[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

QUINONESULFURIMINES

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In a previous paper published with Eugen Riesz[2] the results of experiments carried out in order to get quinoid substances of the type R—S—N═R═O were reported.[3] These substances are derived from quinoneimines in which the imido hydrogen is replaced by an aryl sulfide group. For this configuration, the name quinonesulfurimines has been proposed.

It seemed to us that a quinonesulfurimine substituted with an auxochrome group might be an interesting dye of a new type.

There are two possible ways of easily modifying the 4-chloro-2-nitrophenyl-quinonesulfurimine to obtain the necessary auxochrome group for this purpose. The first is the formation of an external auxochrome group by the reduction of the substance mentioned above to give 4-chloro-2-aminophenyl-quinonesulfurimine. The second possibility is the introduction of an auxochrome group in the quinoid ring.

The results of the attempts to reduce the 4-chloro-2-nitrophenyl-4′-hydroxysulfuranilide, and the preparation and properties of the 4-chloro-2-nitrophenyl-2′-hydroxy-quinonesulfurimine will be reported in this paper.

Zincke[4] first prepared the aryl sulfur chlorides and found that some of their derivatives were split by the action of alkalies and acids between the sulfur and the adjacent atom or group. Thus, the regeneration of the 4-chloro-2-nitrophenyl-1-sulfur chloride by the action of hydrochloric acid on the corresponding amide, and the formation of the 4,4′-chloro-2,2′-nitrophenyl-disulfuroxide by the action of alkali upon this amide have been observed. Furthermore, it has been shown in the first paper concerning the quinonesulfurimines that the 4-chloro-2-nitrophenyl-4′-hydroxy-anilide, on reduction and acetylation, yielded the 6-chloro-1-methylbenzothiazole.[2] To avoid this splitting of the molecule, we used aluminum amalgam in neutral alcohol-ether solution to reduce the nitro group of the anilide mentioned above, but even in this case we found the sulfur-nitrogen linkage broken. *p*-Aminophenol was isolated in nearly quantitative yield. Likewise, when 4-chloro-2-nitrophenylsulfuramide was reduced with the same reducing agent, large quantities of ammonia were obtained. This fact might be explained by assuming the inter-

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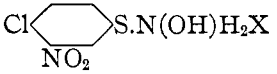
[2] Gebauer-Fülnegg and Riesz, *Monatsh.*, **47**, 57 (1926).

[3] The possible formulations of the actual structure of the different aryl sulfur chlorides and aryl sulfuranilides will be discussed in a future paper.

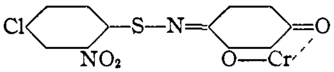
[4] Zincke and Baeumer, *Ann.*, **416**, 86 (1918).

mediate formation of the unstable base  which, on further reduction, gave off ammonia and *p*-aminophenol, respectively.

Other different reducing agents, such as phenylhydrazine, ferrous salts in ammoniacal solution, and hydrogen sulfide with ammonia, failed to effect the desired reduction.

A convenient compound for the formation of a quinonesulfurimine containing an auxochrome group in the quinoid ring is aminoresorcinol. Its hydrochloride[5] was coupled with 4-chloro-2-nitrophenylsulfur chloride in the presence of barium or magnesium carbonate; the corresponding anilide was formed. As the free base, aminoresorcinol, is highly unstable toward the oxygen of the air,[6] especially in the presence of alkali, this step must be carried out very carefully in an atmosphere of carbon dioxide. The structure of the resulting anilide was proved by the determination of its molecular weight, and reducing acetylation which yielded tetra-acetyl-aminoresorcinol[7] and 4-chloro-ethenyl aminothiophenol. As this anilide and the related substances are crystallized only with difficulty, we tried to prepare a crystallizable silver salt, but only succeeded in obtaining it in an amorphous form. The values obtained from the Carius determination for silver, sulfur and chlorine indicated that the salt was precipitated with one molecule of silver acetate.

We oxidized the anilide first with sodium dichromate in acetic acid solution to the corresponding quinoid compound, but the substance thus prepared, even after several purifications, always contained chromium. This observation led us to the conclusion that the oxidized anilide might be used as a mordant dye. We succeeded in confirming this assumption by dyeing with this quinone animal fibers previously treated with chromium salts. There are two possible formulas for this chromium complex.



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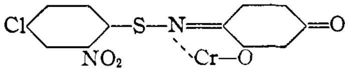

II

I would be analogous, for example, to the alizarin formula proposed by Scholl,[8] which assumes the formation of complex rings between the metal and the hydroxyl and carbonyl groups of the anthraquinone; however, as in our case, the carbonyl and hydroxyl groups are in the *meta* position, Formula II seems more probable.

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[5] It has been shown [Gebauer-Fülnegg and Fleck, *Am. Photographic J.*, in press] that 4-aminoresorcinol hydrochloride is a photographic developer of high energy and good toning qualities.

[6] Weselsky, *Ann.*, **164,** 5 (1872).

[7] Henrich and Wagner, *Ber.*, **35,** 4195 (1902).

[8] Georgievics, "Handbuch der Farbenchemie," Franz Deuticke, Leipzig and Wien, **1922,** 5th ed., p. 233.

When the anilide is oxidized with hydrogen peroxide, the corresponding monomolecular quinoid substance with a free hydroxyl group is formed.

By reducing acetylation of the quinone, tetra-acetylaminoresorcinol and 4-chloro-ethenyl aminothiophenol are formed, indicating that the quinone has the same configuration as the anilide. With chromium salts this quinone can be transformed into the chromium-containing complex previously obtained by oxidation with sodium dichromate.

The quinone shows not only distinct coloring properties as a mordant dye, but also acts as a weak acid dye. In both cases brownish colors result.

As it has been shown that the sulfur-nitrogen linkage is not strong, the sulfurquinone-imine dye has, in this case at least, only theoretical interest.

Experimental Part

Reduction of 4-Chloro-2-nitrophenyl-4'-hydroxysulfuranilide.—The anilide was prepared[2] by refluxing an ethereal solution of equal quantities of 4-chloro-2-nitrophenylsulfur chloride and *p*-aminophenol; after filtration and evaporation of the solution, the viscous residue was crystallized from benzene. It formed red leaves; m. p., 118–119°. Four g. of this anilide dissolved in 50 cc. of alcohol plus 50 cc. of ether was reduced with 6.5 g. of aluminum amalgam. This mixture was refluxed for four hours, then filtered and evaporated by vacuum distillation in an atmosphere of carbon dioxide to prevent reoxidation which occurs in the air. The residue was extracted with benzene, but was found to be only partially soluble; the residue, m. p. 184° (mixed melting point with *p*-aminophenol, 184°), gave a ferric chloride test and was identified as *p*-aminophenol. As this substance was formed in nearly quantitative yield, 1.3 g., it was evident that the sulfur-nitrogen linkage is broken even by reduction in neutral solution.

Preparation of 4-Chloro-2-nitrophenyl-2',4'-dihydroxysulfuranilide.—The 4-aminoresorcinol hydrochloride used in this preparation was obtained[9] by the reduction of benzene-azoresorcinol with tin and hydrochloric acid. The other component, 4-chloro-2-nitrophenylsulfur chloride, was prepared[4] in the usual way by the chlorination of the corresponding disulfide.

To prepare the anilide, 9.1 g. of 4-aminoresorcinol hydrochloride and 12.1 g. of 4-chloro-2-nitrophenylsulfur chloride were dissolved in 100 cc. of moist ether free from alcohol and treated with 10 g. of magnesium carbonate in an atmosphere of carbon dioxide. The mixture was shaken occasionally and was refluxed for three hours. The dark colored solution was then filtered from a considerable residue, dried with anhydrous sodium sulfate, and evaporated in a vacuum. This left a tarry product partially soluble in boiling benzene. The benzene extract was evaporated in a vacuum and the crude product thus obtained was dissolved in chloroform and precipitated by ligroin as an orange-brown, amorphous powder. This substance was very soluble in acetone and in alcohol, less so in ether and in chloroform, and was insoluble in carbon tetrachloride, in toluene and in ligroin. It was found difficult to obtain it in crystalline form in quantities sufficient for analysis, so a silver salt was prepared for this purpose. The amorphous substance appeared to melt at 133°, with decomposition. The method of preparation, the molecular-weight determination and the nitrogen combustion indicate the formation of 4-chloro-2-nitrophenyl-2',4'-dihydroxysulfuranilide.

Anal. Subs., 0.1202: N_2, 9.9 cc. (22°, 730 mm., over 50% KOH). Calcd. for $C_{12}H_9O_4N_2SCl$: N, 8.96. Found: 9.28.

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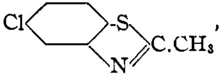
[9] Meyer and Kreis, *Ber.*, **16**, 1329 (1883).

Mol. wt. Subs., 0.0444, in camphor, 0.5625: Δt, 9.5°. Calcd. for $C_{12}H_9O_4N_2SCl$: mol. wt., 312. Found: 332.

SILVER SALT.—The anilide in alcoholic solution treated with silver carbonate or silver acetate gives a voluminous precipitate. The latter reaction was used. The salt was easily soluble only in pyridine and the higher alcohols, such as butyl alcohol, and was also difficult to obtain in crystalline form. Analysis showed that it apparently crystallizes with one molecule of silver acetate.

Anal. Subs., 0.1865: $BaSO_4$, 0.0627; AgCl, 0.1145. Calcd. for $C_{12}H_7O_4N_2SCl\cdot Ag_2.CH_3COOAg$: S, 4.63; Ag, 46.68. Found: S, 4.62; Ag, 46.31.

REDUCING ACETYLATION OF THE ABOVE ANILIDE.—In order to confirm the structure of the anilide, a reducing acetylation was performed. Three g. of the amorphous anilide was dissolved in 50 cc. of glacial acetic acid, to which was added 15 g. of acetic anhydride, 9 g. of anhydrous sodium acetate and 7 g. of zinc dust. The mixture was refluxed for three hours. After distilling the liquid portion in a vacuum, the mixture was extracted with boiling benzene. This solution was evaporated, the residue was washed with water and then distilled with steam. The distillate gave a milky emulsion which deposited white crystals. These were dissolved in low-boiling ligroin, from which large, transparent crystals were obtained; m. p., 68°. This product was identified as 4-chloro-ethenyl aminothiophenol, 

, identical with that obtained[2] by the reducing acetylation of the similar 4-chloro-2-nitrophenyl-4'-hydroxysulfuranilide.

The residue from the steam distillation contained the tetra-acetyl derivative of aminoresorcinol.[7] It was extracted with boiling benzene and precipitated very slowly, according to the literature, from a mixture of benzene and ligroin (50% of each); b. p., 70–80°; m. p., 106–108°.

OXIDATION.—Equal weights of the 4-chloro-2-nitrophenyl-2',4'-dihydroxysulfuranilide and sodium dichromate were dissolved in a small amount of glacial acetic acid and were well mixed. The solution was diluted to 500 cc. with water, and sodium acetate was added to precipitate the colloidal suspension. The precipitate was washed, dried, dissolved in pyridine and reprecipitated with ligroin as an amorphous brown powder. It is slightly soluble in alcohol, in acetone and ethyl acetate, and does not crystallize readily. Borax bead tests indicated, even after several reprecipitations, a chromium-containing complex.

We therefore oxidized the anilide by shaking a solution of it with the calculated amount of 30% hydrogen peroxide in ether. The molecular weight in camphor of the subsequent compound, a nitrogen combustion, and the Carius determination for sulfur and chlorine indicated the presence of 4-chloro-2-nitrophenyl-2'-hydroxyquinonesulfurimine.

Anal. Subs., 0.1304, 0.1065: $BaSO_4$, 0.0968, 0.0783; AgCl, 0.0598, 0.0481. Subs., 0.1451: N_2, 11.8 cc. (22°, 750 mm., over 50% KOH). Calcd. for $C_{12}H_7O_4N_2ClS$: S, 10.31; Cl, 11.43; N, 9.02. Found: S, 10.20, 10.10; Cl, 11.34, 11.17; N, 9.29.

Mol. wt. Subs., 0.0246; in camphor, 0.2738: Δt, 12.0°. Calcd. for $C_{12}H_7O_4N_2ClS$: mol. wt., 310. Found: 299.

If this quinone is treated with soluble chromium salts in acetic acid solution, the above-mentioned chromium-containing complex is formed.

A reducing acetylation was performed on this quinone in the same manner as described for the anilide, identical reduction products being obtained, and identified by mixed-melting-point determinations.

DYEING PROPERTIES.—Animal fibers previously treated in the usual manner with chromium salts were dyed in an 8% solution of the quinone in alcohol or pyridine containing 1% acetic acid, 10% sodium sulfate and sufficient water to dissolve the latter.

TABLE I

COLOR REACTIONS

Compound	Concd. sulfuric acid	Dil. alkali
4-Chloro-2-nitrophenyl-4′-hydroxysulfuranilide	Violet solution, brown on standing	Greenish-brown precipitate
4-Chloro-2-nitrophenyl-2′,4′-dihydroxysulfuranilide	Clear, Bordeaux blue solution	Clear, olive-green solution
4-Chloro-2-nitrophenyl-2′-hydroxyquinonesulfurimine	Dissolved slowly to a brownish-red solution	Brown-red, turbid solution

After boiling the liquid for 45 minutes, the fibers were removed, washed with water and with soap solution. The material was found to be dyed a brown color. Wool was also dyed if the quinone were used as an acid dye in a bath containing 8% quinone, 10% sulfuric acid, 2% sodium sulfate, 0.5% sodium carbonate and water. The intensity of the resulting color was much less than before and the shade more yellowish.

The authors wish to express to Professor Lauder W. Jones their appreciation of his advice during this investigation.

Summary

It has been shown that the sulfur-nitrogen linkage of the *p*-hydroxyanilide of 4-chloro-2-nitrophenylsulfur chloride is split even by reduction in neutral solution with aluminum amalgam. The preparation of an anilide of 4-aminoresorcinol with 4-chloro-2-nitrophenylsulfur chloride, its oxidation product, the 4-chloro-2-nitrophenyl-2′-hydroxysulfurquinoneimine, and their properties have been reported. It has been shown that this oxidation product is a dye and represents a new type of indophenol dyes.

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ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. IV. CONDENSATION OF SOME SECONDARY ALCOHOLS WITH PHENOL

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The experiments described here constitute a continuation of our study of the dehydrating and catalytic effect of anhydrous aluminum chloride in the condensation of aromatic alcohols with aromatic compounds. A previous article[1] describes the condensation of methylphenyl carbinol, ethylphenyl carbinol and benzhydrol with benzene with the formation of diphenylethane, diphenylpropane and triphenylmethane. We have now extended our studies to include the condensation of the same three alcohols with phenol.

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[1] Huston and Friedemann, THIS JOURNAL, **40**, 785 (1918).