

**THE PREPARATION OF SOME NEW AZO
DERIVATIVES OF GUAIACOL I**

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THE PREPARATION
OF
SOME NEW AZO DERIVATIVES OF GUAIACOL I

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OF GUAIACOL I

INTRODUCTION

The literature records but few investigations of the preparation and properties of guaiacol coupled with diazotized amines. This would seem rather odd in view of the decided value that the azo derivatives of a number of closely related phenols have proved to possess, not only as dyes, but also as antiseptics and bactericides. The preparation of the free bases of benzene-azo-guaiacol and guaiacol dis-azo benzene have been reported¹, and a number of acetyl derivatives of azo guaiacol compounds have been investigated², but the guaiacol compounds analagous to such dyes as methyl orange, Congo red, and Orange-II are not described in the literature.

In this investigation a number of dyes have been prepared by coupling guaiacol with various diazotized amines. Some of the physical properties of these compounds have been noted. In all cases the sodium salt of the dye has been prepared, and in a few instances the free base has been satisfactorily isolated, although in the majority of instances the free base was precipitated as a viscous, tarry substance which resisted attempts at recrystallization. In an attempt

¹Jacobson, Jaenicke and Meyer: Ber. 29, 2685.

²Columbans and Leonardi: Atti. Accod. Lincei 16 (ii),

to secure an easily recrystallizable modification of the dyes, the acetyl derivatives of a few were prepared, but these only assumed crystalline form in the case of the acetyl derivatives of benzidine azo guaiacol and p- toluidine azo guaiacol.

PREPARATION OF THE DYES

The majority of the amines employed in this investigation were readily soluble in dilute acid and could be diazotized by the slow addition of sodium nitrite solution to the amine dissolved in slightly more than the theoretical quantity of dilute acid. The temperature of the diazotization was considered in the light of some recent investigation¹, and in the cases of sulfanilic acid and p-aminoazobenzene, excellent yields of the dyes were obtained by diazotization above room temperature, the advantage being a decreased time of diazotization. With the other amines the conventional diazotization temperatures of 0° to 5° were employed. The technique was altered slightly for sulphanilic acid and the naphthylamine sulphonic acids since these amines exhibit solubility only in basic solution. These amines were dissolved in the theoretical quantity of sodium hydroxide solution containing the calculated quantity of sodium nitrite, and the proper amount of acid was added slowly. With the other amines the nitrite was added until the first evidence of a bluish coloration was obtained on starch-KI paper from a sample of the solution.

Since it has been shown² that the presence of free mineral acid in solutions of diazo chlorides and aromatic phenols definitely retards the coupling, this reaction was

¹Snow: Ind. Eng. Chem. 24, 1420 (1932).

²Cain and Thorpe: Synthetic Dyestuffs, p.49.

carried out by placing the guaiacol in solution in a decided excess of sodium hydroxide and adding the diazo chloride slowly to this solution, thus maintaining the alkalinity of the solution at all times.

Spontaneous precipitation of the dyes occurred but in two instances, p-toluidine and sulphanilic acid, when the dye solution was relatively dilute. The dye could be readily precipitated by the addition of a saturated salt solution but this was undesirable because of salt contamination of the precipitated dye which would interfere with the analysis. It was found that the dye could be precipitated salt-free without the addition of a saturated salt solution by diazotizing and coupling in relatively concentrated solutions, so that the total volume of the dye solution would be small. In most cases a precipitate formed immediately because of insufficient solubility of the dye. The yields under such conditions were variable and usually low, but the remainder of the dye could be precipitated by salt with but a minimum degree of salt contamination.

The free bases were prepared by the addition of acid to the unprecipitated dye solution after coupling. An extremely viscous substance would precipitate, and after several days standing it usually solidified, forming a brittle mass. This tarry substance could be recrystallized in a few instances from diluted alcohol. It exhibited definite crystalline form.

The acetyl derivatives were prepared by refluxing the

free base of the dye with a solution of acetic acid anhydride in glacial acetic acid for several hours. Upon cooling and dilution with several volumes of water, the acetyl compound precipitated and could be recrystallized either from alcohol or glacial acetic acid.

The quantitative solubility relationships of the dyes in various solvents were not determined, but it was noted that the sodium salts, with the exception of those from sulphanilic acid and p-toluidine, were soluble not only in many organic solvents including hydrocarbons, carbon tetrachloride, and alcohols, but also water. The free bases exhibited solubility only in the usual organic solvents.

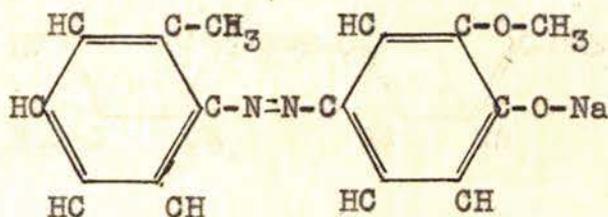
The dyes are treated individually with regard to preparation in the following paragraphs. They are listed according to the amine which was diazotized and coupled with the guaiacol. The empirical formula of the dye (free base) follows the name of the amine.

o-Toluidine (Na Salt) ($C_8H_{15}O_2N_2$)

A solution of 10 grams of o-toluidine in 20 cc hydrochloric acid (Sp. Gr. 1.18) and 100 cc of water was made, cooled to 5° C, and diazotized by the slow addition of a solution of 6.5 grams sodium nitrite in 25 cc water. The diazo solution was then added to 11.6 grams guaiacol dissolved in a solution of 20 grams sodium hydroxide in 100 cc water. The resulting solution was allowed to stand for two days before filtration to insure complete coupling and to allow sufficient

time for maximum precipitation. Light brown powder, melting point above 360° C, giving the following upon analysis: A sample of 0.2717 gram gave 0.02869 gram nitrogen. (Dumas) Found: N, 10.56%. Theory: N, 10.61%.

The structural formula for the compound is as follows:

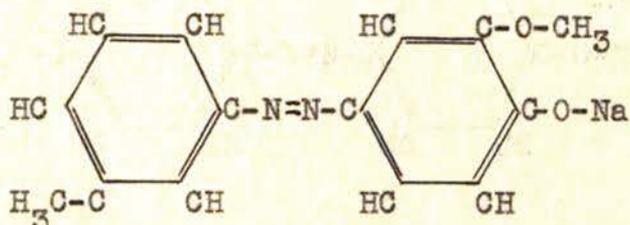


m-Toluidine (Na Salt) ($C_{14}H_{15}O_2N_2$)

A solution of 10 grams *m*-toluidine in 20 cc concentrated hydrochloric acid (Sp. Gr. 1.18) and 100 cc water was made, cooled to 5° C, and diazotized by the slow addition of a solution of 6.5 grams sodium nitrite in 25 cc water until diazotization was complete. The diazo solution was then added to 11.6 grams guaiacol contained in a solution of 20 grams sodium hydroxide in 100 cc water. The resulting solution was allowed to stand for two days to insure complete coupling and precipitation. The solution was then filtered. The filtrate was treated with a saturated salt solution to precipitate the remainder of the dye. Filtration of the dye which had been salted out was extremely slow because of its finely divided state; however this was facilitated by a preliminary digestion on a water bath. Yield, almost quantitative, light brown powder, melting point above 360° C, giving the

following upon analysis: A sample of 0.3005 gram gave 0.0323 grams nitrogen. (Dumas) Found: N, 11.08%. Theory: N, 10.61%.

The above analyzed compound has the following structural formula:



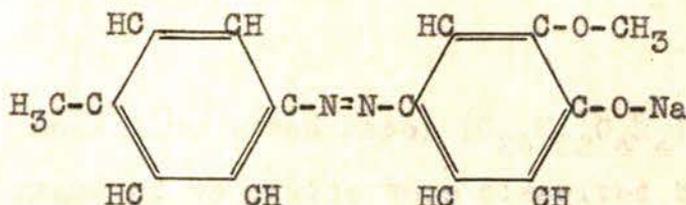
p-Toluidine (Na Salt) ($\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_2$)

A solution of 10 grams p-toluidine in 20 cc hydrochloric acid (Sp. Gr. 1.18) and 200 cc water was made, cooled to near 5°C , and diazotized by the addition of 6.5 grams sodium nitrite in 25 cc water. The diazo solution was then added to 11.6 grams guaiacol in a solution of 20 grams sodium hydroxide in 200 cc water. After standing for 5 days, long crystalline needles developed in the solution. The crystals were allowed to grow for an additional 2 days before filtration. It is to be noted that both a larger volume of amine and guaiacol solution was employed in this preparation because experiment had shown that the dye would assume better crystalline form in the less concentrated solutions. Addition of a saturated salt solution to the filtrate after the primary filtration did not produce an appreciable quantity of the dye. Yield, rather low, of light brown, long needles, melting point above 360°C , giving the following analysis:

A sample of 0.2408 gram gave 0.02668 gram nitrogen. (Dumas)

Found: N, 11.08%. Theory: N, 10.61%.

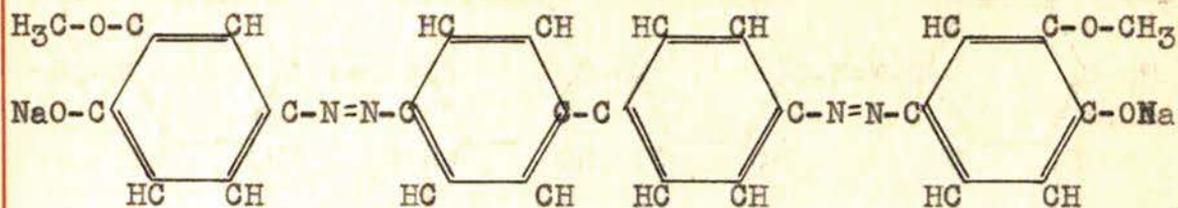
The structural formula for the compound is as follows:



Benzidine (Na Salt) ($C_{26}H_{22}O_4N_4$)

Ten grams of benzidine were dissolved in 30 cc hydrochloric acid (Sp. Gr. 1.18) and 250 cc water by vigorous agitation. This solution was tetrazotized after being cooled to near 5° C by the slow addition of 7.5 grams sodium nitrite in 25 cc water. The tetrazotized solution was then slowly added to 12.8 grams guaiacol contained in a solution of 20 grams sodium hydroxide in 150 cc water. After standing for several days the greater portion of the dye had precipitated. It was then filtered. Addition of a saturated salt solution to the filtrate resulted in the precipitation of the majority of the remainder of the dye. The yield was almost theoretical, dark brown amorphous powder, melting point above 360° C, and gave the following analysis: A sample of 0.3071 gram gave 0.0347 gram nitrogen. (Dumas) Found: N, 11.30%. Theory: N, 11.24%.

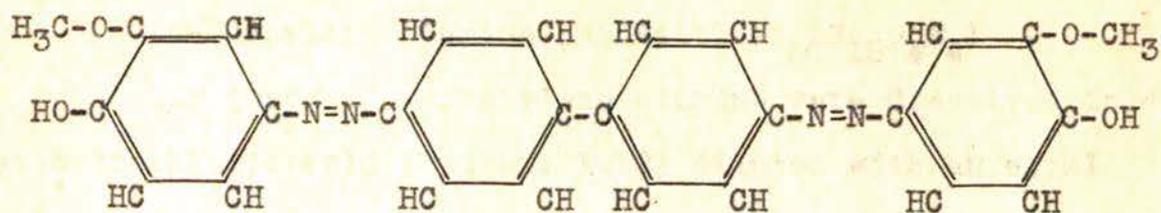
The structural formula for the compound is as follows:



Benzidine (Free Base) ($C_{26}H_{22}O_4N_4$)

Ten grams of benzidine were dissolved by vigorous agitation in a solution of 30 cc of hydrochloric acid (Sp. Gr. 1.18) and 250 cc water. This solution was tetrazotized after cooling to near $5^{\circ}C$ by the addition of 7.5 grams sodium nitrite dissolved in 25 cc water. The resulting solution was coupled with a solution of 14 grams guaiacol and 4.5 grams sodium hydroxide in 220 cc water. About two hours were allowed for complete coupling after which 20 cc of hydrochloric acid were added to the solution with stirring. The free base immediately separated as a light brown powder, very slightly soluble in water. Attempts to recrystallize the free base from alcohol, hydrocarbons, and glacial acetic acid were tried without success, the dye in every instance being thrown out of solution in an amorphous state. Yield, almost quantitative, a light brown powder giving the following analysis: A sample of 0.2401 gram gave 0.02987 gram nitrogen. (Dumas) Found: N, 12.45%. Theory: N, 12.38%.

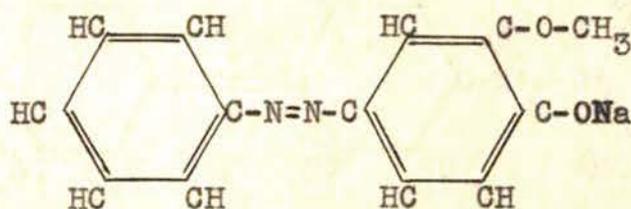
The structural formula of the compound is as follows:



Aniline (Na Salt) ($C_{12}H_{13}O_2N_2$)

Ten grams aniline were dissolved in a solution of 20 cc hydrochloric acid (Sp. Gr. 1.18) and 100 cc water. This solution was cooled to near $5^{\circ} C$ in an ice-salt bath and diazotized by the addition of a solution of 7.5 grams sodium nitrite in 25 cc water. The diazo solution was then added to 12.4 grams guaiacol contained in a solution of 15 grams sodium hydroxide in 100 cc water. The solution was allowed to stand for three days before filtration. By this time a small portion of the dye had precipitated and was of sufficient purity for analysis. Addition of a saturated salt solution to the filtrate separated an additional quantity of the dye; however the yield was relatively low. The dye was a dark reddish brown powder, melting above $360^{\circ} C$, and giving the following analysis: A sample of 0.2108 gram gave 0.02511 gram nitrogen. (Dumas) Found: N, 11.91%. Theory: N, 11.81%.

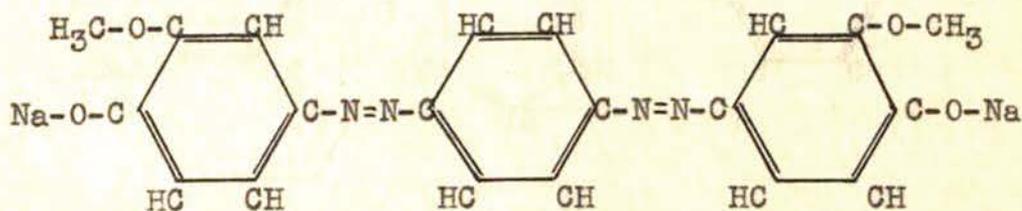
The structural formula of the compound is as follows:



p-Phenylene Diamine (Na Salt) ($C_{20}H_{18}O_4N_4$)

Ten grams of p-phenylene diamine were dissolved in 40 cc hydrochloric acid (Sp. Gr. 1.18) diluted with an equal volume of water by vigorous stirring and continued agitation. When solution was complete an additional 50 cc water were added. This amine solution was cooled to $0^{\circ}C$ and tetrazotized by the addition of a solution of 12.8 grams sodium nitrite in 35 cc water over a period of about 30 minutes. Coupling was effected by adding the tetrazo solution to 20.2 grams guaiacol contained in a solution of 20 grams sodium hydroxide in 150 cc water. After standing for three days, a considerable portion of the dye had precipitated and was readily filtered. The remainder of the dye was precipitated by the addition of a saturated salt solution to the filtrate. A preliminary digestion of the dye suspension on the water bath facilitated the subsequent filtration. Yield, high, of a reddish brown, amorphous powder, melting point above $360^{\circ}C$, giving the following analytical results: A sample of 0.2003 gram gave 0.02670 gram nitrogen. (Dumas) Found: N, 13.33%. Theory: N, 13.27%.

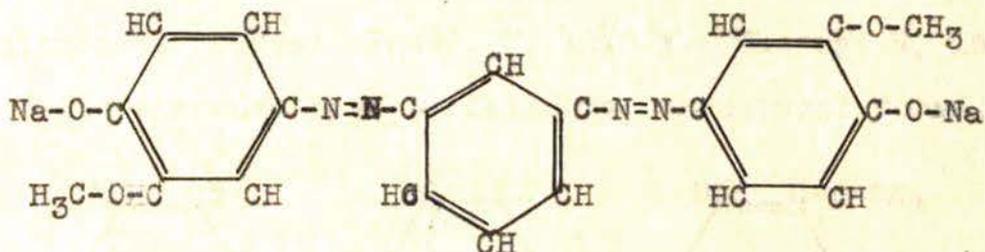
The structural formula of the compound is as follows:



m-Phenylene Diamine (Na Salt) ($C_{20}H_{18}O_4N_4$)

A solution was made of ten grams m-phenylene diamine in 40 cc hydrochloric acid (Sp. Gr. 1.18) and 75 cc water. The temperature of the solution was reduced to below $5^{\circ}C$ and tetrazotization conducted by the addition in small quantities of a solution of 12.8 grams sodium nitrite in 75 cc water. The tetrazo solution was then added to 20.2 cc of guaiacol contained in a solution of 20 grams sodium hydroxide in 150 cc water. The solution was allowed to stand for five days before filtration, and by this time about half of the dye had precipitated. The remainder of the dye could be removed from solution by the addition of a saturated salt solution to the filtrate. Yield, rather poor, as evidenced by an excessive amount of frothing after coupling, indicative of loss of nitrogen. Reddish-brown, amorphous powder, melting point above $360^{\circ}C$, giving the following analysis: 0.2151 gram of the substance gave 0.02841 gram nitrogen. (Dumas) Found: N, 13.21%. Theory: N, 13.27%.

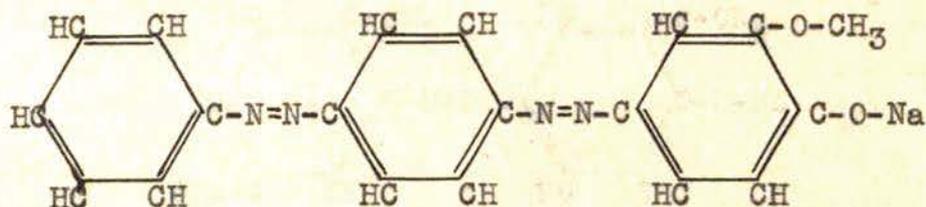
The structural formula of the compound is as follows:



p-Aminoazobenzene (Na Salt) ($C_{19}H_{16}O_2N_4$)

Twenty grams of p-aminoazobenzene were dissolved in 20 cc of hydrochloric acid (Sp. Gr. 1.18) diluted with an equal volume of water. When solution was complete, an additional 150 cc water were added. The amine was diazotized both at the conventional diazotization temperature of $5^{\circ}C$ and at slightly above room temperature (30°). In each case diazotization was conducted by the slow addition of a solution of 7.5 grams sodium nitrite in 50 cc water. The higher temperature of diazotization was productive of as high a yield as the lower one. The higher temperature of diazotization was advantageous in that it reduced the time of diazotization to about one-fourth. The diazotized amine was coupled with 11.3 grams guaiacol contained in a solution of 10 grams sodium hydroxide in 200 cc water. Precipitation occurred immediately; however the solution was allowed to stand 24 hours after which it was filtered. Additional salt solution added to the filtrate did not precipitate an appreciable quantity of the dye. Brown powder, melting point above $360^{\circ}C$, and presenting upon analysis: 0.2303 gram of the substance gave 0.03625 gram nitrogen. (Dumas) Found: N, 15.74%. Theory: N, 15.81%.

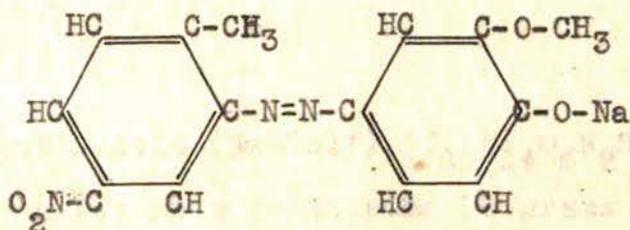
The compound has the following structural formula:



4-Nitro 2-Amino Toluene (Na Salt) ($C_{14}H_{13}O_4N_3$)

The amine was placed in solution by dissolving 10 grams in 15 cc hydrochloric acid (Sp. Gr. 1.18) and 75 cc of water. This solution was cooled to near $5^{\circ} C$ and diazotized by the slow addition of a solution of 4.6 grams sodium nitrite in 25 cc water. The diazo solution was then added to 7.2 cc of guaiacol contained in a solution of 15 grams sodium hydroxide in 75 cc water. The dye was allowed to stand for four days before filtration. Inasmuch as the precipitated dye was finely divided, a preliminary digestion on the water bath was resorted to in order to expedite the filtration. This was not successful as the dye was found to decompose at temperatures above $90^{\circ} C$. The amount of dye precipitated spontaneously was small in spite of the high concentrations of the solutions of the intermediates; however addition of a saturated salt solution to the filtrate removed considerable more of the dye from solution. Brownish-red, amorphous powder, melting point above 360° , presenting the following analytical results: 0.3101 gram of the substance gave 0.04230 gram nitrogen. (Dumas) Found: N, 13.64%. Theory: N, 13.59%.

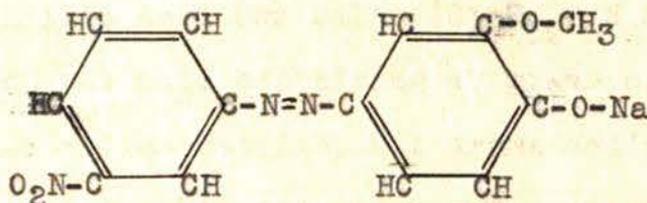
The following is the structural formula of the compound:



m-Nitraniline (Na Salt) ($C_{13}H_{11}O_4N_3$)

A solution of 10 grams of m-nitraniline in 15 cc of hydrochloric acid (Sp. Gr. 1.18) was made and diluted with 75 cc water. It was then cooled to below $5^{\circ}C$ and diazotized by the slow addition of a solution containing 5 grams sodium nitrite dissolved in 25 cc water. Coupling was effected by adding the diazo solution to 7.8 grams guaiacol contained in a solution of 10 grams sodium hydroxide in 100 cc water. The maximum amount of precipitation was deemed to have occurred after three days standing. An additional quantity of the dye was removed from solution by the addition of a saturated salt solution to the filtrate, but digestion was necessary before filtration of that portion of the dye which had been salted out. Yield, high, of a maroon, amorphous powder, melting point above $360^{\circ}C$, presenting the following analytical data: A sample of 0.2515 gram gave 0.03597 gram nitrogen. (Dumas) Found: N, 14.30%. Theory: N, 14.23%.

The structural formula of the compound is as follows:

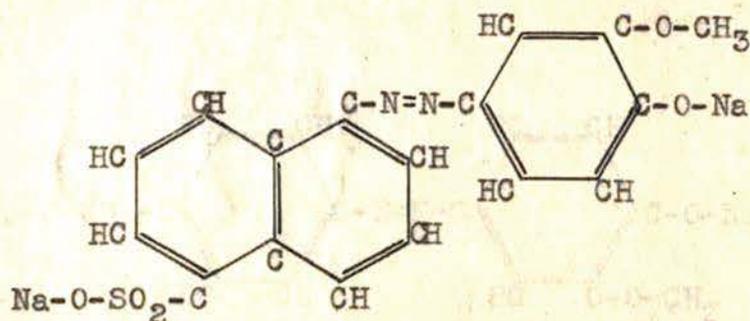


Laurent's Acid (Na Salt) ($C_{17}H_{14}O_5N_2S$)

A solution was made containing 10 grams of Laurent's acid (1-naphthylamine 5-sulphonic acid), 1.7 grams sodium

hydroxide, 2.9 grams sodium nitrite, and 150 cc water. This solution was cooled to 5° C and diazotized by the slow addition of 10 cc hydrochloric acid (Sp. Gr. 1.18). The diazo solution resulting was added 4.5 cc guaiacol contained in a solution of 10 grams sodium hydroxide in 150 cc water. The solution was allowed to stand for five days before filtration. About half of the dye had precipitated spontaneously and the remainder was removed from solution by the addition of a saturated salt solution to the filtrate. Brown powder, melting point above 360° C, presenting upon analysis: A sample of 0.3404 grams gave 0.02353 grams nitrogen. (Dumas) Found: N, 6.911%. Theory: N, 6.964%.

The compound has the following structural formula:

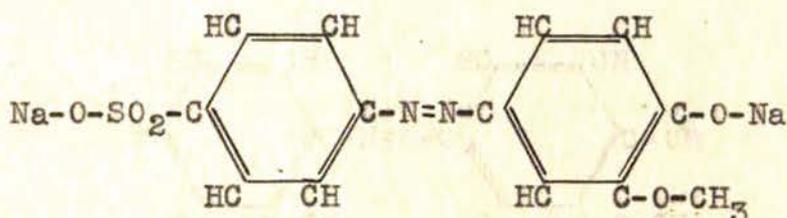


Sulphanilic Acid (Na Salt) ($C_{13}H_{12}O_5N_2S$)

A solution was made containing 10 grams of sulphanilic acid, 3.6 grams sodium nitrite, 2.1 grams sodium hydroxide, and 150 cc water. Diazotization was conducted at slightly above room temperature (after preliminary experimentation) by adding 15 cc hydrochloric acid (Sp. Gr. 1.18) slowly. The resulting diazo solution was coupled by addition to 6.5 grams guaiacol contained in a solution of 10 grams

sodium hydroxide in 150 cc water. The dye precipitated immediately but was allowed to stand for two hours to assure complete coupling. After filtration of the portion of the dye which had precipitated spontaneously an additional quantity was obtained by addition of a saturated salt solution to the filtrate. The color of this portion, precipitated by the use of salt, was considerable darker than that of the portion precipitated spontaneously, a fact probably indicative of occlusion of impurities by the precipitated particles. Orange powder, melting point above 360° C, giving the following analytical results: 0.2277 gram of the substance gave 0.01814 gram nitrogen. (Dumas) Found: N, 7.968%. Theory: N, 7.955%.

The following is the structural formula of the compound:



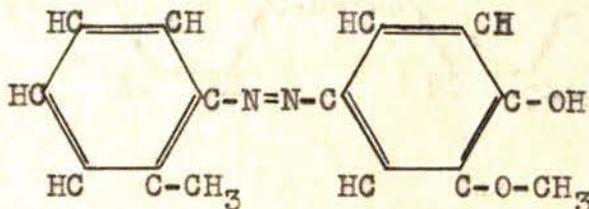
o-Toluidine (Free Base) ($\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_2$)

A solution of 10 grams o-toluidine in 20 cc hydrochloric acid and 200 cc water was made, cooled to 5° C, and diazotized by the slow addition of a solution of 6.5 grams sodium nitrite in 25 cc water. The diazo solution was then added to 11.6 grams guaiacol contained in a solution of 5 grams sodium hydroxide in 100 cc water. The dye solution was allowed to stand for two hours to assure complete coupling,

after which 20 cc of hydrochloric acid were added with vigorous stirring. The free base was precipitated in the form of a viscous, tarry substance which became somewhat brittle after standing for 24 hours. This tarry substance was dissolved in the smallest possible quantity of alcohol and was reprecipitated by diluting the alcohol in the cold until the first evidence of precipitation, after which the solution was heated to boiling and allowed to cool slowly for the formation of crystals. The crystals were quite well-formed after about 5 hours. Light brown needles, melting point 220-225° C, presenting the following analysis: A sample of 0.3011 gram gave 0.04893 gram nitrogen. (Dumas) Found: N, 16.25%.

Theory: N, 16.36%.

The compound has the following structural formula:

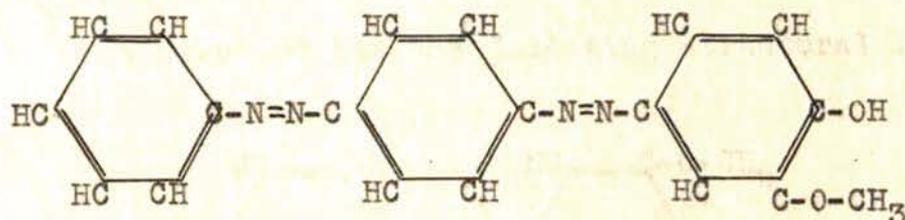


p-Amino-Azo-Benzene (Free Base) (C₁₉H₁₆O₂N₂)

Ten grams p-amino-azo-benzene were dissolved in 10 cc hydrochloric acid (Sp. Gr. 1.18), diluted with an equal volume of water and when solution was complete, an additional 100 cc water were added. Diazotization was conducted at room temperature by the slow addition of a solution of 3.8 grams sodium nitrite in 25 cc water. The resulting diazo solution

was added to 5.6 grams guaiacol contained in a solution of 5 grams sodium hydroxide in 100 cc water. Two hours were allowed for complete coupling. Ten cc of hydrochloric acid were then added to the solution, whereupon the free base of the dye precipitated. Attempts to obtain the free base in crystalline form by recrystallization from alcohol, glacial acetic acid, aromatic hydrocarbons, and carbon tetrachloride were not successful, the compound in every instance precipitated in an amorphous state. Dark brownish-black powder, decomposed below 100° C, giving upon analysis: 0.2091 gram of the substance gave 0.0350 gram nitrogen. (Dumas) Found: N, 16.74%. Theory: 16.86%.

The structural formula for the compound is as follows:

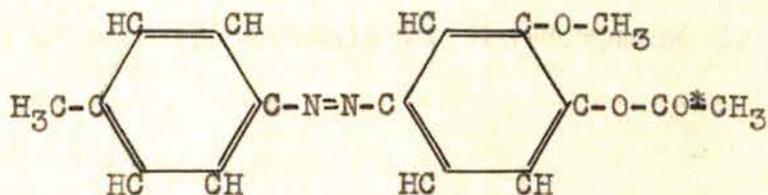


Acetyl Derivative of p-Toluidine (C₁₆H₁₆O₃N₂)

The free base of p-toluidine coupled with guaiacol was prepared by placing 10 grams of the amine in solution in 20 cc hydrochloric acid (Sp. Gr. 1.18) and 150 cc water, cooling to near 5° C, and diazotizing with a solution of 6.5 grams sodium nitrite in 25 cc water. The diazo solution was coupled by addition to a solution of 11.6 grams guaiacol, 5 grams sodium hydroxide, and 100 cc water. Addition of 20 cc hydro-

chloric acid to the solution resulted in the precipitation of the free base which was then filtered and dried. Twelve grams of the free base were then placed in a 500 cc round-bottom flask and a solution of 25 grams acetic acid anhydride and 10 grams glacial acetic acid added. The mixture was refluxed at a temperature of 135-145° for five hours, whereupon it was poured into an evaporating dish to cool. Dilution with three volumes of water resulted in the precipitation of the acetyl compound, which was then filtered and dried. It could be re-crystallized readily from either diluted alcohol or glacial acetic acid. Orange, crystalline plates, melting point 103-103.5° C, giving the following analysis: A sample of 0.3500 gram gave 0.03447 gram nitrogen. (Dumas) Found: N, 9.849%. Theory: N, 9.856%.

The compound has the following structural formula:

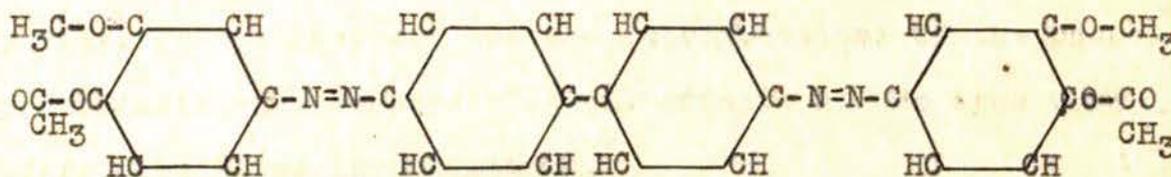


Acetyl Derivative of Benzidine (C₃₀ H₂₆ O₆ N₄)

Ten grams of benzidine were dissolved in a solution of 30 cc hydrochloric acid in 200 cc water and to this solution after cooling to near 5° C was added slowly, 7.5 grams sodium nitrite in 50 cc water. The resulting tetrazo solution was added to 14 grams guaiacol contained in a solution of 4.5

grams sodium hydroxide in 100 cc water. Two hours were allowed for complete coupling to occur. Ten cc of hydrochloric acid were then added, whereupon the free base immediately precipitated as a light brown powder. Fifteen grams of the dried powder were placed in a 500 cc round-bottom flask and a solution of 60 grams acetic acid anhydride and 20 grams glacial acetic acid added. The mixture was allowed to reflux for five hours at a temperature of 135-145° C. At the end of this time the solution was poured into an evaporating dish to cool. Fine crystals were precipitated upon dilution of this solution with three volumes water. These crystals were recrystallized from 250 cc of glacial acetic acid. Brownish-orange, crystalline plates, melting point 184-185° C, insoluble in water but soluble in organic solvents. Analysis presented the following data: A sample of 0.2001 gram gave 0.02069 gram nitrogen. (Dumas) Found: N, 10.34%. Theory: N, 10.40%.

The structural formula of the compound is as follows:



CONCLUSIONS

1. A number of azo dyes have been prepared by coupling guaiacol with various diazotized amines, a monotony of color being presented inasmuch as the dyes ranged in color from orange to maroon, the tendency towards brownish red.

2. The free bases of the dyes were found to precipitate in the form of a viscous, tarry material which could be recrystallized satisfactorily in only a few instances.

3. The dyes (sodium salts) were found to be soluble in both water and a large number of organic solvents, while the free bases exhibited solubility only in the usual organic solvents.

4. The acetyl derivatives of p-toluidine coupled with guaiacol and benzdine coupled with guaiacol were isolated in crystalline form. The products of acetylation of a number of the other dyes were thrown out of solution in the form of an oil which decomposed upon distillation at a reduced pressure of 100 mm. mercury.

5. It was suspected that each of the dyes prepared had more or less antiseptic value because of the phenolic hydroxyl groups present, but the determinations of the phenol coefficients and the physiological effects of the dyes were deferred to later investigation.

BIBLIOGRAPHY

Books

Cain and Thorpe: Synthetic Dyestuffs.

Literature Cited

Columbans and Leonardi: Atti. Accod. Lincei 16, (ii),
639-648.

Jacobson, Jaenicke and Meyer: Ber. 29, 2685.

Snow: Ind. Eng. Chem. 24, 1420 (1932).