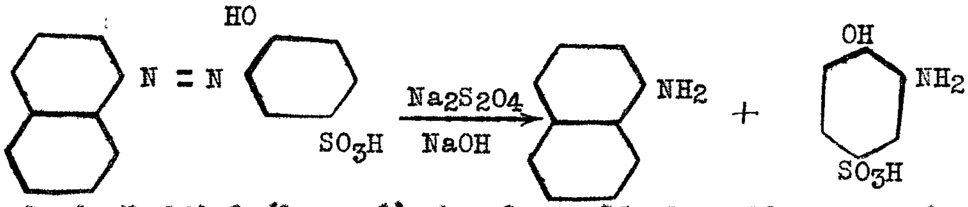
1-naphthylamine, 11.7 gm., (0.0653 mole), was diazotized according to the procedure of Bamberger (1). Diazotization temperature was held at 15 to 18°C. The reaction was slow at lower temperatures. The solution gave a red-purple color when spot-tested with alkaline 2-naphthol.

This diazonium solution was added to a rapidly stirred, chilled (0 to 5°C.) solution of 0.0952 mole phenol-4-sulfonic acid, (Page 6), containing 115 gm. (0.926 mole) sodium carbonate monohydrate. After standing 48 hours at 0 to 5°C., coupling was complete as indicated by a negative spot test with alkaline 2-naphthol.

The solution, after acidification to Congo Red with A.C.S. grade hydrochloric acid, was chilled (0 to 5°C.) and filtered. Red-brown, crude Naphthyl-(1 azo 6)-phenol-4-sulfonic acid, 19.8 gm., 73.9% of theoretical based on 1-naphthylamine, was obtained. The almost colorless filtrate was discarded.

Identity was established by reduction to 1-naphthylamine and 2-amino phenol-4-sulfonic acid, see below. Purity was estimated at 58%.

REDUCTION OF NAPHTHYL-(1 AZO 6)-PHENOL-4-SULFONIC ACID



Crude Naphthyl-(1 azo 6)-phenol-4-sulfonic acid, prepared above, 10.0 gm. (0.0305 mole), was dissolved in 120 cc. distilled water containing 5.3 gm. (0.132 mole) A.C.S. grade sodium hydroxide pellets by heating to 40 to 50°C. The insoluble, 4.2 gm. (melting point = 207 - 208°C.) indicated that the crude azo dye was approximately 58% pure and the reduction charge was corrected to 5.8 gm. (0.0177 mole).

C.P. sodium hyposulfite, 14.1 gm. (0.067 mole), was added, with stirring, to the filtrate at room temperature. The red solution turned pink. It was chilled (0 to 5°C.), filtered, and the cake was dissolved in a mixture of 2.6 cc. A.C.S. grade hydrochloric acid in 40 cc. of distilled water.

1-naphthylamine oxidized quickly in air and was recovered as the more stable hydrochloride as follows:

An equal volume of aqueous, saturated sodium sulfate solution was added, the mixture was chilled to 0 to 5°C. and filtered. 2.3 gm. of 1-naphthylamine hydrochloride was obtained, 71.5% of theoretical.

Identity was established by converting a sample to 1-naphthylamine by sludging in water and alkalising to phenolphthalein. The insoluble 1-naphthylamine melted at 48 - 50°C. and no change in melting point was observed when a sample was mixed with known 1-naphthylamine.

The reduction filtrate, when acidified to Congo Red with A.C.S. grade hydrochloric acid, concentrated to half volume, chilled (0 to 5°C.) for 48 hours and filtered, yielded 1.2 gms. of pale pink 2-amino phenol-4-sulfonic acid, 35.8% of theoretical. Identity tests agreed with those in Beilstein (2) and microscopic comparison with 2-amino phenol-4-sulfonic acid substantiated composition.

EXPERIMENTAL RESULTS

A total of six coupling reactions were run. Each involved two separate processes: (1) preparation of the diazonium salt, and (2) coupling of the diazonium salt. The various compounds prepared, methods, and yields are summarised in Table I, Page 27.

In addition to the diazotisations listed in Table I, Page 27, others were carried out and were abandoned because they would not couple with phenol-4-sulfonic acid. Their preparation and properties are presented in Table II, Page 28.

Reduction of the azo compounds listed in Table I, Page 27, gave a variety of products. Some exhibited benzidine rearrangements,

Table I -- Azo Compounds Prepared by Coupling Reactions

Diazotized Compound	Diazotization Procedure	Coupled To	Product	Yield
Aniline	direct (23)	Phenol-4-sulfonic acid	2-phenyl-azo-phenol-4-sulfonic acid XI	96.7%
p-nitro aniline	direct (23)	Phenol-4-sulfonic acid	4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid XII	93.1
2-amino phenol-4-sulfonic acid	inverted (22)	2-naphthol	naphthol-2-(1 azo 6)-phenol-4-sulfonic acid XIII	98.2
2-amino phenol-4-sulfonic acid	inverted (22)	1-naphthol	naphthol-1-(4 azo 6)-phenol-4-sulfonic acid XIV	52.8
2-naphthylamine	direct (26)	phenol-4-sulfonic acid	naphthyl-(2 azo 6)-phenol-4-sulfonic acid XV	75.5
1-naphthylamine	direct (1)	phenol-4-sulfonic acid	naphthyl-(1 azo 6)-phenol-4-sulfonic acid XVI	42.8

TABLE II -- Diazonium Compounds that do not Couple with Phenol-4-sulfonic Acid

Diazotised Compound	Diazotisation Procedure	Properties
1-amino-2-naphthol	sodium acetate inhibited (15)	red-violet solution in acetic acid. Violet gum in water. Couples to alkaline 2-naphthol to produce blue-black dye.
1-amino-2-naphthol	acetylation of hydroxyl (16)	did not diazotise.
1-amino-2-naphthol-4-sulfonic acid	copper sulfate inhibited (25)	yellow-gray solid. HCl insol. Easily couples with alkaline 2-naphthol to produce purple dye.
2-amino phenol-4-sulfonic acid	inverted (22)	white solid. HCl insol. Easily couples to alkaline 2-naphthol to produce a red-brown dye, Page 14.

Table III -- Reduction of Azo Derivatives of Phenol-4-Sulfonic Acid

Azo Compound	Reduction Method	Reaction	Product	Yield
2-phenyl-azo-phenol-4-sulfonic acid	Raney nickel catalyst	Benzidine rearrangement	4, 4' diamino-3-hydroxy-diphenyl-6-sulfonic acid	68.7%
4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid	Alkaline sodium hyposulfite	semidine rearrangement	probably 2,5-diamino-2'-hydroxy-diphenylamine-6-sulfonic acid	18.8
Naphthol-2-(1azo 6)-phenol-4-sulfonic acid	Alkaline sodium hyposulfite	fission	1-amino-2-naphthol	70.5
			2-amino phenol-4-sulfonic acid	69.3
Naphthol-1-(4 azo 6)-phenol-4-sulfonic acid	Alkaline sodium hyposulfite	fission	1-amino-4-naphthol	17.6
			nothing else isolated	
Naphthyl-(2 azo 6)-phenol-4-sulfonic acid	Alkaline sodium hyposulfite	fission	2-naphthylamine	64.8
			2-amino phenol-4-sulfonic acid	46.1
Naphthyl-(1 azo 6) phenol-4-sulfonic acid	Alkaline sodium hyposulfite	fission	1-naphthylamine	71.5
			2-amino phenol-4-sulfonic acid	35.8

others formed semidines, and others split and gave the desired amines. Reduction results are summarized in Table III, Page 29.

DISCUSSION

There were two problems to be overcome before a satisfactory solution to this investigation could be reached: (1) selection of an amine that could be diazotized and coupled to phenol-4-sulfonic acid, and (2) thereby produce an azo compound that would split, when reduced, and not rearrange.

The problem was further complicated when it became evident that phenol-4-sulfonic acid was a weak acceptor and required a strong diazonium salt coupler.

DIAZOTIZATION -- Four general techniques were used for diazotization in this investigation: direct method, inverted method, sodium acetate inhibited method, and copper sulfate inhibited method. Each procedure reference is listed, Table I, Page 27 and Table II, Page 28; and directions as given in the literature were used, except for slight modifications as were deemed necessary.

The direct method was applied to those amines, aniline, p-nitro aniline, and the naphthylamines, that were strongly basic and whose salts were soluble in aqueous acid.

The sulfonic acids, except for 1-amino-2-naphthol-4-sulfonic acid, were diazotized by the inverted method which is designed for those amines which are weakly basic or whose salts are almost insoluble in aqueous acid.

The 1-amino-2-naphthols were diazotized under inhibited conditions to prevent the nitrous acid from oxidizing them to naphthoquinone (13). Sodium acetate and copper sulfate were used successfully as inhibitors, but a "pre-acetylation of the hydroxyl group" recommended by Kroeber and Jagerspacher (16) failed.

COUPLING -- The coupling ability of the various diazonium compounds, in aqueous solution alkaline to red litmus, with phenol-4-sulfonic acid is:

aniline > p-nitro aniline > 2-naphthylamine > 1-naphthylamine

This order is based on yields from the coupling reaction, Table I, Page 27, presuming that side reactions, such as self coupling and decomposition are negligible. Coupling yields varied from 98% for the aniline diazonium compound to 43% for the 1-naphthylamine diazonium compound.

Phenol-4-sulfonic acid is a weak acceptor, compared to 2-naphthol, and coupling may not take place or proceed to a reasonable yield unless a strong coupling diazonium salt is used.

The diazonium compounds listed below would not couple with phenol-4-sulfonic acid in acid or alkaline solution, see Table II., Page 28, and are rated on ability to couple with 2-naphthol:

2-amino phenol-4-sulfonic acid > 1-amino-2-naphthol-4-sulfonic acid ⋙ 1-amino-2-naphthol

1-amino-2-naphthol would have been an excellent solution to this investigation if it could have been coupled to phenol-4-sulfonic acid, but it is such a poor coupler that its reaction with 2-naphthol, a very strong acceptor is slow. The azo dye, prepared in reverse by coupling diazotized 2-amino phenol-4-sulfonic acid with 2-naphthol, reduced easily and split into 1-amino-2-naphthol and 2-amino phenol-4-sulfonic acid, see Table III, Page 29.

REDUCTION -- Products and techniques of reduction are summarized in Table III, Page 29.

Whitmore and Revukas (28) announced fission of azo benzene, a compound which may be reduced to benzidine, by reduction with raney nickel catalyst and hydrogen under pressure. Their procedure was applied in this investigation to 2-phenyl-azo-phenol-4-sulfonic acid without success. The same benzidine rearrangement produced in reductions with stannous chloride and hydrochloric acid was obtained, with 69% yield.

Except for 2-phenyl-azo-phenol-4-sulfonic acid, reductions were performed by adding sodium hyposulfite to the strong alkaline solution of the azo dye. Weakly basic or neutral solutions may produce hydrazo compounds (18).

Blocking the 4-position with a nitro group did not promote fission and 4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid did not split when reduced. Positive identification was not completed, but either a benzidine or semidine was produced. A semidine is more likely since Jacobson (17) reported that semidines resulted when 4 and 4'-hydrazo benzene positions were occupied with bromo, ethoxy, iodo, or methyl groups.

Fission of 1-azo derivatives of 2-naphthol (5) and 2-naphthol acetate (11) has been reported. This investigation of naphthol-2-

(1 azo 6)-phenol-4-sulfonic acid describes a similar fission with a 70% yield. As was previously indicated, Page 31, this dye would be an excellent source material for 2-amino phenol-4-sulfonic acid if a method for coupling the 1-amino-2-naphthol diazonium compound to phenol-4-sulfonic acid could be developed.

A new synthesis for 2-amino phenol-4-sulfonic acid is described: Coupling of the diazonium salt of either 1- or 2-naphthylamine to phenol-4-sulfonic acid, followed by reduction of the resultant azo compound. Of the two amines, 2-naphthylamine is preferable. It is higher melting and more stable, and gave a 76% higher coupling yield. The 1- and 2-naphthylamine derivatives were split in alkaline sodium hyposulfite to produce 2-amino phenol-4-sulfonic acid, 46% and 36% yields respectively, and the corresponding 1- and 2-naphthylamine, 65% and 72% yield respectively.

SUMMARY

Procedures for the preparation and reduction of some 2-azo derivatives of phenol-4-sulfonic acid are given.

Phenol-4-sulfonic acid is a weak acceptor in a coupling reaction and requires a strong diazonium salt coupler.

Order of coupling of the various diazonium salts studied, with phenol-4-sulfonic acid is proposed:

aniline > p-nitro aniline > 2-naphthylamine >
1-naphthylamine

The diazo-oxides studied did not couple with phenol-4-sulfonic acid. Their ability to couple with 2-naphthol is proposed:

2-amino phenol-4-sulfonic acid > 1-amino-2-naphthol-4-sulfonic acid >>> 1-amino-2-naphthol

Raney nickel catalyst and hydrogen under pressure reduction of 2-phenyl-azo-phenol-4-sulfonic acid produced a benzidine, 4-4'-diamino 3-hydroxy-diphenyl-6-sulfonic acid.

Blocking the 4-position with a nitro group did not promote fission and 4-nitro phenyl-(1 azo 6)-phenol-4-sulfonic acid did not split when reduced in alkaline sodium hyposulfite. A semidine or benzidine was produced.

Reduction of Naphthyl-(2 azo 6)-phenol-4-sulfonic acid and Naphthyl-(1 azo 6)-phenol-4-sulfonic acid in alkaline sodium hyposulfite is presented as a heretofore undescribed method for the preparation of 2-amino phenol-4-sulfonic acid. These azo derivatives can be prepared by coupling the naphthylamine diazonium salt with phenol-4-sulfonic acid.

LITERATURE CITED

1. Bamberger, Ber., 55, 3383-92 (1922).
2. Beilstein, Handbuch der Organischen Chemie, XIV, System 1926, (814), 1931.
3. Ibid., (853), 1931.
4. Ibid., XVI, System 2158, (293), 1931.
5. Blatt, A.H., "Organic Synthesis", vol. 2, p. 35, John wiley & Sons, London (1941).
6. Ibid., vol. 4, p. 430, John Wiley & Sons, London (1934).
7. Ibid, p. 39.
8. Covert, L.W., and Adkins, H., J. Am. Chem. Soc., 54, 4116 (1932).
9. Cummings, Hooper, and Wheeler, "Systematic Organic Chemistry", p. 322, D. Van Nostrand Co., New York (1931).
10. De Jonge and Dijkstra, Rec. Trav. Chim., 67, 328-43 (1948).
11. Ghigi, E., Helv. Chim. Acta., 23, 428-30 (1940).
12. Gillman, H. "Organic Synthesis"., vol. 1, 1st. ed., p. 53, John Wiley & Sons, New York (1932).
13. Grandmougin and Michel, Ber., 25, 972-85 (1892).
14. Hodgson, H.H., and Birtwell, S., J. Chem. Soc., 321-3 (1943).
15. Ibid., 539-40 (1944).
16. Kroeber and Jagerspacher, U.S. Patent 797, 441 (May 23, 1905).
17. Jacobson, P., Ann., 427, 142-221 (1922).
18. Pearl, I.A., J. Org. Chem., 10, 205-210 (1945).
19. Robinson, R., J. Chem. Soc., 220 (1941).
20. Sandmeyer, U.S. Patent 793, 743 (Sept. 30, 1904).

21. Saunders, K.H. "The Aromatic Diazo-Compounds and their Technical Applications", 2nd. ed., Edward Arnold & Co., London (1949).

22. Ibid., p. 10.

23. Ibid., p. 6.

24. Ibid., p. 28-31.

25. Ibid., p. 30.

26. Scheid, Ber., 34, 1813 (1901).

27. Shreve, R.N., "Dyes Classified by Intermediates", P. 80-1, Chemical Catalogue Co., (1922).

28. Whitmore, W.F., and Revukas, A., J. Am. Chem. Soc., 59, 1500-3 (1937).