

UNIVERSITY OF CINCINNATI

May 22 1940

I hereby recommend that the thesis prepared under my supervision by Clara Louise Healy entitled The sulfonation of secondary aromatic amines for use as redox indicators.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Ralph E. Cesper
Hoke S. Greene, chairman

**The Sulfonation of Secondary Aromatic
Amines for Use as Redox Indicators**

A dissertation submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

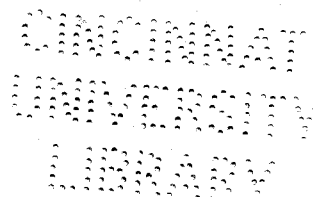
1940

by

Clara L. Deasy

A.B. University of Cincinnati 1937

M.Sc. University of Cincinnati 1939



UMI Number: DP15722

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI®

UMI Microform DP15722

Copyright 2009 by ProQuest LLC.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 E. Eisenhower Parkway
PO Box 1346
Ann Arbor, MI 48106-1346

ACKNOWLEDGEMENT

The author wishes to express to
Dr. Ralph E. Oesper her thanks and
deepest appreciation for the advice
and criticism which he has offered.

TABLE OF CONTENTS

Introduction 1
History 2
Experimental Work 27
Summary 69
Bibliography 70

26 Ag '40

INTRODUCTION

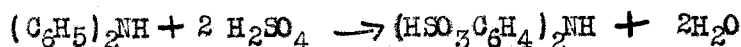
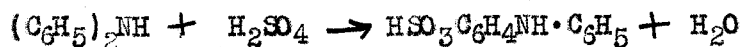
The purpose of this study was to find organic compounds which could function as redox indicators, that is, substances which immediately show striking and reversible color changes at the attainment of definite oxidation potentials. Since many of the indicators now in use are only slightly soluble in water, it seemed worthwhile to attempt the preparation of derivatives which would not possess this disadvantage. In general, this can be accomplished by introducing a sulfonic acid group into the molecule. Accordingly, the sulfonic acid derivatives of some indicators already in use were prepared and tested for indicator properties.

The results of the study are given in the following pages.

HISTORY

Diphenylamine monosulfonic acid. Preparation.

Diphenylamine monosulfonic acid(4?) was first prepared in 1872 by Merz and Weith ^(1) by the action of concentrated sulfuric acid on diphenylamine. The reaction did not occur until 150 - 170° was reached, and even at these temperatures it is incomplete. The sulfonation mixture was treated with hot water, neutralized with barium carbonate, and filtered. The filtrate deposited the barium salt of diphenylamine monosulfonic acid as small shining crystals. The mother liquor after evaporation deposited the readily soluble barium salt of diphenylamine disulfonic acid.



The free monosulfonic acid was obtained by treating a suspension of the barium salt with dilute sulfuric acid, and on evaporating the solution was deposited as white crystals, that turn blue on exposure to air. The acid is quite stable, however, Heating with hydrochloric acid decomposes it only at temperatures above 200°, the chief products being diphenylamine and sulfuric acid.

.....
(1)

Merz and Weith, Ber. 5, 283 (1872); 6, 1511 (1873).

Merz and Weith also prepared the lead and the potassium salts of the monosulfonic acid. The lead salt, which is only slightly soluble in cold water, was formed by treating the free acid with lead carbonate. The potassium salt was prepared by double decomposition between the barium salt and potassium carbonate, and was purified by recrystallization from alcohol. It forms white, lustrous plates, easily soluble in cold water, but only slightly soluble in cold alcohol.

(2)

Gnehm and Werdenberg reinvestigated the sulfonation of diphenyl amine, since they found that the method of Merz and Weith gave very poor yields. They first tried the action of concentrated sulfuric acid (66 Bé.), of sulfuric acid monohydrate, and of oleum on diphenylamine.

The results of Gnehm and Werdenberg in the sulfonation obtained with the concentrated acid are given in Table I. The following procedure was used: 30 g. diphenylamine was added with stirring over a 15 minute period to 60 g. sulfuric acid (66° Bé.). The mixture was then held at the desired temperature for the indicated length of time. The resulting dark colored mass was cooled, treated with water, and the sulfonation products obtained as barium salts.

.....

(2)

Gnehm and Werdenberg, Z. angew. Chem. 12, 1027, 1051 (1899).

TABLE I

Diphenyl- amine g.	H ₂ SO ₄ g.	Temper- ature	Time Hrs.	Yield of Ba salt g.	% Ba	% Ba salt of monosul- fonic acid	% Ba salt of disul- fonic acid	Res- idue g.
30	60	140° C	0.5	32	29.13	5	95	13
30	60	130°	1.5	18	29.26	4	96	20
30	60	115°	1.5	3	29.00	6	94	28
30	60	98°	5.0	1	29.18	5	95	29
30	60	150°	3.0	65	28.10	18	82	3

The residue consisted of unchanged diphenylamine and of other un-sulfonated bases, probably related to carbazole. It is evident from Table I that sulfonation of diphenylamine with concentrated sulfuric acid produces chiefly the disulfonated product, and a large part of the amine remains unchanged.

The results of sulfonation of diphenylamine with sulfuric acid monohydrate and with a mixture of oleum and sulfuric acid monohydrate are given in Tables II and III respectively. The procedure was essentially the same as the one described in the discussion of the sulfonation with concentrated sulfuric acid.

Since the foregoing did not give high yields of the desired monosulfonic acid, other methods were tried by Gnehm and Werdenberg. It was found better to start with acetyl diphenylamine, because it is more readily sulfonated than the amine. Acetyldiphenylamine

TABLE II

Diphenyl-amine g.	H ₂ SO ₄ · H ₂ O g.	Temperature	Time Hrs.	Yield of Ba salt g.	%Ba	% Ba salt of monosulfonic acid-g.	% Ba salt of disulfonic acid-g.	Residue g.
30	60	110-20 ^o C	2.00	30	28.83	7	93	10
30	60	110-20 ^o	2.00	26	29.00	6	94	14
50	100	110-20 ^o	2.50	40	29.50	0	100	30
80	170	125 ^o	3.25	90	29.30	0	100	30
95	170	105 ^o	2.25	13	28.47	15	85	90
100	180	105 ^o	2.25	13	29.37	0	100	94
100	180	110-115 ^o	2.50	50	29.32	0	100	70
100	200	140 ^o	3.50	160	29.43	0	100	20

TABLE III

Diphenyl-amine g.	H ₂ SO ₄ · H ₂ O g.	Oleum 80% g.	Temperature	Time Hrs.	Yld. of Ba salt g.	%Ba	%Ba salt of monosulfonic acid-g.	% Ba salt of disulfonic acid-g.	Residue g.
10	30	10	0-5 ^o C	.5	0	0	0	0	10
10	20	10	20 ^o	.5	3	27.36	25	75	8
15	25	15	20-25 ^o	.5	7	29.20	4	96	11
20	30	20	20 ^o	.5	8	28.54	14	86	15

can be prepared, and the acetyl group hydrolyzed off to give the desired diphenylamine monosulfonic acid. The hydrolysis can also be carried out without previous isolation of the acetyl compound. Since

there is no advantage in isolating the intermediate product, the following procedure was recommended by Gnehm and Werdenberg: The reaction is carried out in a porcelain beaker provided with a cork fitted with a thermometer and a stirrer. 200 g. fuming sulfuric acid (20%) is cooled to 5°, and 100 g. acetyldiphenylamine ⁽³⁾ ₍₃₎ added in small portions with constant stirring. The mixture is stirred for two hours at 45° on the water bath. It is then poured into 250 cc. water and boiled for three hours. The hydrolysis of the acetyl compound is then complete. The insoluble unreacted diphenylamine is separated by pouring the mixture into a large volume of water and filtering. The filtrate is neutralized with barium carbonate, the barium sulfate filtered off, and the barium diphenylamine monosulfonate separated from the more soluble barium acetate by fractional crystallization. The average yield is 80% theoretical; 17% of the diphenylamine is recovered unchanged.

(4)
Sarver and Kolthoff prepared barium diphenylamine sulfonate for use as a redox indicator by the same method. Their product analyzed 21.88% Ba (calculated for anhydrous barium diphenylamine monosulfonate, 21.64% Ba). Since they were primarily interested in
.....

(3)
A. Claus, Ber. 14, 2365 (1881).

(4)
Sarver and Kolthoff, J. Am. Chem. Soc., 53, 2902 (1931).

the purity of the product, they made no special attempt to get a maximum yield.

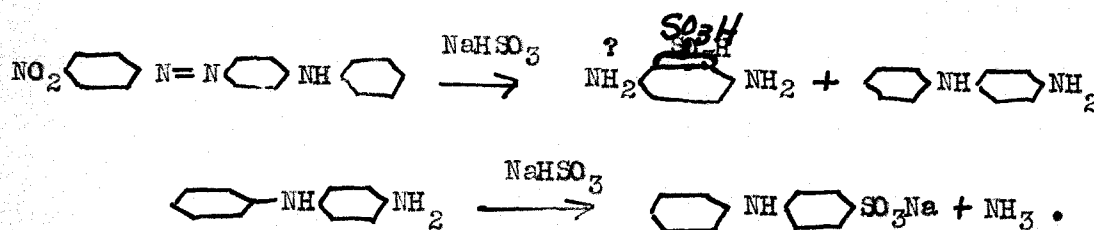
(5)
Gnehm and Werdenberg prepared the copper and sodium salts of diphenylamine monosulfonic acid. The copper salt, prepared by adding an equivalent amount of copper sulfate to the barium salt, is fairly soluble in water. It crystallizes in blue plates, which begin to decompose at 100°. The sodium salt was formed by adding an equivalent quantity of sodium carbonate to the barium salt. It is quite soluble in water. When crystallized from 30% alcohol, it forms white shining plates. They also isolated the free diphenylamine monosulfonic acid by the action of hydrogen sulfide on the copper salt. The acid was readily soluble in water and alcohol, and insoluble in ether.

(6)
Vorohtzov prepared diphenylamine monosulfonic acid by a method which does not involve direct sulfonation. 4-nitro-4'-anilino-azobenzene, prepared from diazotized p-nitraniline and diphenylamine, was found to react with an aqueous-alcoholic solution of sodium bisulfite to form yellow-grey crystals of diphenylamine monosulfonic acid. Ammonia was also identified as a product of the reaction. According to Vorohtzov, the reaction may be approximately represented;

.....

(5)
loc.cit. ref. (2)

(6)
N. Vorohtzov, J.Russ.Phys.Chem.Soc. 47, 1669 (1915); Chem. Ab. 10, 2896 (1916); Ann.chim. 7, 50 (1917).



No yields are reported.

(7)
 Dziewonski and Russocki studied the sulfonation of diphenylamine and confirmed the conclusions of Merz and Weith regarding the proportions of diphenylamine mono- and disulfonic acids formed by the action of concentrated sulfuric acid on diphenylamine. They also investigated the use of chlorosulfonic acid as a sulfonating agent. At temperatures below 90°, an unstable crystalline addition product, $\text{ClSO}_3\text{H} \cdot \text{NH}(\text{C}_6\text{H}_5)_2$, is formed in nitrobenzene solution. This decomposes rapidly at higher temperatures, giving nuclear substitution products, either mono- or disulfonated diphenylamine being obtained according to the proportions of chlorosulfonic acid and amine used. The results are given in Table IV.

TABLE IV

Mols of ClSO_3H per mol of $(\text{C}_6\text{H}_5)_2\text{NH}$	Diphenylamine monosulfonic acid	Mol % of Diphenylamine disulfonic acid	Diphenylamine (unreacted)
0.5	25	5	70
1.0	38	22	40
1.5	34	50	16
2.0	0	99-100	0

(7) Dziewonski and Russocki, Bull.intern.acad.polonaise, 1929A, 506; Chem.Ab., 25, 1503 (1931).

(8)
Straka and Oesper prepared a diphenylamine monosulfonic acid, which, since its action as a redox indicator is not the same, is probably an isomer of the acid previously described. The acid was prepared by heating 50 g. acetyl diphenylamine with 40 g. of an old sample of ethyl sulfate on a water bath for 5 hours. The solution was then refluxed with a solution of sodium ethylate prepared by dissolving 7 g. sodium in 200 cc. ethyl alcohol. When the original dark solid had become white, the alcohol was removed by distillation, the solid residue was dissolved in water, and the solution extracted with ether to remove any unreacted diphenylamine. After the ether was removed by aeration, the solution was treated with concentrated sodium hydroxide solution until a permanent turbidity was obtained. On standing, the solution deposited a voluminous white precipitate, the sodium salt of diphenylamine monosulfonic acid.

(9)
Cohen and Oesper showed that ordinary ethyl sulfate did not give the above product, but that it could be obtained with n-butyl sulfate. The p-toluidine salt of this diphenylamine monosulfonic acid was found to melt at 196-197°.

.....
(8)
Straka and Oesper, Ind.Eng.Chem. (Anal.Ed.) 6, 465 (1934);
Straka, Ph.D. Thesis, University of Cincinnati, (1934).
(9)
Cohen and Oesper, Ind.Eng.Chem. (Anal.Ed.) 8, 364 (1936);
Cohen, Ph.D. Thesis, University of Cincinnati, (1936).

Diphenylamine monosulfonic acid. Use as redox indicator:

(10)

Sarver and Kolthoff were the first to introduce diphenylamine monosulfonic acid as a redox indicator. They showed that it had several advantages over the unsulfonated amine: solubility in water, a strikingly sharp color change, and ability to function in the presence of tungstates.

The oxidized form, diphenylbenzidine sulfonic acid violet, has a reddish violet color resembling permanganate. Its absorption spectrum in the visible range resembles that of diphenylbenzidine violet, although it absorbs more in the red. The speed of formation of the color depends on the oxidation potential of the solution. Thus, with permanganate in acid solution (normal potential, 1.59 v. against normal hydrogen electrode at $[H^+]=1$), the color develops instantly. With dichromate (normal potential, 1.3 v. against normal hydrogen electrode at $[H^+]=1$), even at high hydrogen ion concentrations and with a relatively great excess of oxidizing agent, the color change is slower than with diphenylamine, but the presence of ferrous iron accelerates the rate of oxidation tremendously (induced reaction). The violet color is very marked, and titrations can be made even in highly colored solutions where diphenylamine can not be used. The color change in an iron-dichromate titration

.....
(10)

Sarver and Kolthoff, J. Am. Chem. Soc., 53, 2902 (1931).

takes place at a potential of about .83 - .84 v. (against the normal hydrogen electrode) in sulfuric acid solutions between 0.5 and 2.0 normal.

(11)

Kolthoff and Sarver also extensively studied the use of diphenylamine sulfonic acid in iron-dichromate titrations. They recommend using 7 to 10 drops of .2% solution of barium diphenylamine sulfonate in a volume of 100 to 250 cc. when .1 N dichromate is used as titrant. The solution should be .25 to 3.0 N with sulfuric or hydrochloric acid. Approximately 10 cc. of 25% phosphoric acid should be present for each 50 cc. of solution to reduce the oxidation potential of the ferric - ferrous ion system.

Although the indicator correction in iron-dichromate titrations is somewhat greater for the sulfonated compound than for diphenylamine, Kolthoff and Sarver recommend the use of the sulfonate because of its other advantages.

(12)

Willard and Young were the first to suggest the use of sodium diphenylamine sulfonate for the determination of vanadium in steels containing tungsten, whose presence interferes with the indicator action of diphenylamine. The sample, after solution is complete, is oxidized with permanganate in the cold and the excess permanganate is destroyed by sodium azide. After the excess of azide is removed by

.

(11)

Kolthoff and Sarver, J. Am. Chem. Soc., 53, 2906 (1931).

(12)

Willard and Young, Ind. Eng. Chem. (Anal. Ed.) 4, 187 (1932).

boiling, the vanadic acid is titrated with ferrous sulfate, using sodium diphenylamine sulfonate as indicator. An indicator correction, which may be determined by standardizing the solution against a standard steel, must be used. If the indicator before use is subjected to oxidation with dichromate until the color has become purple, and is then just decolorized with ferrous solution, no blank correction is necessary.

(13)

Willard and Young also recommend the use of this indicator for the determination of chromium and vanadium in tungsten steels.

(14)

Kolthoff and Lingane used diphenylamine sulfonic acid in the determination of uranium. The hexavalent uranium was reduced to the quadrivalent state in a Jones reductor, excess of ferric solution was added, and the ferrous iron thus formed was titrated with dichromate. It was necessary to add the ferric iron because the uranyl ion inhibits the speed of oxidation of the indicator. The procedure may be applied to the indirect determination of small amounts of sodium by precipitating the sodium as sodium zinc uranyl acetate, and determining the uranium as before.

(15)

Bennett recommends the use of the barium salt of diphenylamine

.....
(13

Willard and Young, Ind.Eng.Chem.(Anal.Ed.) § 5, 154, 158 (1933).

(14

Kolthoff and Lingane, J.Am.Chem.Soc. 55, 1871 (1933).

§ 15

W.Bennett, J.Am.Chem.Soc., 56, 277 (1934).

sulfonic acid for the determination of uranium using permanganate, since the use of the indicator made the color change so distinct that the usual correction for the masking of the end-point by the green uranium solution was not necessary.

Diphenylamine sulfonic acid may also be used as indicator in the determination of cobalt ⁽¹⁶⁾. The cobalt is oxidized by sodium perborate, the excess of perborate being removed by boiling. The solution is then treated with excess ferrous iron, and the excess ferrous iron is titrated with dichromate, using diphenylamine sulfonic acid as indicator.

In the colorimetric determination of nitrates, diphenylamine and diphenylbenzidine may with advantage be replaced by the sodium salt of diphenylamine sulfonic acid ⁽¹⁷⁾. The chief advantage lies in the fact that the color developed is more stable.

Lang recommends diphenylamine sulfonic acid in the determination of manganese ⁽¹⁸⁾, when reducing trivalent manganese with ferrous sulfate. The indicator is particularly useful in the presence of tungsten, but it can be used only for small amounts of manganese.

.....
(16)

Sarver, Ind.Eng.Chem. (Anal.Ed.) 5, 275 (1933).

(17)

Kolthoff and Nojonen, J.Am.Chem.Soc., 55, 1448 (1933).

(18)

Lang, Z.anal.Chem. 102, 8 (1935).

(19)
Lang and Gottlieb use diphenylamine sulfonic acid in the titration of quinquevalent molybdenum with vanadate solution. The direct titration is not possible with diphenylamine, and it is necessary to add excess vanadate and back-titrate with ferrous solution. This is avoided with the sulfonated compound. If the indicator is pre-oxidized, the color change arises more rapidly.

(20)
Stegeman and Englis recommend the indicator in the determination of reducing sugars. The cuprous oxide, precipitated by the action of reducing sugars on Fehling's solution, is dissolved in dichromate, and the excess dichromate determined with ferrous sulfate, using barium diphenylamine sulfonate as indicator.

.....
(19)

Lang and Gottlieb, Z.anal.Chem. 104, 1 (1936).

(20)

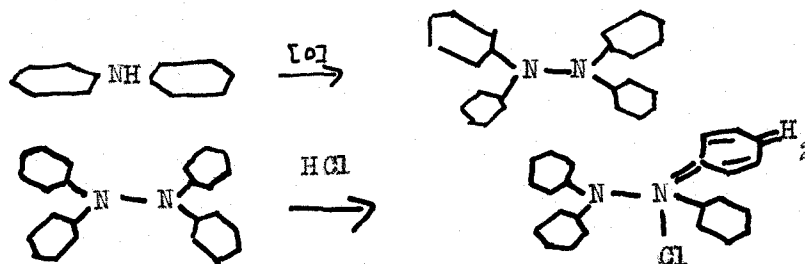
Stegeman and Englis, J.Assoc.Official Agr.Chem. 19, 480 (1936);
Chem.Ab. 30, 7067 (1936).

Diphenylamine monosulfonic acid. Mechanism of color change:

The mechanism of the reaction by which diphenylamine sulfonic acid is converted into the highly colored oxidation product has been studied to some extent, but most of the work has been done with the parent substance, diphenylamine, since it is believed that both the reactions are essentially the same.

The first explanation came from Baeyer, who postulated that the color was due to a salt of the then unknown diphenylhydroxylamine (21). This he believed to be analogous to triphenylcarbinol, which was known to form colored salts.

(22)
Wieland, after considerable study of the question, put forth the following explanation. The first product of the oxidation of diphenylamine is tetraphenylhydrazine, which adds acids to form quinoid-like salts.



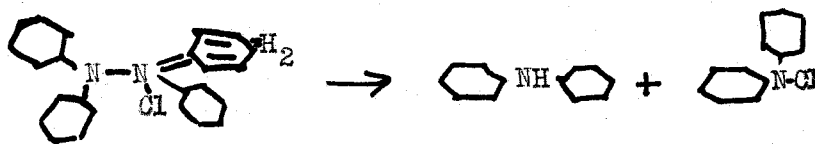
This unstable salt decomposes to form one molecule of diphenylamine and one molecule of diphenylchloramine.

(21)

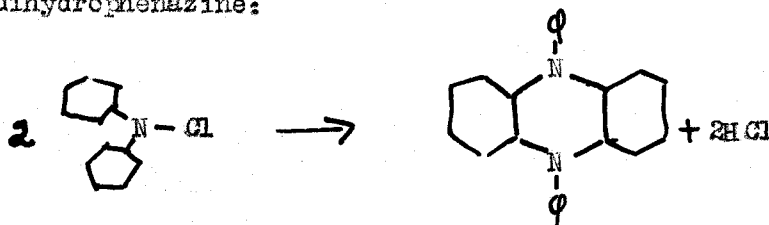
A. Baeyer, Ber. 38, 583 (1905).

(22)

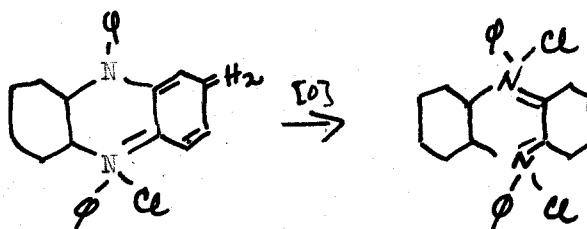
Wieland, Ber. 39, 1499, 3036 (1906); 41, 3478 (1908); 43, 3260 (1910); 45, 495 (1912); 52, 886 (1919); Ann. 381, 200 (1911).



Two molecules of the chloramine thus formed then condense to give diphenyldihydrophenazine:



This substance adds hydrochloric acid forming a green, quinoid, salt-like addition product,



which oxidizes to give the corresponding perazonium compound, the supposed observed blue oxidation product.

(23)

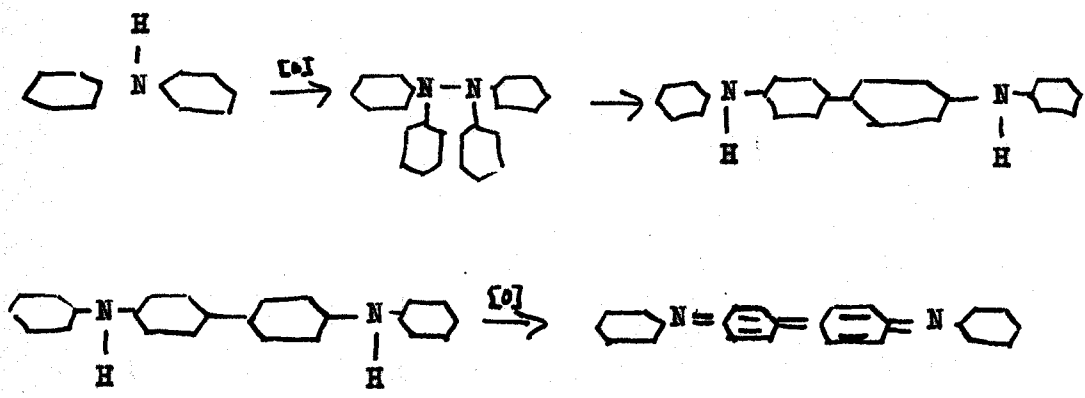
Kehrmann and Micewicz and Kehrmann and Roy (24) postulated that the first stage of the reaction is the formation of tetraphenylhydrazine, which rearranges in acid solution to diphenylbenzidine. The diphenylbenzidine is then oxidized to a quinoid compound, diphenylbenzidine violet, which is blue.

(23)

Kehrmann and Micewicz, Ber. 45, 2641 (1912).

(24)

Kehrmann and Roy, Ber. 55, 156 (1922).



(25)
 Wieland himself later rejected his first proposal and accepted the mechanism just given, but he omitted the formation of tetraphenylhydrazine as an intermediate.

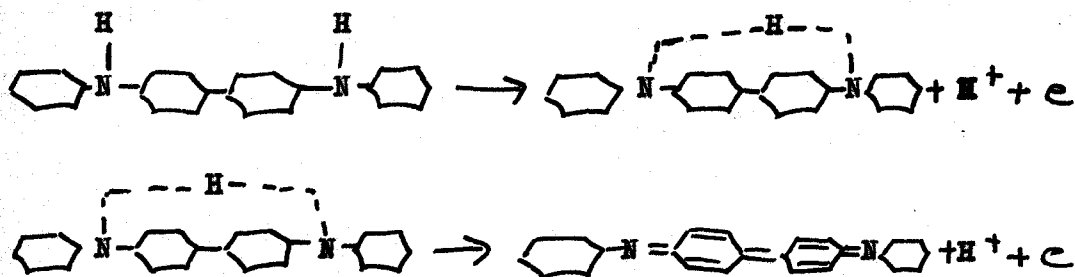
Kehrmann and his coworkers also postulated that the slightly soluble green compound which is sometimes formed as an intermediate in the oxidation of diphenylamine is a molecular compound of diphenylbenzidine and diphenylbenzidine violet. According to more recent views, the green insoluble compound is not a di- but a monomolecular compound of the semiquinone type, in which only one electron has been lost. Sarver and Kalthoff (27) by means of potentiometric titrations

(25)
 H. Wieland, Ber. 46, 3298 (1913).

(26)
 Michaelis, Chem.Rev. 14, 243 (1935); Weitz, Z. Electrochem. 34, 538 (1936).

(27)
 Sarver and Kalthoff, J. Am. Chem. Soc., 59, 24 (1937).

showed that in the case of diphenylbenzidine sulfonic acid (an intermediate in the oxidation of diphenylamine sulfonic acid) the semiquinone and not the meriquinone was formed:



While the foregoing explanation is rather generally accepted, (28) two other mechanisms have been offered. Madelung, Reiss, and Herr studied the blue and violet compounds obtained from the para substituted derivatives of di- and triphenylamine and from the corresponding benzidine compounds, and concluded that the color is not produced by a quinoid structure but by addition compounds of the amines with inorganic salts, whose structures can be interpreted by the Werner (29) Theory. Weitz and Schwechten postulated a similar explanation, but they regard nitrogen as the central atom of the ammonium-like complex, whereas Madelung, Reiss, and Herr believe the metal atom is the central atom.

(28) Madelung, Reiss, and Herr, Ann. 454, 7 (1927).

(29) Weitz and Schwechten, Ber. 59, 2307 (1926); 60, 545 (1927).

Diphenylamine disulfonic acid:

Diphenylamine disulfonic acid (4, 4') was first prepared by
 (30)
 Merz and Weith in 1872. The direct sulfonation of diphenylamine
 with concentrated sulfuric acid was found to give both the mono-
 and disulfonated amines, which were separated as the barium salts.
 The barium salt of the monosulfonic acid is only slightly soluble
 in cold water, while that of the disulfonic acid is readily soluble.
 The mother liquor remaining after the deposition of the barium salt
 of the monosulfonic acid is treated with alcohol, and the resulting
 precipitate of the barium salt of the disulfonic acid is dissolved
 in a little water. Flower-like crystals of the dihydrate separate
 if the aqueous solution is allowed to stand over concentrated sul-
 furic acid.

(31)

Gnehm and Werdenberg obtained the barium salt of the di-
 sulfonate by heating diphenylamine (80 g.) with sulfuric acid mono-
 hydrate (17 g.) for 3 hours at 130-140°, and also by heating di-
 phenylamine (100 g.) with oleum (200 g.) for 3 hours at 110-120°.

The potassium salt was obtained by adding an equivalent amount
 of potassium carbonate to a solution of the barium salt. On adding

(30)

Merz and Weith, Ber. 5, 283 (1872); 6, 1513 (1873).

(31)

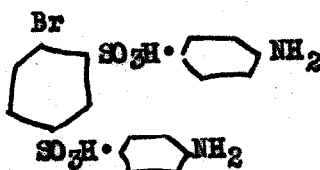
Gnehm and Werdenberg, Z. angew. Chem. 12, 1051 (1899).

alcohol to the filtrate, white crystals with 1.5 molecules of water appeared. The copper salt was formed by evaporating the filtrate obtained from the double decomposition of solutions of the barium salt and of copper sulfate. It is readily soluble in water and contains 4 molecules of water of crystallization.

On evaporating a solution formed by passing hydrogen sulfide into an aqueous solution of the copper salt, a thick dark blue syrup is obtained which does not solidify, although under the microscope it appeared to consist chiefly of small needles. It is readily soluble in alcohol and water.

Djiewoński and Russocki ⁽³²⁾ obtained the disulfonic acid by the action of excess chlorosulfonic acid on a solution of diphenylamine in nitrobenzene at 110-115°. The product was obtained as the magnesium salt, which has 2.5 molecules of water of crystallization. The anilide melts at 239°.

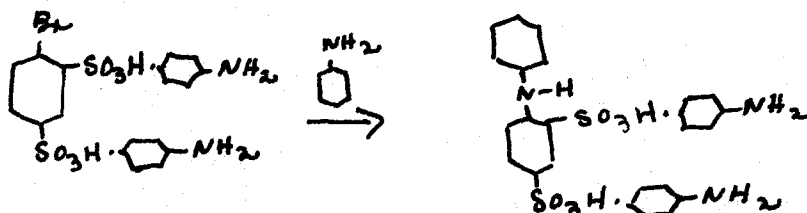
Diphenylamine disulfonic acid (2,4) was first prepared by Fischer ⁽³³⁾ in 1891 by the action of aniline on 1-brombenzenedisulfonic acid (2,4). The first product obtained is the aniline salt,



.....
(32) Djiewoński and Russocki, Bull. intern. acad. polonaise, 1929A, 506; Chem. Ab., 25, 1503 (1931).

(33) P. Fischer, Ber. 24, 3807 (1891).

which crystallizes from water, in which it is readily soluble, in lustrous plates. It is almost insoluble in alcohol, but is soluble in glycerin. Condensation occurs when the salt is refluxed in glycerin solution for several hours.



The reaction mixture was treated with barium hydroxide, the excess aniline removed by steam distillation, and the excess barium hydroxide removed by passing in carbon dioxide. The neutral barium salt of di(phenylaminedisulfonic acid (2,4) precipitates as an amorphous yellowish mass with three molecules of water.

The anilide of the acid forms yellow crystals, melting at 221-222°. It is best prepared by heating bromobenzene disulfonylchloride (2,4) with excess aniline. The reaction mixture is dissolved in a little alcohol, the solution is poured into a dilute hydrochloric acid solution, and the yellow precipitate of the anilide is recrystallized from alcohol. It is quite soluble in alcohol, more difficultly soluble in glacial acetic acid, and slightly soluble in glycerin and water.

Naphthidine Sulfonic Acids:
(34)

Straka and Oesper investigated the properties of naphthidine as a redox indicator, and showed that it functions excellently under the conditions of the usual analytical procedures for iron and chromium. It gives a deep red color with a slight excess of dichromate, the color development being induced by the oxidation of ferrous salts.

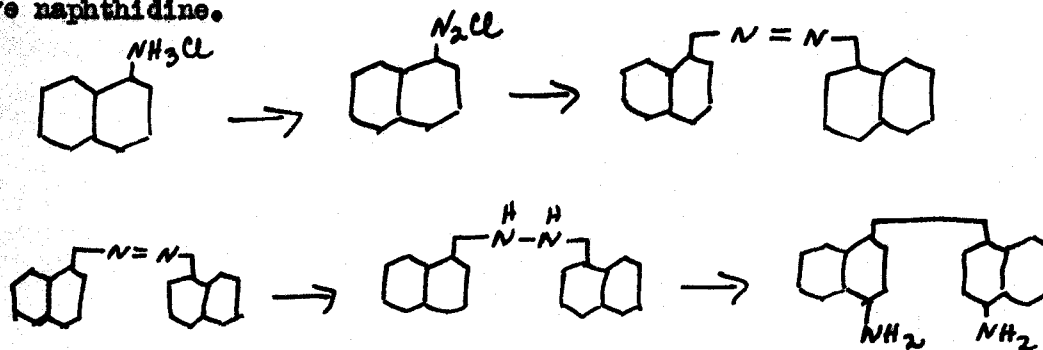
The red oxidation product is stable for a period of 1.5 to 2 minutes after the first excess drop of oxidizing agent has been added, and then gradually fades. Since a color is produced with ferric ions alone, it is necessary to use phosphoric acid to reduce their concentration and oxidation potential. Mercury salts do not interfere with the development and discharge of the color, a fact of importance if stannous chloride is used to reduce the ferric iron as a preliminary to the dichromate titration. Comparative ferrous iron-dichromate determinations with naphthidine, ferricyanide, diphenylamine, and diphenylbenzidine as indicators prove the reliability of naphthidine, which shows a distinct advantage in that the red is in greater contrast to the green of the chromic ion than is the blue developed by the other two internal indicators.

(35)
Cohen and Oesper have developed an improved method for the preparation of naphthidine, which involves the preparation of azo-

• • • • •
(34) Straka and Oesper, Ind.Eng.Chem. (Anal.Ed.), 2, 465 (1934);
Straka, M.A. Thesis, University of Cincinnati (1932).

(35) Cohen and Oesper, Ind.Eng.Chem. (Anal.Ed.) 2, 306 (1936); Cohen,
Ph.D. Thesis, University of Cincinnati (1936).

naphthalene from α -naphthylamine, the reduction of the azo to the hydrazone compound, and the rearrangement of the hydrazone naphthalene to give naphthidine.



Naphthidine is only slightly soluble in water, a disadvantage in its use as a redox indicator. It was thought that naphthidine sulfonic acids would possess all the advantages of naphthidine as a redox indicator, together with the additional advantage of solubility in water. It was expected that the naphthidene sulfonic acids could be prepared in a manner analogous to the preparation of naphthidine.

(36)

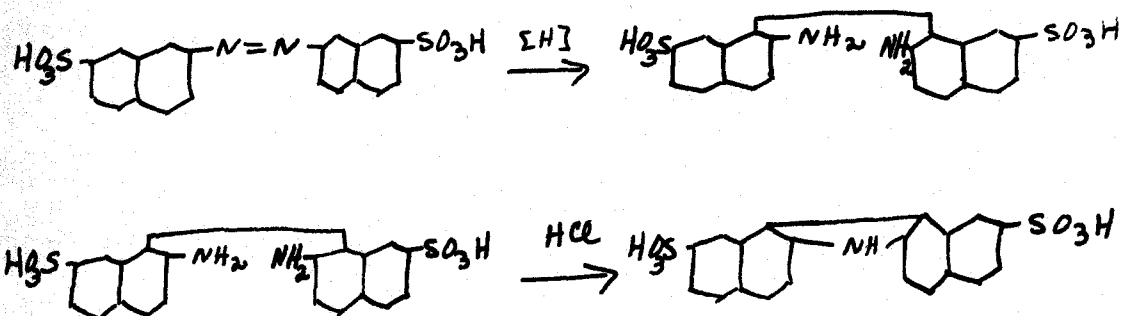
Lange showed that diazonium salts of naphthalene and its derivatives give the corresponding azo compounds when treated with sulfuric acid or its salts.

(36)

M. Lange, D.R.P. 78225, Frđl. 4, 1016.

In this way the sodium salt of azonaphthalene (1,1') disulfonic acid (4,4') was obtained from naphthylamine (1) sulfonic acid (4). The product appeared as small yellow plates, slightly soluble in cold water, and difficultly soluble in hot water. Similarly naphthylamine(2) sulfonic acid (6) produced the sodium salt of azonaphthalene (2,2') di-sulfonic acid (6,6'), bright yellow plates, difficultly soluble in water. (37)

It has been found that sulfonic acid derivatives of(1,1') and (2,2') azonaphthalene when treated with alkaline or acid reducing agents add two atoms of hydrogen to disminodinaphthylsulfonic acids, which may split out ammonia, forming the corresponding dinaphthoiminesulfonic acids.

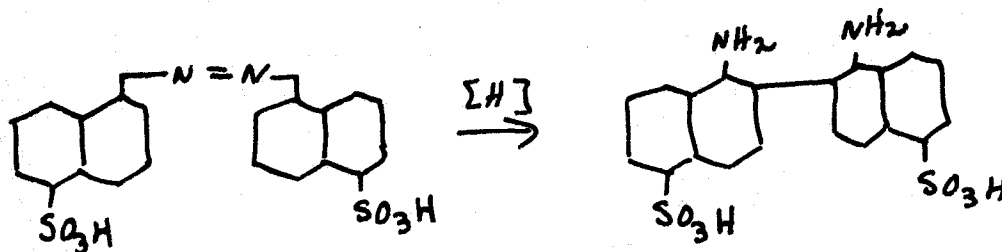


Thus, when azonaphthalene (1,1') disulfonic acid (5,5') is reduced

.....
 (37)

Kalle and Co., D.R.P. 343149, Fwdl. 13, 296 (1921).

with stannous chloride in concentrated hydrochloric acid solution, an acid is obtained in the form of colorless needles, difficultly soluble in hot water. Its alkali salts are readily soluble in water. With nitrous acid it gives a yellow, difficultly soluble diazo compound. On heating with dilute hydrochloric acid at 140° , ammonia is split out. A weakly alkaline solution of the acid on standing with sodium amalgam forms diamino (1,1') dinaphthyl (2,2'). From these reactions it may be concluded that the acid is diamino (1,1') dinaphthyl (2,2') disulfonic acid (5,5').



Iron or zinc and dilute mineral acids can also be used as reducing agents in this reaction.

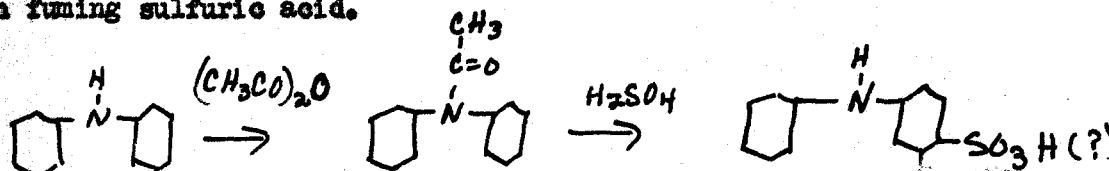
Dinaphthoimine(1,1') disulfonic acid (4,4') is obtained on reduction of azonaphthalene (1,1') disulfonic acid (4,4') with an alkaline solution of sodium hydrosulfite or with zinc dust and

sodium hydroxide. This acid cannot be diazotized, and forms dinaphtho-
imine (1,1') on heating with mineral acids at 130°. Similarly
azonaphthalene (2,2') disulfonic acid (7,7') undergoes reduction
as shown in the equation previously given.

EXPERIMENTAL

Diphenylamine Sulfonic Acids:

The preparation of diphenylamine monosulfonic acid by the method
(38)
of Kolthoff and Sarver was repeated. This method involves the
acetylation of diphenylamine and sulfonation of the acetylated amine
with fuming sulfuric acid.



Kolthoff recommends Claus' (39)
method of preparation of acetyl-
diphenylamine, in which equimolecular quantities of diphenylamine
and acetic anhydride are refluxed for one hour in the presence of a
few drops of sulfuric acid. Kaufmann (40)
states that a better yield and
a purer product can be obtained by refluxing diphenylamine and the
calculated quantity of acetic anhydride in xylene solution for two
hours. Both methods were tried. If commercial diphenylamine was used,

.....

(38) Kolthoff and Sarver, J. Am. Chem. Soc., 53, 2902, (1931).

(39) A. Claus, Ber. 14, 2365 (1881).

(40) A. Kaufmann, Ber. 42, 3480 (1909).

a brown product which could not be recrystallized from ether, as suggested by Claus, was obtained by both methods. However, if the amine is first purified by distillation, Kaufmann's method was found to give a pure white product in 57% yield.

Kolthoff's method of sulfonation was then tried. The sulfonation mixture was heated with water after the sulfonation had occurred to hydrolyze the acetyldiphenylamine sulfonic acid to diphenylamine sulfonic acid and the unreacted acetyldiphenylamine to diphenylamine. The diphenylamine obtained in this way was weighed, in order to determine the extent of the sulfonation. In one trial, 87% of the original acetyl diphenylamine was recovered unsulfonated as diphenylamine after hydrolysis. In another trial, a 21.7% yield of the barium salt of the monosulfonic acid was obtained. This calculation of the yield is based on the total acetyldiphenylamine used.

Since the foregoing method gave rather unsatisfactory results, it was decided to attempt to prepare the diphenylamine sulfonic acid by other procedures. Direct sulfonation with N-pyridinium sulfonic acid (41) was first tried. It has already been shown that this compound is an excellent sulfonating agent.

N-pyridinium sulfonic acid, $C_5H_5NSO_3$, was prepared according to the method of Baumgarten and Marggraff. The acid was obtained as pure white crystals in 85% yield.

.....
(41)

Baumgarten, Ber. 59, 1166, 1977 (1926); Baumgarten and Marggraff, Ber. 64, 1584 (1931).

The action of N-pyridinium sulfonic acid on acetyldiphenylamine was first tried.

32.5 g. acetyldiphenylamine was heated at 160-170° with 41 g. N-pyridinium sulfonic acid for 8 hours. The reaction mixture was then poured into 600 cc. water, hydrolyzed by boiling for 8 hours, and the solution was filtered. 26.0 g. unreacted diphenylamine was recovered in this way. Since the 32.5 g. original acetyldiphenylamine used would give on hydrolysis 26.0 g. diphenylamine, it is evident that N-pyridinium sulfonic acid has practically no action on acetyldiphenylamine.

The action of N-pyridinium sulfonic acid on diphenylamine was next tried.

8.5 g. diphenylamine and 7.9 g. N-pyridinium sulfonic acid were heated for 1 hour on the water bath and then on the oil bath at 140° for 3-4 hours. Hot water was added to the green, glassy mixture, and the insoluble, unreacted diphenylamine was filtered off. The water solution was extracted with ether in order to remove the last traces of diphenylamine. Concentrated sodium hydroxide solution was then added until the solution became turbid. The heavy pale yellow gelatinous precipitate which formed on standing was filtered off, dissolved in ethyl alcohol, and reprecipitated by the addition of ether. The salt was again dissolved in alcohol, carbon dioxide was passed in until

there was no further precipitation of sodium carbonate, and the filtrate was concentrated to incipient crystallization. Since no appreciable amount of precipitate was formed on cooling, ether was added. The white precipitate which formed was filtered off and dried.

With excess dichromate in hydrochloric acid solution, a water solution of the salt gave a deep purple color, similar to that given by Kolthoff's indicator.

The p-toluidine salt of the diphenylamine sulfonic acid thus obtained was prepared according to the method of Fieser⁽⁴²⁾. After one recrystallization from water, the salt melted at 198-199°. The p-toluidine salt of Kolthoff's diphenylamine sulfonic acid was also prepared by the same method, and melted at 198-199°. A mixed melting point of the two p-toluidine salts exhibits no depression. The two sulfonic acids are therefore identical. Cohen and Oesper showed that⁽⁴³⁾ the diphenylamine sulfonic acid prepared by the action of butyl sulfate on diphenylamine gives a p-toluidine salt melting at 196-197°, and forms an oxidized product which differs in color from that produced from Kolthoff's acid. The two sulfonic acids are therefore isomers.

.....
(42)

L. Fieser, *Experiments in Organic Chemistry*, New York: Heath and Co. (1935), p. 140.

(43)

Cohen and Oesper, *Ind. Eng. Chem. (Anal. Ed.)* **8**, 364 (1936); Cohen, Ph.D. Thesis, University of Cincinnati (1936).

Sulfonation of diphenylamine with N-pyridinium sulfonic acid gives excellent yields, as was shown by Table V. However, the

TABLE V

Diphenyl- amine g.	N-pyridin- ium sul- fonic acid g.	Time Hours	Temperature	Diphenylamine recovered un- sulfonated g.
17	24	6	150-170°	3.7
17	32	6	150-170°	1.6

isolation of the diphenylamine sulfonic acid as the sodium salt offered difficulties. The salt separates from the solution on the addition of sodium hydroxide as a gelatinous precipitate, and is quite contaminated with alkali. It was found impossible to recrystallize the sodium salt from water, since it is too soluble, and, on, evaporation of the solution, it forms a gelatinous mass. If the sodium salt is dissolved in ethyl alcohol and reprecipitated with ether, it forms a white powder, but there is a 50% loss. Similar results were obtained using methyl alcohol.

It was therefore decided to attempt the isolation of the diphenylamine sulfonic acid as the barium salt. The following procedure was used. Diphenylamine and N-pyridinium sulfonic acid were heated to the stated temperature for the stated length of time. The green, glassy

reaction mixture was dissolved in water, the insoluble unreacted diphenylamine filtered off, and excess O.P. barium carbonate added. The suspension was heated for 30 minutes, cooled, and filtered. The filter cake that contained barium diphenylamine sulfonate, barium sulfate, and barium carbonate was extracted with hot water. On cooling, a precipitate of barium diphenylamine sulfonate was formed. Evaporation of the solution gave a further yield of salt. The results obtained are given in Table VI.

TABLE VI

Diphenyl- amine g.	N-pyridin- ium sulfon- ic acid-g.	Temper- ature	Time Hrs.	Diphenyl- amine recovered g.	Extrac- tion liquid cc.	Vol. after evapo- ration	Ba * g.
15	30	150-170°	2.5	1.7	800	100	6.5
15	30	150-170°	5.0	1.9	800	dryness	10.0
15	45	150-170°	2.5	0.5	800	"	9.0
15	60	150-170°	2.5	0.0	800	"	10.0
15	30	130°	0.5	1.0	800	"	3.5

* Theoretical yield of barium diphenylamine monosulfonate from 15 g. diphenylamine is 28.1 g.

It is evident from Table VI that a considerable fraction of the diphenylamine sulfonic acid formed is not obtained with this procedure, since the discrepancies between the amount of diphenylamine recovered

unsulfonated and the amount of barium diphenylamine sulfonate obtained are quite great. Since the barium salt of Kolthoff's acid was known to be only slightly soluble in cold water, and since this would be practically completely isolated by the procedure used, it was thought that either another isomeric monosulfonic acid having a soluble barium salt was formed in the reaction, or that possibly di- or trisulfonation was occurring.

To test this possibility, 15 g. diphenylamine was heated with 30 g. N-pyridinium sulfonic acid at 130° for 2.5 hours. The reaction mixture was treated with 100 cc. hot water, the unreacted diphenylamine (1 g.) filtered off, and excess barium carbonate added. The suspension was then heated to boiling and filtered hot. On cooling, 3.5 g. of the white barium salt precipitated. After a second extraction of the mixture of barium salts with the mother liquor, 2 g. additional of barium salt was obtained; a third extraction yielded nothing. The solution was then evaporated to dryness. 26.5 g. of a pale green solid were thus obtained, making the total yield of probably impure product 32 g. The theoretical yield of barium diphenylamine monosulfonate from 15 g. diphenylamine is 28.1 g.

The above experiment shows that sulfonation of diphenylamine with N-pyridinium sulfonic acid gives at least two products, one forming a barium salt slightly soluble in water, and the other a barium salt readily soluble in water.

Similar results were obtained when strontium carbonate was sub-

stituted for barium carbonate, indicating that there is likewise a great difference in the solubilities of the strontium salts of the two products. The strontium salt of the acid giving the slightly soluble barium salt was prepared by double decomposition between a solution of the slightly soluble barium diphenylamine monosulfonate and strontium sulfate. The strontium salt was obtained as white shining crystals. Analysis gave the following results: .3446 g. gave .1106 g. strontium sulfate, corresponding to 15.31% strontium. (Calculated for $C_{24}H_{26}N_2S_2O_6 Sr$, 15.01% strontium.)

The two sulfonated products were prepared and separated in the following manner, to determine whether the acid having the soluble barium salt was a mono- or polysulfonated diphenylamine. 10 g. diphenylamine and 20 g. N-pyridinium sulfonic acid were heated at 170° on an oil bath for 1 hour. The mixture was then boiled with 150 cc. water, cooled, and the unreacted diphenylamine (1.5 g.) filtered off. The filtrate was diluted to 700 cc., excess C.P. barium carbonate was added, and the mixture was heated for 30 minutes and filtered hot. The filtrate was evaporated on the steam bath to 50-60 cc., and the light grey precipitate, A, which had formed was filtered off. When dried it weighed 4.5 g. The filtrate was then evaporated to dryness. 15.5 g. of a light grey powder, B, was thus obtained.

Precipitate A was analyzed for barium by heating a weighed portion (dried at 110° for 2 hours) with concentrated sulfuric acid. .5420 and .5205 g. gave .1957 and .1882 g. barium sulfate respectively, corresponding to 21.25% and 21.28% barium, or an average of 21.27% barium. The calculated percentage of barium in barium diphenylamine monosulfonate, $C_{24}H_{20}N_2S_2O_6Ba$, is 21.68%, which indicates that A is the monosulfonate.

The p-toluidine salt of A was prepared according to the method of Fieser. It formed pale purple crystals, melting at 200-201° after one recrystallization from water. Since the p-toluidine salt of Kolthoff's indicator has a melting point of 198-199°, and since the solubilities of the barium salt and the color of the oxidized form are apparently the same, the two salts are probably identical.

Precipitate B was analyzed for barium by the same method as was used for A. .6437 and .5549 g. samples of B gave .2389 and .2048 g. barium sulfate respectively, corresponding to 21.84 % and 21.72% barium, or an average of 21.78% barium. (Calculated for barium diphenylamine monosulfonate, $C_{24}H_{20}N_2S_2O_6Ba$, 21.68% barium.) This salt is also, therefore, a barium diphenylamine monosulfonate, and is an isomer of A. The p-toluidine salt could not be prepared either by the method of Fieser or of Kamm .

.....
(44)
O. Kamm, Qualitative Organic Analysis. New York: Wiley and Co. (1923). p. 157.

This salt is probably identical with the diphenylamine sulfonic acid prepared by Straka and Oesper ⁽⁴⁵⁾ and Cohen and Oesper ⁽⁴⁶⁾, since it gives with dichromate and hydrochloric acid a red-purple color, not identical with the color obtained with Kolthoff's indicator.

It was next decided to try the effect of solvents on the reaction between diphenylamine and N-pyridinium sulfonic acid. For this purpose, benzene was suitable, since it dissolves diphenylamine readily and N-pyridinium sulfonic acid to a lesser extent.

The effect of N-pyridinium sulfonic acid on benzene alone was first tried. 5 g. N-pyridinium sulfonic acid and 50 cc. benzene were heated on the water bath for 2 hours. The solution was then treated with 100 cc. water, the water layer separated, and excess C.P. barium carbonate added. The solution was heated to boiling, filtered while hot, and evaporated to dryness. 0.4g. of a white solid which contained barium was obtained as a residue. This small amount of sulfonation product indicates that the action of N-pyridinium sulfonic acid on benzene is practically negligible.

10 g. diphenylamine, 20 g. N-pyridinium sulfonic acid and 100 g. anhydrous benzene were heated for one hour on the water

• • • • •
(45)

Straka and Oesper, Ind.Eng.Chem. (Anal.Ed.) 6, 465 (1934).

(46)

Cohen and Oesper, Ind.Eng.Chem. (Anal.Ed.) 9, 364 (1936).

bath. The benzene layer was light yellow, and there was a yellowish semi-solid mass on the bottom of the flask. The benzene was decanted off, and the residue heated with 150 cc. water in which it dissolved. The benzene was extracted with 20 cc. portions of water until no more diphenylamine sulfonic acid was present, as was shown by the fact that a few drops of the last wash portion gave only a faint purple color with excess dichromate and dilute hydrochloric acid. This wash liquid was added to the 150 cc. of water in which the residue had been dissolved; the total volume of water solution at this point was 250 cc. 37.2 g. G.P. barium carbonate (50% excess) was added and the mixture heated to boiling for 30 minutes. The solution was then filtered and the residue was washed with water until free from barium diphenylamine sulfonate. The volume of solution at this point was 400 cc. The solution was evaporated on the steam bath, but no precipitate appeared until the volume had reached approximately 100 cc. The solution was evaporated almost to dryness, and gave 14.7 g. of a light grey powder.

The product was analyzed for barium in the usual way and with the following results. .4928 g. and .5513 g. gave .2635 and .2957 g. of barium sulfate respectively, corresponding to 31.47% and 31.56% barium, an average of 31.52% barium. The result indicates that the product consists of a mixture of 49.7% barium diphenylamine trisulfonate and 50.3% of barium diphenylamine disulfonate. (Calculated

for barium diphenylamine disulfonate, $C_{12}H_{10}NS_2O_6Ba$, 29.53% barium;

for bariumdiphenylamine trisulfonate, $C_{12}H_7N_2S_3O_6Ba_3$, 33.55%

barium.

When these results are compared with those obtained under analogous conditions when no solvent is used, it is seen that the presence of benzene facilitates sulfonation of diphenylamine, since with benzene a polysulfonate and not a monosulfonate is formed.

Another run was made in benzene solution using a molar ratio of diphenylamine to N-pyridinium sulfonic acid of approximately 1:1 instead of the 1:2 previously used. 10 g. diphenylamine and 10 g. N-pyridinium sulfonic acid in 100 g. anhydrous benzene were carried through the previous procedure. 9.3 g. of a light grey powder was thus obtained. The analytical results were: .5729 g. and .5988 g. gave .2843 and .2983 g. barium sulfate respectively, corresponding to 29.20 and 29.32% barium, or an average of 29.26% barium. This analysis agrees with the theoretical value for the disulfonated salt (29.52% barium), indicating that under these conditions the pure disulfonated compound is obtained.

When a ratio of approximately 1 mol diphenylamine to 3 mols N-pyridinium sulfonic acid was used, the other conditions of reaction being the same, 16.9 g. of a light grey powder was obtained from 10 g. diphenylamine and 30 g. N-pyridinium sulfonic acid in

100 g. anhydrous benzene. The product was analyzed with the following results. .6433 and .5754 g. gave .3410 and .3052 g. barium sulfate respectively, corresponding to 31.19% and 31.21% barium, or an average of 31.20% barium. These results indicate that the product consists of a mixture of barium diphenylamine disulfonate (58.4%) and barium diphenylamine trisulfonate (41.6%).

The effect of nitrobenzene on the sulfonation was next tried. 10 g. diphenylamine, 10 g. N-pyridinium sulfonic acid, and 100 g. nitrobenzene were heated on a water bath for one hour. The nitrobenzene layer was brown, and there was a yellow semi-solid mass on the bottom. The nitrobenzene was decanted and the deposit treated with 150 cc. hot water in which it dissolved. The nitrobenzene layer was then extracted with 20 cc. portions of water until a test portion gave almost no purple color with dichromate and dilute hydrochloric acid. The wash liquid was combined with the 150 cc. of solution in which the deposit had been dissolved. The volume at this point was 275 cc. 18.6 g. C.P. barium carbonate (50% excess) was added, the mixture was heated for 45 minutes, and filtered while hot. The residue was washed with hot water until a test portion of the wash solution gave only a faint indicator color. The volume at this point was 600 cc. The solution was evaporated on a steam bath to 100 cc. and the 2.5 g. of light grey-purple powder formed up to this point was filtered off. Analysis

of this product for barium by the usual method gave the following results. .4811 g. and .4881 g. gave .1790 and .1817 g. barium sulfate respectively, corresponding to 21.90% and 21.91% barium. The theoretical percentage of barium in the monosulfonated product is 21.68%, which indicates that the above product is barium diphenylamine monosulfonate.

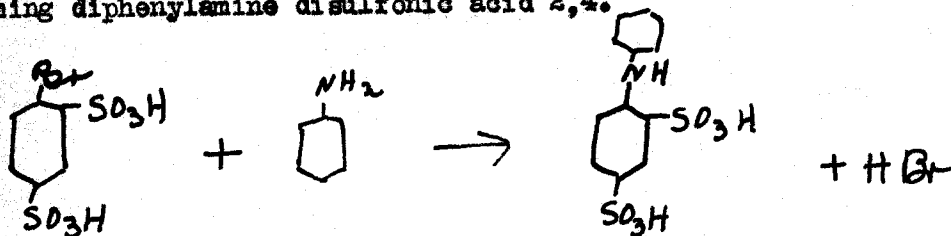
The solution was evaporated to dryness, and 6.5 g. of a light grey powder was thus obtained. Analysis for barium in the usual way gave the following results. .3931 g. and .5736 g. gave .1798 and .2621 g. barium sulfate respectively, corresponding to 26.92% and 26.89 % barium respectively, or an average of 26.91% barium. These results indicate that the product is a mixture of barium diphenylamine monosulfonate (33.3%) and barium diphenylamine disulfonate (66.7%).

Another experiment with nitrobenzene as solvent using higher temperatures was tried. 10 g. diphenylamine, 10 g. N-pyridinium sulfonic acid, and 100 cc. nitrobenzene were refluxed for 1 hour. The reaction mixture was black, and appreciable quantities of a black solid residue insoluble in hot water were formed. The mixture was treated with 200 cc. water, and the water layer separated. 700 cc. water and 18.6 g. barium carbonate C.P. (50% excess) were

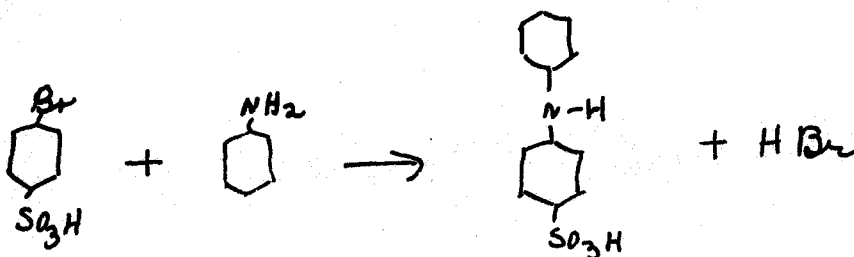
added, and the solution was heated for 45 minutes and filtered while hot. The solution was decolorized by heating with animal charcoal and was evaporated to dryness. 1.8 g. pale tan precipitate was thus obtained. This was not analyzed.

From the above results it is seen that while the use of benzene as a solvent facilitates sulfonation of diphenylamine, nitrobenzene appears to have a deleterious effect.

The direct synthesis of diphenylamine monosulfonic acid was next attempted. Fischer (47) has shown that the sulfonic acid groups ortho and para to the bromine in 1-bromobenzene disulfonic acid 2,4 render the halogen sufficiently reactive to condense with aniline forming diphenylamine disulfonic acid 2,4.



It was thought possible that one sulfonic acid group para to the bromine would have the same effect, although to lesser degree, in activating the halogen, so that the following reaction might occur:



.....
(47) P. Fischer, Ber. 24, 3807 (1891)

The p-brombenzene sulfonic acid was prepared by two methods.

(48)
Ray and Dey obtained the acid in 85% yield by heating brombenzene with the exact quantity or excess of concentrated sulfuric acid and a trace of iodine at 100° for 2 hours. The acid was obtained as the barium salt, from which it was liberated by sulfuric acid. The free acid is deliquescent and forms needles melting at 102-3°.

The method of Ray and Dey was tried, but the yield obtained was only 27.4% of the theoretical. The acid was not pure white, but slightly brown, undoubtedly due to decomposition, and melted at 91-95°, probably because of the presence of moisture.

(49)
Huntress and Carten prepared p-brombenzene sulfonyl chloride by dissolving brombenzene in chloroform and treating with excess chlorosulfonic acid. They report that fluoro- and iodobenzene, as well as several other dihalogenated benzenes, give corresponding sulfones along with the sulfonyl chlorides, but make no mention of this occurring in the case of brombenzene.

Their procedure was carried out, but on a larger scale, 20 g. of brombenzene being used. The product obtained was recrystallized from benzene, and heated with water for several hours to hydrolyze the sulfonyl chloride to the sulfonic acid. Some of the product, however, did not dissolve. The solution was filtered, and the

.....

(48) Ray and Dey, J.Chem.Soc., 117, 1405 (1920).

(49) Huntress and Carten, J.Am.Chem.Soc., 62, 511 (1940).

filtrate, on evaporation, gave 3 g. p-brombenzene sulfonic acid, M.P. 101°. (Literature, 102-103°) The white crystalline product which did not dissolve was filtered off and dried. 4.5 g. was thus obtained (M.P. 172-3°). This was undoubtedly p-p'dibromdiphenylsulfone (M.P., Literature, 172°), which was formed along with the sulfonyl chloride.

The condensation of p-brombenzene sulfonic acid with aniline was then tried. 3.6 cc. aniline, 6.5 g. p-brombenzene sulfonic acid, and 10 cc. glycerin were heated on a reflux for 5 hours. The mixture became red-brown, but the water-soluble material had no indicator action, indicating that the condensation had not occurred.

15 cc. aniline, 3 g. p-brombenzene sulfonic acid and 3 g. potassium carbonate, together with a trace of copper powder, were refluxed for 25 hours. The mixture, which was deep purple, was steam distilled to remove the excess aniline. A few drops of the solution gave with excess dichromate in hydrochloric acid solution the characteristic violet color of diphenylamine sulfonic acid. However, when the solution was heated with animal charcoal, and filtered, it became colorless and was without indicator action. The amount of diphenylamine sulfonic acid obtained in the condensation is, therefore, negligible, and is entirely adsorbed on the charcoal.

A second method for the preparation of p-diphenylamine sulfonic

acid was attempted, the condensation of aniline and sulfanilic acid in the presence of either copper powder (Ullmann condensation), or (50) of benzoic acid or both.

8 g. sulfanilic acid, 40 cc. aniline, and .5 g. benzoic acid were refluxed for several hours. The mixture was extracted with a dilute solution of sodium hydroxide. On acidifying a test portion, and treating with excess dichromate, no indicator action was observed, and the expected condensation had not therefore occurred.

Similar experiments were performed using 8 g. sulfanilic acid, 6 g. aniline hydrochloride, 20 cc. aniline, and .5 g. copper powder, and others using 8 g. sulfanilic acid, 40 cc. aniline, .5 g benzoic acid and .5 g. copper powder. Again the condensation did not occur, since the dilute alkali soluble portion did not possess any indicator action.

.....
(50)

Bayer and Co., D.R.P. 71168, Frdl. 5 516.

Other Secondary Amines and Their Sulfonation Products:

Phenyl- α -naphthylamine:

Phenyl- α -naphthylamine was prepared in 1872 by Girard and (51) Vogt by heating a mixture of α -naphthylamine and aniline hydrochloride for 36 hours in a sealed tube at 230°. The crude product was vacuum distilled, the salt was then formed by passing dry hydrogen chloride into the benzene solution, and the product obtained by treating the hydrochloride with alkali was again distilled. The purified amine melted at 58° and was slightly yellow, but on exposure to air turned red.

(52) Streiff prepared phenyl- α -naphthylamine by heating aniline and α -naphthylamine hydrochloride in a sealed tube for 30 to 36 hours at 240°. Purification was accomplished by distillation and recrystallization from alcohol. The pure product melted at 62°.

(53) Friedlander obtained phenyl- α -naphthylamine in 26% yield

.....
(51) Girard and Vogt, Bull. soc. chim. [2], 18, 67 (1872).

(52) J. Streiff, Ann 209, 152 (1882).

(53) E. Friedlander, Ber. 16, 2075 (1883).

by heating a mixture of α -naphthol, aniline, and calcium chloride in a sealed tube. After distillation, the product was recrystallized from ligroin and then from aqueous alcohol (M.P. 60°).

(54)

Iodine was later found to be a catalyst for the condensation. Knoevenagel prepared the amine in 85% yield by heating α -naphthol, aniline, and a little iodine at $180-200^{\circ}$, and by heating α -naphthylamine, aniline, and iodine at $225-250^{\circ}$. The phenyl- α -naphthylamine was purified by vacuum distillation.

(55)

Hodgson and Marsden found that ammonium iodide was a better catalyst than iodine. They prepared phenyl- α -naphthylamine in 95.2% yield (unpurified) by refluxing aniline (210 g.), α -naphthylamine (221 g.), and ammonium iodide (1.25 g.) for 12 hours, the temperature rising to $180-230^{\circ}$. The crude product, after one recrystallization from ligroin, melted at 59° .

Since phenyl- α -naphthylamine should be similar to diphenylamine in indicator action, it was prepared and tested. The method of Hodgson and Marsden was used. The product, a heavy black oil, was treated with 10% hydrochloric acid several times, then with dilute sodium hydroxide to remove the acid, and finally with pure water.

.....
(54)

H. Knoevenagel, J. prakt. Chem. 2, 89, 17 (1914). Knoll and Co., D.R.P. 241853, Fndl. 10, 180.

(55)

Hodgson and Marsden, J. Chem. Soc., 1181 (1936).

The amine appeared to be produced in fairly high yield, but in the subsequent purification the loss was considerable. Hodgson and Marsden had recommended ligroin as solvent for the recrystallization, but the heavy oil was practically insoluble in the ligroin available. The crude product was found to be quite soluble in hot gasoline, but it did not separate on cooling. The amine separated from the gasoline solution as an amorphous mass on standing. It was found that the amine could be satisfactorily purified by dissolving it in boiling ethyl alcohol, adding water dropwise until the solution was just turbid, heating the solution until clear, and cooling. When the product was recrystallized in this manner five times, a light tan crystalline material was obtained which melted at 59.5-60°. The yield of purified product was 14% of the theoretical.

A dilute solution of the amine in concentrated sulfuric acid was prepared. A few drops of this solution gave a blue-green color similar to that of diphenylamine when treated with excess dichromate in the presence of hydrochloric acid. The color was discharged by the addition of ferrous sulfate.

p-tolyl-*o*-naphthylamine:

(55) Girard and Vogt prepared *p*-tolyl-*o*-naphthylamine by heating *o*-naphthylamine and *p*-toluidine hydrochloride in a sealed tube at 260°, The *p*-tolyl-*o*-naphthylamine melted at 78°, and was colorless but turned red on exposure to air.

(57) Friedlander obtained *p*-tolyle *o*-naphthylamine by heating one mole of *o*-naphthol with two moles *p*-toluidine and one mole calcium chloride in a sealed tube at 280°. The amine was purified by distillation and recrystallization from alcohol (M.P. 78.5 - 79°). (56)

Iodine was later found to be a catalyst for the condensation. Knoevenagel prepared *p*-tolyl-*o*-naphthyl amine by heating *o*-naphthylamine and *p*-toluidine at 260-270° in the presence of a small amount of iodine. The product was purified either by crystallization from alcohol or by vacuum distillation.

(59) Hodgson and Marsden showed that ammonium iodide was a better catalyst for the condensation. The *p*-tolyl-*o*-naphthyl amine was obtained in 49% yield (unpurified) by refluxing *o*-naphthylamine (44.2 g)

p-toluidine (42 g.), and ammonium iodide (.25 g.) for 12 hours, the temperature rising to 250°. After one recrystallization from ligroin

.....
(56) Girard and Vogt, Bull. soc. chim. 2, 18, 68 (1872).

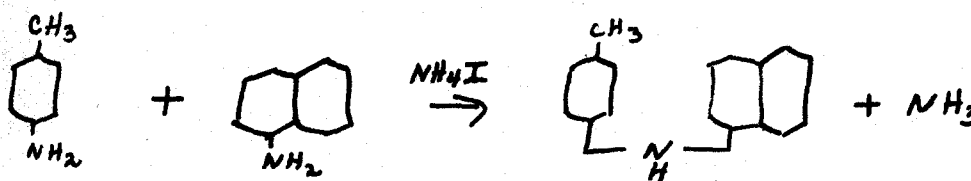
(57) E. Friedlander, Ber. 16, 2081 (1883).

(58) E. Knoevenagel, J. prakt. Chem. 2, 92, 23 (1914); Knoll and Co., D.R.P. 241853, Ptdl. 10, 180.

(59) Hodgson and Marsden, J. Chem. Soc., 1161 (1928).

the amine melted at 78°.

p-tolyl- α -naphthylamine should be similar in indicator properties to diphenylamine. It was therefore prepared and tested for use as a redox indicator. The method of Hodgson and Marsden was also used for the preparation.



The heavy black oil obtained was first steam distilled to remove unchanged primary amines. It was found that p-tolyl- α -naphthylamine could not be recrystallized from the ligroin available as recommended, since it was only slightly soluble in this solvent. Hot gasoline dissolved it readily, but the amine did not separate on cooling. On standing, the solution deposited an amorphous mass.

Recrystallization from aqueous alcohol was next attempted. The amine was dissolved in hot alcohol, water was added dropwise until a turbidity resulted, and the solution was then heated to boiling until clear, a small amount of alcohol being added if necessary. After several recrystallizations in this way, the amine still precipitated as an amorphous black solid. Vacuum

distillation of the amine was therefore tried. The distillate was a light brown oil, which solidified on standing to a light brown crystalline solid. This was recrystallized twice from aqueous alcohol. The resulting light tan crystalline solid melted at 77.5° (lit. $78-79^{\circ}$). The yield of purified p-tolyl- α -naphthylamine was 24% of the theoretical, losses in purification accounting for the low yield.

A dilute solution of the amine in concentrated sulfuric acid gave a blue color with excess dichromate in hydrochloric acid solution, similar to that given by diphenylamine.

d-d'-dinaphthylamine

(60)
Girard and Vogt prepared *d-d'*-dinaphthylamine by heating *d*-naphthylamine and its hydrochloride in a sealed tube at 150°. The amine, after vacuum distillation, melted at 113°.

(61)
Landshoff found that the compound was formed by the action of methyl chloride on *d*-naphthylamine. The product was purified by repeated distillations and finally recrystallized from alcohol

(62)
(M.P. 111°). Calm prepared the amine by heating a mixture of *d*-naphthol, sodium acetate, and ammonium chloride for 8 hours at 270°. Repeated vacuum distillations and recrystallizations from alcohol gave a product melting at 111°. In some cases a crystalline product could not be obtained.

(63)
Benz obtained the amine in 67% yield by heating a mixture of

.....

(60)
Girard and Vogt, Bull. soc. chim. 2 18, 68 (1872).

(61)
Landshoff, Ber. 11, 638 (1878).

(62)
A. Calm, Ber. 15, 615 (1862).

(63)
G. Benz, Ber. 16, 16 (1863).

α -naphthol and zinc ammonium chloride in a sealed tube at 260°. The amine was purified by repeated vacuum distillations followed by repeated recrystallizations from alcohol (M.P. 111°).

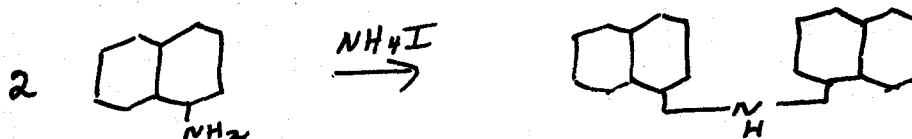
(64)

Meyer and Hofmann prepared the amine by heating α -naphthylamine and its hydrochloride in an autoclave. The crude product was repeatedly recrystallized from alcohol, and the amine was then dissolved in acetic acid and precipitated by cautious addition of water (M.P. 115°).

(65)

Hodgson and Marsden used ammonium iodide as catalyst. They heated α -naphthylamine (57.2 g) and ammonium iodide for 15 hours, the temperature rising to 250°. The crude α -dinaphthylamine (51.5 g.) was recrystallized once from ligroin (M.P. 110°).

Since it was decided to test α -dinaphthylamine for indicator action, the amine was prepared according to the Method of Hodgson and Marsden.



The heavy black oil obtained could not be recrystallized from

.....
(64)

Meyer and Hofmann, *Monatsh.* 27, 706 (1916).

(65) Hodgson and Marsden, *J. Chem. Soc.*, 1161 (1938).

ligroin or from gasoline, since it was only slightly soluble in the former and very readily soluble in the latter even at room temperature. The amine was dissolved in hot alcohol and water was added dropwise until a turbidity occurred; the solution was then heated until clear and allowed to cool. The amine separated as a black oil, even after the attempted recrystallization was repeated 3 or 4 times. The amine was therefore vacuum distilled. The distillate was a dark brown oil which solidified to a dark crystalline solid on standing. The product was recrystallized several times from aqueous-alcohol, and then twice from a glacial acetic acid - water mixture. The purified amine was a tan crystalline product, which melted at $111-2^{\circ}$ (Lit. 115°). Yield, 7% of theoretical.

A dilute solution of the amine in concentrated sulfuric acid gave a blue-purple color with excess dichromate in hydrochloric acid solution.

Sulfonated Secondary Amines:

Phenylnaphthylamine (1) sulfonic acid (3) can be prepared by heating naphthylamine (1) sulfonic acid (3) with aniline and aniline hydrochloride at 140°⁽⁶⁶⁾. The acid and its sodium salt are somewhat soluble in water.

Phenylnaphthylamine (1) sulfonic acid (4) can be prepared by heating naphthionic acid with aniline and aniline hydrochloride at 160° for 10 hours.⁽⁶⁷⁾ The acid, which is isolated as the calcium salt, forms colorless plates, somewhat soluble in water. The sodium salt is readily soluble in water.

Better yields of the acid are obtained by heating a mixture of naphthol (1) ethyl ether sulfonic acid (4) with aniline to boiling for 15 minutes.⁽⁶⁸⁾

Phenylnaphthylamine (1) sulfonic acid (5) is prepared by heating naphthylamine (1) sulfonic acid (5) with aniline and aniline hydrochloride at 100-140°.⁽⁶⁹⁾ The acid is slightly soluble

.....

(66) Bayer and Co., D.R.P. 70349, Frdl. 3, 513.

(67) Idem.

(68) Witt and Schneider, Ber. 34, 3184 (1901).

(69) Loc.cit.ref. (66).

in water. The sodium salt forms plates, difficultly soluble in water.

Phenyl-naphthylamine (1) sulfonic acid (6) is prepared by heating naphthylamine (1) sulfonic acid (6) with aniline and aniline hydrochloride at 160-170°, (70) or by heating naphthylamine (1) disulfonic acid (4,6) with aniline in the presence of a small amount of benzoic acid. (71) The acid is practically insoluble in water. Its sodium salt forms plates, difficultly soluble in water.

Phenyl-naphthylamine (1) sulfonic acid (7) is prepared by heating naphthylamine (1) sulfonic acid (7) with aniline and aniline hydrochloride at 160-170° (72), or by heating naphthylamine (1) disulfonic acid (4,7) with aniline in the presence of a small amount of benzoic acid. (73) The acid is difficultly soluble in water. The sodium salt forms needles, readily soluble in water.

• • • • •

(70)
Loc.cit.ref. (66).

(71)
Akt.-Ges.f. Anilin f., D.R.P. 159,353 ; Frdl. 8, 168.

(72)
Loc.cit.ref. (66).

(73)
Loc.cit.ref. (71).

Phenyl-naphthylamine (1) sulfonic acid (8) is prepared by heating naphthylamine (1) sulfonic acid (8) with aniline and aniline hydrochloride at 160-170°⁽⁷⁴⁾, by heating the acid with aniline and aniline hydrochloride in the presence of water at 140° under pressure⁽⁷⁵⁾, or by heating naphthylamine (1) disulfonic acid (4,8) with aniline at 180°⁽⁷⁶⁾. The acid forms plates, difficultly soluble in water. The sodium salt is very readily soluble in water.

Since N-pyridinium sulfonic acid sulfonates diphenylamine, its action on phenyl- α -naphthylamine was investigated. It was found that phenyl- α -naphthylamine monosulfonic acid could be prepared in this way.

8 g. phenyl- α -naphthylamine and 8.4 g. N-pyridinium sulfonic acid were heated at 150-170° for 5 hours. The reaction mixture was cooled, treated with 50 cc. hot water, and the insoluble phenyl- α -naphthylamine filtered off. Concentrated

.....

(74) Loc.cit.ref. (66).

(75) Kalle and Co., D.R.P. 170630, *Frdl. S.* 168.

(76) Loc.cit.ref. (71).

sodium hydroxide was added to the filtrate until it was turbid. After standing, the solution deposited a white precipitate. This was heated with 200 cc. ethyl alcohol, the solution filtered, and 150 cc. ether added to precipitate the salt. A white powder weighing 2 g. was obtained in this way.

The product was analyzed for sodium in the following manner. A weighed sample was heated to carbonization in a platinum crucible, a few crystals of ammonium sulfate and a few drops of water were added, and the contents of the crucible were ignited cautiously. .4030 g. and .3436g. gave .0923 and .0774 g. sodium sulfate respectively, corresponding to 7.41% and 7.29% sodium, an average of 7.55% sodium. (Calculated for sodium phenyl- α -naphthylamine mono-sulfonate, $C_{16}H_{12}NSO_3Na$, 7.17% sodium.)

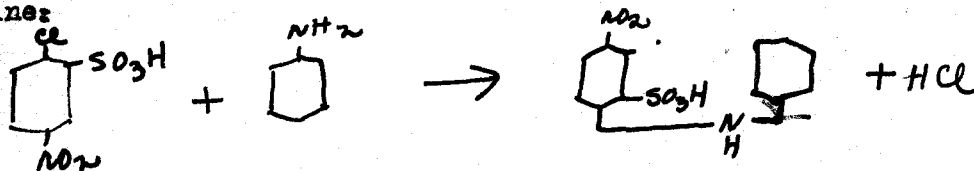
Corresponding attempts were made to prepare the sulfonated p-tolyl- α -naphthylamine and $\alpha\alpha'$ -dinaphthylamine, but these sulfonic acids could not be isolated as the sodium salts by the foregoing procedure.

(4) nitrodiphenylamine sulfonic acid (2) :
(77)

Walden and Edmonds have shown that p-nitrodiphenylamine functions as a redox indicator, giving a reddish-violet oxidation product with strong oxidizing agents. Its oxidation potential was found to be about 0.2 volts higher than that of diphenylamine sulfonic acid. Six dinitro derivatives of diphenylamine were also studied by these workers, but no color change was observed when these materials were treated with ceric or permanganate ions, or with sodium bismuthate in acid solution. Apparently the oxidation potential required is raised so much by the second nitro group that these powerful oxidizing agents are incapable of producing the reaction.

It was decided to prepare a diphenylamine derivative containing one nitro and one sulfonic acid group, and to test it for indicator action. For this purpose, (4) nitrodiphenylamine sulfonic acid (2) was chosen.

Fischer (78) prepared (4) nitrodiphenylamine sulfonic acid (2) by heating (2) chloro (5) nitrobenzene sulfonic acid with excess aniline:



(77)

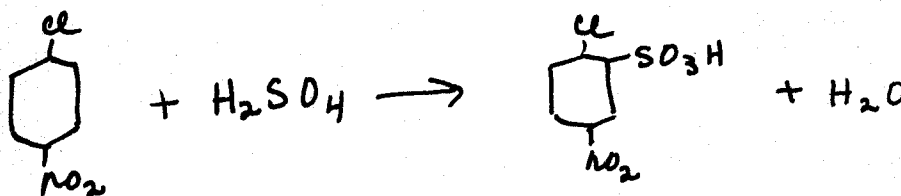
Walden and Edmonds, Chem.Rev. 16, 81 (1935).

(78)

P. Fischer, Ber. 24, 3798 (1891).

(79)

Ullmann and Dahmen prepared the acid by heating the sodium salt of (2) chloro (5) nitrobenzene sulfonic acid with aniline at 180-5° in the presence of glycerin and calcium carbonate. The acid was found to form olive-green plates from hydrochloric acid solution, and to be very readily soluble in alcohol and in water. The (2) chloro (5) nitrobenzene sulfonic acid to be used in the preparation of (4) nitrodiphenylamine sulfonic acid (2) was prepared according (80) to the method of Ullmann and Jungel by heating p-chlornitrobenzene with 20% fuming sulfuric acid for 6 hours at 160°.



The sodium salt of the (2) chloro (5) nitrobenzene sulfonic acid was then condensed with aniline according to the method of Ullmann and Dahmen previously discussed. The resulting green-yellow sodium salt of (4) nitrodiphenylamine sulfonic acid (2) is readily soluble in water. A dilute solution of the salt was tested for indicator action with .1 N dichromate in hydrochloric acid solution. It was found that a red oxidation product is produced immediately, but the color fades

..... V.

(79)

Ullmann and Dahmen, Ber. 41, 3746 (1908).

(80)

Ullmann and Jungel, Ber. 42, 1077 (1909).

very quickly. For this reason, (4) nitrodiphenylamine sulfonic acid (2) is not suitable for use as a redox indicator.

2-7 diamino fluorene:

Since 2-7 diamino fluorene can replace benzidine successfully
(81) in many qualitative tests, it was thought that it might also
function, as does benzidine, as a redox indicator. It has already
(82) been found by Guglielmelli and Ruiz that 2-7 diamino fluorene
gives a blue-green color when treated with a very dilute chloride
solution, and a deep blue precipitate with potassium permanganate.
The presence of oxidase or peroxidase in milk or blood can also
(83) be detected by it. Schmidt and Hinderer reported its use in
the detection of persulfates and peroxidases, and mention that it
has the advantages over benzidine of greater sensitivity and solu-
(84) bility. Like diphenylamine, it gives an insoluble tungstate.

2-7 diamino fluorene was prepared from fluorene by nitration
with fuming nitric acid and reduction of the dinitro to the diamine
(85) compound according to the method of Schmidt and Hinderer . It

.

(81) Feigl, Qualitative Analysis by Spot Tests; Inorganic and Organic Applications. Trans. by J. Matthews. New York; Nordemann (1939), p. 208.

(82) Guglielmelli and Ruiz, Anales asocn. quim. Argentina, 17, 189 (1929); Chem. Ab. 24, 1057 (1930).

(83) Schmidt and Hinderer, Ber. 65, 87 (1932).

(84) Loc. cit. ref. (82).

(85) Schmidt and Hinderer, Ber. 64, 1793 (1931).

was found that the nitration gave a good yield of the dinitro compound, but in the purification, which required recrystallization from large quantities of glacial acetic acid, a considerable amount of the product was lost. The yield of purified 2-7 dinitro fluorene was 25.8%.

The dinitro fluorene was reduced with tin and hydrochloric acid to the diamino compound, which precipitated as the tin double salt. 2-7 diamino fluorene hydrochloride was obtained by passing hydrogen sulfide into the solution of the tin double salt and evaporating the solution to crystallization.

2-7 diamino fluorene hydrochloride is a white crystalline solid, readily soluble in water. A solution of the hydrochloride gradually turns green on exposure to air. In neutral or slightly alkaline solution it gives a blue-green color with oxidizing agents. An acid solution treated with excess dichromate gives a blue-green color which is reversibly discharged by ferrous ions, provided acetate is present. In an unbuffered acid solution no definite color change can be observed. In order to get a color change in an iron-dichromate titration when the amine is used as indicator, tartrates or fluorides must be present to reduce the ferric ion concentration, and sodium acetate must be used if acid is present. Even when these precautions were taken, however, reproducible end points could not be obtained with .1 M dichromate

and .1 N ferrous sulfate solutions, although sharp color changes were observed. The results varied over a range of 1%.

Because of the necessity of using neutral or slightly alkaline solutions and the vacillation of the end point, 2-7 diamino fluorene cannot be used as an indicator in iron-dichromate titrations.

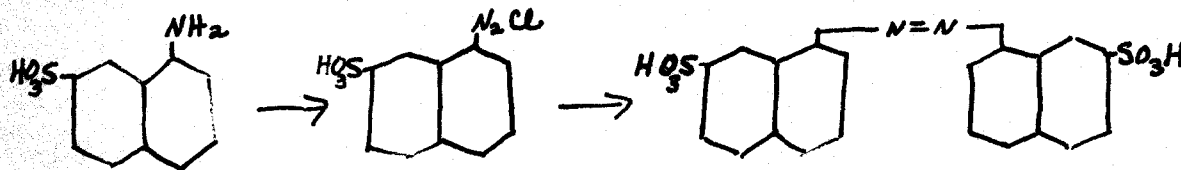
Naphthidine Sulfonic Acids:

(86) (87)
Straka and Oesper and Cohen and Oesper have shown

that naphthidine, NH_2  NH_2 , is a highly satisfactory

redox indicator. Since however, it has the disadvantage of being but slightly soluble in water, it was decided to attempt the preparation of a sulfonic acid derivative, which would be expected to be soluble.

Naphthidine disulfonic acid (6,6') (or possibly the unrearranged hydrazo compound) was prepared by diazotization of naphthylamine (1) sulfonic acid (7), and treatment of the diazo compound with sodium sulfite, forming azonaphthalene(1,1') disulfonic acid (7,7'). The azo compound was reduced, rearrangement probably taken place at the same time, with tin and hydrochloric acid.

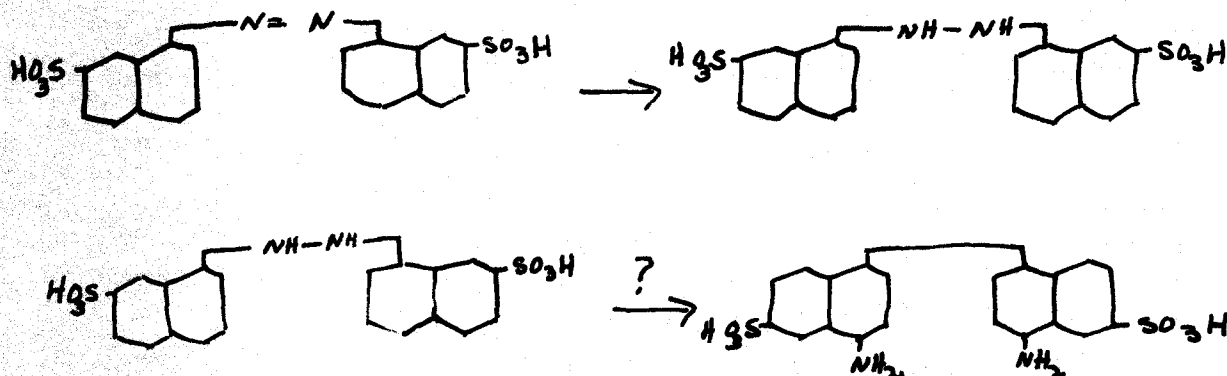


.....
(86)

Straka and Oesper, Ind.Eng.Chem. (Anal.Ed.) 6, 465 (1934);
Straka, Ph.D. Thesis, University of Cincinnati (1934).

(87)

Cohen and Oesper, Ind.Eng.Chem. (Anal.Ed.) 8, 364 (1936);
Cohen, Ph.D. Thesis, University of Cincinnati (1936).



Commercial naphthylamine (1) sulfonic acid (7) was purified (88) in the following manner. The acid was dissolved in strong sodium carbonate solution, heated with animal charcoal, and filtered. The free acid was precipitated with hydrochloric acid, filtered, and washed. This purification was repeated twice. The acid was then practically white, but on exposure to air turned purple.

The acid was diazotized and treated with sodium sulfite to form the azo compound according to the method of Lange (89). 22 g. naphthylamine (1) sulfonic acid (7) was suspended in 400 cc. water, 30 cc. concentrated hydrochloric acid was added, the mechanical stirrer was started, and the solution was cooled to 0° .

(88) Whitmore and Gebhart, Ind. Eng. Chem. (Anal. Ed.) 10, 654 (1938).

(89) Lange, D.R.P. 78225, Fndl. 4, 1016.

A cold solution of 7 g. sodium nitrite in 80 cc. water was then slowly stirred in. A cold solution of 25 g. sodium acetate in 100 cc. water was slowly run in, the temperature still being maintained at 0-5°. A cold solution of 15 g. sodium sulfite in 150 cc. water was then slowly added. Nitrogen was evolved, and the solution became red-brown. On making the solution alkaline with sodium hydroxide, the sodium salt of azonaphthalene (1,1') disulfonic acid (7,7') was obtained as a red-orange powder. The solution was heated to coagulate the precipitate, cooled, and filtered. The sodium salt was recrystallized once from water. 7.5 g. of the purified salt was obtained in this way.

The salt was analyzed for sulfur by the Parr Bomb method. .2079 g. and .2893 g. gave .2020 g. and .2736 g. barium sulfate respectively, corresponding to 13.34% and 12.98% sulfur, or an average of 13.16% sulfur. (Calculated for sodium azonaphthalene(1,1') disulfonate (7,7'), $C_{20}H_{12}N_2S_2O_6Na_2$, 13.18 % sulfur.)

The sodium salt of the azo compound was reduced to the hydrazo compound according to the method of Kalle and Co. (90). Rearrangement in the acid solution to the naphthidine compound probably occurred at the same time.

.....
(90)

Kalle and Co., D.R.P. 545149, Frdl. 13, 296.

10 g. sodium azonaphthalene (1,1') disulfonate (7,7') was heated on a water bath with a solution of 11 g. stannous chloride in 50 cc. concentrated hydrochloric acid for 30 minutes. The red color of the azo compound disappeared, and a white precipitate was formed. The solution was cooled, filtered, and washed with concentrated hydrochloric acid. The product thus obtained was dissolved in a solution of 25 g. potassium carbonate in 400 cc. water. The solution was heated to boiling, and filtered. On cooling, white plates were deposited. The solution was filtered, and the solid product was recrystallized once from water. 2.7 g. of a white shining product, stable in air, was thus obtained.

The product was analyzed for potassium in the following manner. A weighed sample was heated to carbonization in a crucible, a few drops of water and a few crystals of ammonium sulfate were added, and the contents were ignited cautiously. .5313 g. and .6182 g. gave .1774 g. and .2068 g. potassium sulfate respectively, corresponding to 14.98% and 15.00% potassium, or an average of 14.99% potassium. The theoretical value for the potassium salt of either hydrazonaphthalene (1,1') disulfonic acid (7,7') or naphthidine disulfonic acid (6,6'), $C_{20}H_{14}N_2S_2O_6K_2$ is 15.00% potassium.

The product gave a red oxidation product similar to that pre-

duced by naphthidine, when treated with excess dichromate in hydrochloric acid solution. The color is reversibly discharged by ferrous ions.

SUMMARY

- (1) The sulfonation of diphenylamine by N-pyridinium sulfonic acid has been studied. The effect of using benzene and nitrobenzene as solvents for the reaction was determined.
- (2) The strontium salt of a diphenylamine monosulfonic acid has been prepared.
- (3) The following compounds have been prepared and found to function as redox indicators:
 - (a) p-tolyl- α -naphthylamine
 - (b) phenyl- α -naphthylamine
 - (c) $\alpha\alpha'$ -dinaphthylamine
 - (d) a phenyl- α -naphthylamine monosulfonic acid
- (4) 2-7 diamino fluorene was prepared and found to possess indicator action, but quantitative tests showed that it was unsatisfactory in iron-dichromate titrations.
- (5) 4-nitrodiphenylamine sulfonic acid-2 was prepared and found to be unsatisfactory as a redox indicator.
- (6) Naphthidine disulfonic acid (6,6') (or possibly its isomer hydrazonephthalene (1,1') disulfonic acid (7,7')) was prepared and found to function satisfactorily as a redox indicator.

BIBLIOGRAPHY

1. Akt.-Ges.f.Anilinf. D.R.P. 159353, *Frdl.* 8, 166.
2. Baumgarten, *Ber.* 59, 1166, 1977 (1926).
3. Baumgarten and Marggraff, *Ber.* 64, 1584 (1931).
4. A.Baeyer, *Ber.* 38, 583 (1905).
5. Bayer and Co., D.R.P. 70349, *Frdl.* 3, 513.
6. Bayer and Co., D.R.P. 71168, *Frdl.* 3, 516.
7. W. Bennett, *J.Am.Chem.Soc.*, 56, 277, (1934).
8. G.Benz, *Ber.* 16, 16 (1883).
9. W. Bottger, Editor, *Newer Methods of Volumetric Chemical Analysis*. Trans. by R.E. Oesper. New York: Van Nostrand (1938).
10. A.Calm, *Ber.* 15, 615 (1882).
11. A.Claus, *Ber.* 14, 2365 (1881).
12. Cohen, Ph.D. Thesis, University of Cincinnati (1936).
13. Cohen and Oesper, *Ind.Eng.Chem. (Anal.Ed.)* 8, 364 (1936).
14. Djiewonski and Russocki, *Bull. intern.acad.polonaise*, 1929A, 506; *Chem.Ab.* 25, 1503 (1931).
15. Feigl, *Qualitative Analysis by Spot Tests: Inorganic and Organic Applications*. Trans. by J. Matthews. New York: Norde-
mann (1939).
16. L.Fieser, *Experiments in Organic Chemistry*. New York: Heath &
Co. (1935).
17. P.Fischer, *Ber.* 24, 3807 (1891).
18. E.Friedlander, *Ber.* 16, 2075 (1883).
19. Girard and Vogt, *Bull.sec.chim.* 2, 18, 67 (1872).

20. Gnehm and Werdenberg, Z. angew. Chem. 12, 1027, 1051 (1899).
21. Guglielmelli and Ruiz, Anales asocn. quim. Argentina, 17, 189 (1929); Chem. Ab. 24, 1057 (1930).
22. Hodgson and Marsden, J. Chem. Soc. 1181 (1938).
23. Huntress and Garten, J. Am. Chem. Soc. 62, 511 (1940).
24. Kalle and Co., D.R.P. 170630, Frdl. 8, 168.
25. Kalle and Co., D.R.P. 343149, Frdl. 13, 296.
26. O. Kamm, Qualitative Organic Analysis. New York: Wiley and Co. (1923).
27. Kaufmann, Ber. 42, 3480 (1909).
28. Kehrman and Micewicz, Ber. 45, 2641 (1912).
29. Kehrman and Roy, Ber. 55, 156 (1922).
30. Knoevenggel, J. prakt. Chem. 2, 89, 17 (1914).
31. Knoll and Co., D.R.P. 241853, Frdl. 10, 180.
32. Kolthoff and Lingane, J. Am. Chem. Soc. 55, 1871 (1933).
33. Kolthoff and Neponen, J. Am. Chem. Soc., 55, 1448 (1933).
34. Landshoff, Ber. 11, 638 (1878).
35. Lang, Z. anal. Chem. 102, 8 (1935).
36. Lang and Gottlieb, Z. anal. Chem. 104, 1 (1936).
37. Lange, D.R.P. 78225, Frdl. 4, 1016.
38. Michaelis, Chem. Rev. 16, 243 (1933).
39. Michaelis, Oxidation-Reduction Potentials, Trans. by L. Flexner, Philadelphia: Lippincott (1930).

40. Ray and Dey, *J. Chem. Soc.* 117, 1408 (1920).
41. Sarver, *Ind. Eng. Chem. (Anal. Ed.)* 5, 275 (1933).
42. Sarver and Kolthoff, *J. Am. Chem. Soc.* 53, 2902 (1931).
43. Sarver and Kolthoff, *J. Am. Chem. Soc.* 53, 2906 (1931).
44. Sarver and Kolthoff, *J. Am. Chem. Soc.* 59, 24 (1937).
45. Schmidt and Hinderer, *Ber.* 65, 87 (1932).
46. Schmidt and Hinderer, *Ber.* 64, 1793 (1931).
47. Stegeman and Englis, *J. Assoc. Official Agr. Chem.* 19, 480 (1936); *Chem. Ab.* 30, 7067 (1936).
48. Straka and Oesper, *Ind. Eng. Chem. (Anal. Ed.)* 6, 465 (1934).
49. L. Straka, Ph.D. Thesis, University of Cincinnati (1934).
50. J. Streiff, *Ann.* 202, 152 (1882).
51. Ullmann and Dalmen, *Ber.* 41, 3746 (1908).
52. Ullmann and Jungel, *Ber.* 42, 1077 (1909).
53. Vorozhtzov, *J. Russ. Phys. Chem. Soc.* 47, 1669 (1915); *Chem. Ab.* 10, 2896 (1916); *Ann. Chim.* 7, 50 (1917).
54. Walden and Edmonds, *Chem. Rev.* 16, 81 (1935).
55. Weitz, *Z. Electrochem.* 34, 538 (1928).
56. Weitz and Schwechten, *Ber.* 59, 2307 (1926).
57. Weitz and Schwechten, *Ber.* 60, 545 (1927).
58. Whitmore and Gebhart, *Ind. Eng. Chem. (Anal. Ed.)* 10, 654 (1938).
59. Wieland, *Ber.* 39, 1499, 3036 (1906); 41, 3478 (1908); 43, 3260 (1910); 45, 495 (1912); 52, 886 (1919); *Ann.* 381, 200 (1911); *Ber.* 46, 3298 (1913).

60. Witt and Schneider, Ber. 34, 3184 (1901).
61. Willard and Young, Ind.Eng.Chem. (Anal.Ed.) 4, 187 (1932).
62. Willard and Young, Ind.Eng.Chem. (Anal.Ed.) 5, 154, 158 (1933).