

substitution a decrease and *m*-substitution a less marked decrease. The only exception to these rules are our *m*-chloro and *m*-bromo dyes, which show a greater decrease than the corresponding *o*-compounds.

Summary

1. A series of dyes containing the three halogens in the *o*-, *m*- and *p*-positions have been prepared, their spectral absorptions in water solution determined and compared with that of a parent dye containing no halogen.

2. The results show no simple relationship between the dyes attributable to variations in molecular weight but a complicated effect distributed in different portions of the spectrum.

3. The effect of position isomerism is for the most part the same as that observed by other workers.

4. The chief absorption bands appear to be composed of two or more constituent bands. These have in one instance been calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY No. 650]

RESEARCHES ON THIAZOLES. XVI. THE SYNTHESIS AND STUDY OF NEW AMINOTOLUTHIAZOLES AND DERIVATIVES FROM 2,5-DIAMINOTOLUENE-4-THIOSULFURIC ACID

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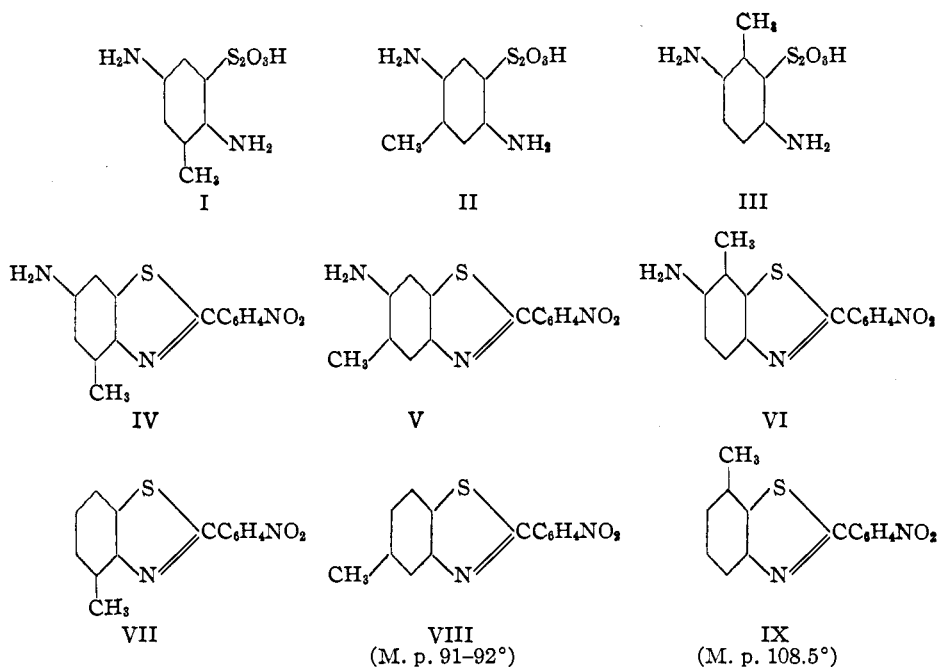
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Following up the work already reported¹ from these laboratories on benzothiazole dyes, incidental and related compounds, it seemed to us desirable to ascertain the tinctorial properties of such dyes when they carried also free amino groups in the molecule, and the present paper is a contribution to the solution of the problem, in that it describes a method by which the necessary intermediates may be synthesized and records some preliminary experiments in the preparation therefrom of dyes of the Columbia Yellow (Colour Index No. 814) class.

The initial material was the 2,5-diaminotoluene, which was converted into a monothiosulfuric acid by the method of Bernthsen.² Theoretically, such a derivative might possess any one of the structures I, II or III, all of which are capable of yielding benzothiazoles. Thus, if condensed with *o*-nitrobenzaldehyde, they should give the thiazoles IV, V and VI, respectively, elimination of whose amino groups should result in the production of VII, VIII and IX.

¹ (a) Bogert and Bergeim, *Color Trade J.*, **15**, 63 (1924); (b) Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926); (c) Bogert and Allen, *THIS JOURNAL*, **49**, 1315 (1927).

² Bernthsen, *Ann.*, **251**, 61 (1889).



Of the last three compounds, VII has not yet appeared in the literature, but VIII and IX have been described by Bogert and Allen.³

When this series of reactions was carried out with our 2,5-diaminotoluene thiosulfuric acid, the nitrotoluthiazole obtained as the final product proved to be identical with VIII. Hence the $\text{—SSO}_3\text{H}$ group in the initial acid must have been in Position 4, *i. e.*, the acid must have had structure II.

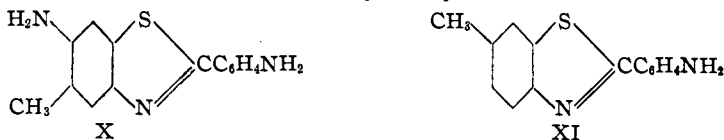
Potentiometric titrations were carried out with the acid and the results plotted graphically. From these results, the ionization constant of the acid was calculated as 5.56×10^{-6} at 25° .

Condensation of the thiosulfuric acid with *o*-, *m*- and *p*-nitrobenzaldehydes, or with 2,4-dinitrobenzaldehyde, led to the formation of the expected toluthiazoles, except in the case of the *p*-nitro compound where two moles of the aldehyde participated in the reaction, resulting in the production of a *p*-nitrobenzalamino, instead of a simple amino group, in Position 6 of the benzothiazole nucleus.

This *p*-nitrobenzalamino group was remarkably resistant to hydrolyzing agents, and this stability was associated in some manner with the presence of the nitro groups, for when the compound was treated with tin and hydrochloric acid, the nitro group on the 2-phenyl nucleus was reduced and the *p*-nitrobenzalamino at 6 simultaneously hydrolyzed to the 6-amino, giving the 2-(*p*-aminophenyl)-5-methyl-6-aminobenzothiazole.

³ Bogert and Allen, THIS JOURNAL, 49, 1320 (1927).

The other 2-aminophenylthiazoles were secured by reduction of the corresponding 2-nitrophenyl derivatives, save the *m*-amino compound, which could not be isolated in sufficient purity for analysis. These products are analogous to the well-known dehydrothio-*p*-toluidine, and the intention is to use them in similar ways as dye intermediates:



The 2-(*p*-aminophenyl) derivative (X), for example, differs from dehydrothio-*p*-toluidine (XI) only in the location of its methyl group, a difference which we have shown in a previous communication^{1c} to be without any great effect upon the shade, and in the presence of an additional amino group upon the benzothiazole portion of the molecule.

Preliminary experiments have shown that the 2-(*o*- and *p*-aminophenyl) derivatives can be converted into direct cotton dyes of the Columbia Yellow class, in which the amino group in Position 6 remains intact: and that these amino Columbia Yellow dyes, when diazotized and coupled, yield azo dyes which are also substantive for cotton.

Experimental Part

2,5-Diaminotoluene-4-thiosulfuric Acid, CH₃(1)(NH₂)₂(2,5)C₆H₂SSO₃H-(4).—The 2,5-diaminotoluene which served as initial material for this research was generously supplied by the Fales Chemical Co. of Cornwall, N. Y., and was an exceptionally high-grade product which, when freshly distilled, formed colorless needles, m. p. 64°, b. p. 273°. It was preserved in the form of its hydrochloride and used as such in the experiments.

For its conversion into the thiosulfuric acid, the method used by Bernthsen⁴ for the preparation of *p*-phenylenediamine thiosulfuric acid was utilized, with one or two modifications. The best results were obtained when the materials were used in the proportion of seven moles of the diamine hydrochloride, seven moles of sodium thiosulfate (Na₂S₂O₃·5H₂O), one mole of potassium dichromate, and 50 g. of aluminum sulfate.

To a solution of 50 g. of diaminotoluene hydrochloride in 120 cc. of water, there was added 50 g. of powdered aluminum sulfate, and then a solution of 64 g. of sodium thiosulfate (Na₂S₂O₃·5H₂O) in 120 cc. of water was stirred in slowly. A copious white precipitate separated, which was probably the thiosulfate of the diamine.⁴ To this mixture, a solution of 10 g. of potassium dichromate in 120 cc. of water was added gradually (during about one minute). The precipitate largely redissolved and the solution turned green at first, changing finally to a dark purplish-green.

After standing for a few minutes, it was filtered and the filtrate, after six to ten hours, separated a small quantity of a dark red amorphous solid, which was likewise filtered out. From the filtrate so obtained, the diamine thiosulfuric acid crystallized after forty-eight to seventy-two hours' standing, in dark steel-gray rhombic crystals; yield, 15%.

This product was purified by suspending the finely powdered material first in alcohol and then in ether for several hours, repeating the treatment until the decanted washings were nearly colorless. This removed the organic impurities. The product

⁴ Wahl, *Compt. rend.*, 133, 1216 (1902).

so purified was washed several times with tepid water and a solution of citric acid, to eliminate any traces of iron which might have been present in the initial diamine, since iron if present is likely to be carried down and retained by the diamine thiosulfuric acid.

The purified compound, when heated in an open crucible, decomposed without melting, swelling up and taking fire.

Anal. Calcd. for $C_7H_{10}O_3N_2S_2$: C, 35.88; H, 4.27; S, 27.40. Found: C, 35.88; H, 4.42; S, 27.64.

In carrying out the above method of preparation, it was found necessary to work with small batches only, since when quantities were used much larger than those stated, the yields were lower and the products less pure.

The location of the thiosulfuric acid group in this compound was proved, as described beyond, by condensing it with *o*-nitrobenzaldehyde to the 2-(*o*-nitrophenyl)-aminotolthiazole, removal of whose amino group yielded the 2-(*o*-nitrophenyl)-5-methylbenzothiazole, from which it follows that the $-SSO_3H$ group must have been in Position 4.

Potentiometric Titration of 2,5-Diaminotoluene-4-thiosulfuric Acid.— In a 100-cc. volumetric flask containing 100 cc. of distilled water there was suspended 0.1 g. of the thiosulfuric acid and this was brought into solution by shaking. This solution was transferred to a pyrex hydrogen gas electrode vessel, the flask being rinsed out with 25 cc. of water and this rinsing added to the main solution. The cell was connected to the saturated calomel electrode by a glass-stoppered salt bridge filled with saturated potassium chloride solution. The titration was conducted at 25° in a gas-tight apparatus, using a Type K potentiometer, in an atmosphere of hydrogen which had been purified by passing over heated copper oxide. The calomel and hydrogen electrodes were standardized by determining potentiometrically the P_H of a 0.104 *N* hydrochloric acid solution. Calculated P_H for 0.104 *N* HCl, 1.01; found, 0.99.

The titrations were carried out by means of a 0.0202 *N* sodium hydroxide solution, the stoichiometrical point for which was 21.3 cc. For reasons explained in what follows, a reverse titration also was conducted using 0.0202 *N* hydrochloric acid. The results of these titrations are presented graphically in the curves shown.

In the course of titration it was noticed that, after reaching a certain stage in the experiment, the potential began to drop to a final equilibrium much lower than the initial one. This phenomenon occurred only within the range of P_H 7.66 (0.6988 volt) to P_H 9.58 (0.8124 volt). These figures represent the initial readings. Final equilibrium corresponding to P_H 7.66, after seventy-five minutes, was 7.51 (or 0.6908 volt), and that corresponding to P_H 9.58 after twelve hours was 9.36 (or 0.7993 volt). The drop of potential took place at every point within this range after the addition of sodium hydroxide, and was a minimum at either of these two points, and maximum at P_H 8.71 (or 0.7612 volt). The final equilibrium corresponding to P_H 8.71 was P_H 7.97 (or 0.7177 volt), after thirty hours, a drop of 0.74 P_H unit (or 0.0435 volt).

The final neutralization equilibrium was easily attained at all points

corresponding to measurements up to P_H 7.66 (or 0.6988 volt), and above P_H 9.58 (or 0.8124 volt).

The phenomenon within the above mentioned range may be due to one of the following causes: (1) decomposition of the diamine thiosulfuric acid with formation of sulfuric acid; (2) poisoning of the electrode by some impurity present in either the thiosulfuric acid or the sodium hydroxide; (3) liberation of hydrochloric acid occluded by the electrode during the process of platinizing in chloroplatinic acid, or occlusion of the diamine thiosulfuric acid in which the electrode was immersed.

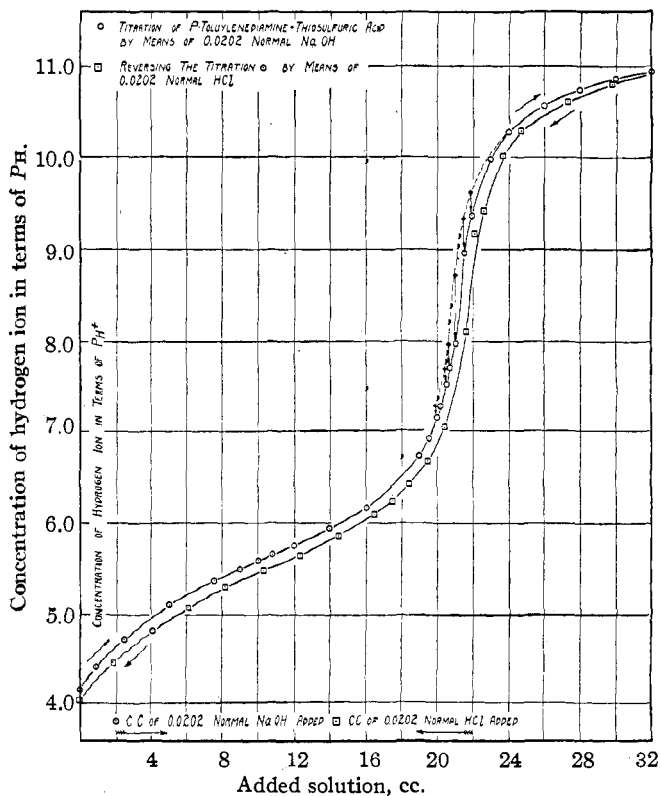


Fig. 1.

It was shown that there was no decomposition of the diamine thiosulfuric acid with formation of sulfuric acid because the final equilibrium remained constant for sixty-three hours and because practically no barium sulfate could be obtained from the solution after standing for twenty-four hours. Poisoning of the electrode was proved not to occur as shown by the smoothness of the curve, the similarity of the reverse titration curve and the constancy of the electrode after eighty hours' standing in solution.

The third hypothesis concerning the drop in potential suggested the liberation of the hydrochloric acid occluded by the electrode during the process of platinizing in chloroplatinic acid solution, and the diamine thio-sulfuric acid occluded by the electrode during the period before reaching the neutralization region. In order to determine whether the electrode contributed to the occurrence of this phenomenon, a new electrode was platinized under similar conditions and used to titrate 25 cc. of 0.1 *N* hydrochloric acid solution diluted to 125 cc. with distilled water. The steady neutralization equilibrium was obtained immediately at each point and no indication of drop of potential was observed during the entire course of titration. The curve plotted from the results was a typical hydrochloric acid titration curve. However, due to the fact that in the measurements of hydrogen electrode potentials in inorganic solutions which are strongly acid, strongly alkaline, or well buffered, it is difficult to observe this phenomenon,⁵ it was necessary to study the measurements of the hydrogen electrode potentials of an organic acid whose ionization constant approximated that of the diamine thiosulfuric acid.

According to Ostwald,⁶ *K*_a for propionic acid from the conductivity measurements is 1.34×10^{-6} . One hundred cubic centimeters of 0.0052 normal propionic acid was titrated by means of 0.0197 normal sodium hydroxide solution. In the course of the titration it was noticed also in this case that after reaching a certain point in the titration, the potential began to drop to a final equilibrium which was much lower than the initial potential. This drift of potential occurred within the range of *P*_H 7.85 (0.7104 volt) to 8.91 (0.7730 volt). The final reading of potential corresponded to 0.7104 at 0.6504, a drop of 0.0170 volt. Beyond this point if any drift of potential was noticed it was upward in trend. A comparison of these results with those obtained from the measurements of the hydrogen electrode potentials of the diamine thiosulfuric acid will at once show a close resemblance and point to a common cause. Beans and Hammett,⁵ from their studies on the hydrogen electrode, conclude that the greatest single cause of this phenomenon is the overwhelming tendency of platinum to occlude substances of an acid nature and to give up the occluded acid slowly but continuously. Therefore, in the light of these observations, the phenomenon observed in this investigation may be attributed to the occlusion of acids.⁷ The molecular weight calculated from the stoichiometrical point of the final equilibrium curve is the one that approximates

⁵ Beans and Hammett, *THIS JOURNAL*, **47**, 1215 (1925).

⁶ Ostwald, *Z. physik. Chem.*, **3**, 170, 241, 369 (1889).

⁷ From the conductivity measurements at 25°, the ionization constant for propionic acid, according to White and Jones [*THIS JOURNAL*, **44**, 197 (1910)], is 1.4×10^{-6} ; Franke [*Z. physik. Chem.*, **16**, 463 (1895)], 1.3×10^{-6} ; Drucker [*ibid.*, **52**, 641 (1905)], 1.3×10^{-6} . The shape of the titration curve plotted from our measurements is similar to that of acetic acid with an ionization constant of 1.86×10^{-6} .

most satisfactorily to the true molecular weight. This relationship is suggestive of the possibility of the diamine thiosulfuric acid having been occluded by the electrode to a greater extent than the hydrochloric acid from the chloroplatinic acid solution during the process of platinizing the electrode.

Ionization Constant of 2,5-Diaminotoluene-4-thiosulfuric Acid.—It has been found that the hydrogen-ion concentration in a weak acid 50% neutralized by a strong base is equal to that of the acid provided the salt is practically completely ionized; that is, the middle point of the titration curve of a given acid lies near the point where the hydrogen-ion concentration is numerically equal to the dissociation constant.

In the titration of the diamine thiosulfuric acid, the middle portion of the titration curve corresponds to 10.65 cc. of the sodium hydroxide, or P_H 5.64, or $C_H = 5.56 \times 10^{-6}$. Hence $K_a = 5.56 \times 10^{-6}$.

2-(*o*-Nitrophenyl)-5-methyl-6-aminobenzothiazole, $CH_3(5)H_2N(6)C_6H_3 \begin{matrix} \diagup S \\ \diagdown N \\ \diagup C \end{matrix}$

$C_8H_4NO_2(o-)$.—A mixture of 10 g. of the diaminotoluene thiosulfuric acid, 8 g. of *o*-nitrobenzaldehyde and 80 cc. of glacial acetic acid was refluxed gently for twenty to thirty minutes and then more strongly for an hour longer. The color of the mixture gradually turned to a dark red, and considerable bumping occurred due to the separation of a cream-colored precipitate, which was possibly the acetate of the desired product. The mixture was filtered hot and more of the precipitate separated from the filtrate as the latter cooled and was added to the original precipitate. Warmed on the water-bath with caustic alkali, this cream-colored substance was changed to a yellow solid. Seven grams of the former gave 5 g. of the latter, which proved to be the compound sought.

The filtrate from the cream-colored precipitates was diluted carefully to incipient turbidity and concentrated at laboratory temperature by allowing a stream of dry air to impinge upon its surface. The thiazole separated gradually and nearly completely. Crystallized from 90% alcohol, it was obtained in yellowish needles, m. p. 144° (corr.); yield 36%.

Anal. Calcd. for $C_{14}H_{11}O_2N_2S$: C, 58.94; H, 3.86; S, 11.24. Found: C, 58.86; H, 3.99; S, 11.38.

The alcoholic solution of these crystals exhibited a very faint purplish-red fluorescence.

A small amount (0.5 g.) of this thiazole was diazotized at 0° and after the diazotized mixture had stood for thirty minutes at that temperature it was filtered and the precipitate suspended in 30 cc. of concentrated formic acid and exposed for three hours to direct sunlight. This suspension was refluxed for ten minutes and the resulting solution poured into cold water. The pale yellow precipitate which separated was removed and crystallized from 60% alcohol in lustrous pale yellow needles, m. p. 91.5–92°, which is the melting point recorded by Bogert and Allen³ for 2-(*o*-nitrophenyl)-5-methylbenzothiazole.

Anal. Calcd. for $C_{14}H_{10}O_2N_2S$: N, 10.37. Found: N, 10.59.

2-(*m*-Nitrophenyl)-5-methyl-6-aminobenzothiazole was synthesized from the diamine thiosulfuric acid and *m*-nitrobenzaldehyde in much the same way as just described for the *o*-nitro isomer.

During the refluxing of the initial mixture, some bumping also occurred, caused by

the separation of by-products. Upon the completion of the heating, the mixture was filtered hot and as the filtrate cooled most of the thiazole separated, due to its sparing solubility in cold glacial acetic acid. The filtrate from this thiazole was diluted to moderate turbidity and then heated. This caused the impurities to redissolve and by filtering the hot solution more thiazole was recovered. Too large dilution during this latter step obviously precipitated more tarry impurities than could be redissolved on heating. The crude thiazole was refluxed in a large volume of glacial acetic acid in the presence of a decolorizing charcoal, to remove tarry impurities, and then crystallized from toluene, from which it separated very slowly in orange-yellow needles, m. p. 233.5° (corr.); yield, 58.5%. In toluene solution it showed a yellowish-red fluorescence.

Anal. Calcd. for $C_{14}H_{11}O_2N_3S$: C, 58.94; H, 3.86. Found: C, 58.76; H, 3.99.

2-(*p*-Nitrophenyl)-5-methyl-6-(*p*-nitrobenzalamino)-benzothiazole, $CH_3(5)(N=$

$C_6H_4NO_2)(6)C_6H_4 \begin{array}{c} S \\ \diagup \quad \diagdown \\ N \end{array} \text{CC}_6H_4NO_2(p)$.—When a mixture of 11 g. of the diamine thio-sulfuric acid, 15 g. of *p*-nitrobenzaldehyde and 75 cc. of glacial acetic acid was refluxed, the reaction seemed to proceed in the same way as noted for the *o*- and *m*-isomers. A dark red solid precipitated which, when removed and crystallized from xylene, yielded fine dark red needles, m. p. 279° (corr.), the xylene solution exhibiting a greenish-yellow fluorescence. More of this material was precipitated from the original acetic acid mother liquor by diluting the latter with alcohol and warming.

Anal. Calcd. for $C_{21}H_{14}O_4N_4S$: C, 60.30; H, 3.32; N, 13.4; S, 7.65. Found: C, 60.00, 60.15, 60.22; H, 3.91, 3.94, 3.68; N, 13.24; S, 7.67.

While these analytical results are reasonably satisfactory so far as C, N and S are concerned, it is not clear why the figures for hydrogen should run so high.

A determination of the molecular weight gave the figures 405.1 and 411.4; calcd., 418.

A careful search for 2-(*p*-nitrophenyl)-5-methyl-6-aminobenzothiazole in the mother liquors from the *p*-nitrobenzal derivative resulted in the isolation, finally, through repeated fractional crystallization, of a very small amount (0.005 g.) of fine bright orange needles, m. p. 312–315°, whose analysis indicated that they were probably the impure amine, but the quantity remaining after the analysis was insufficient for further purification.

Anal. Calcd. for $C_{14}H_{11}O_2N_3S$: C, 58.94; H, 3.86. Found: C, 57.72; H, 3.00.

Attempts to prepare this amine by varying the proportions of initial materials, temperature, length of heating, and other factors, gave only the *p*-nitrobenzal derivative.

This *p*-nitrobenzal derivative was surprisingly stable to hydrolysis, for it was unaltered when refluxed for several hours with either 30% sulfuric or concentrated hydrochloric acid. This stability was evidently associated with the presence of the nitro group for, as described beyond, when subjected to the action of tin and hydrochloric acid, the reduction of the nitro groups was accompanied also by hydrolysis of the *p*-nitrobenzalamino group.

A small amount (1.0 g.) of the 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzalamino)-benzothiazole was treated with 25 cc. of cold concentrated nitric acid for one or two minutes and the mixture then diluted with water. The precipitate separated crystallized from xylene in fine reddish orange needles, which melted at 247.5° (corr.), then congealed and remained unmelted at 300°. The product was apparently an impure mononitro derivative of the *p*-nitrobenzalamino compound.

Anal. Calcd. for $C_{21}H_{13}O_6N_4S$: C, 54.42; H, 2.67. Found: C, 54.24; H, 3.41.

2-(*o,p*-Dinitrophenyl)-5-methyl-6-aminobenzothiazole was prepared by refluxing for an hour and a half a mixture of the diamine thiosulfuric acid (10g.), 2,4-dinitrobenzaldehyde (15 g.) and glacial acetic acid (80 cc.) and filtering hot. The small quantity of insoluble material filtered out was composed largely of the acetate of the thiazole, from which the thiazole itself was recovered by treatment with alkali.

The main portion of the thiazole was obtained from the filtrate by concentrating it cold with the aid of a current of air, adding alcohol to the concentrate, collecting the precipitate and crystallizing it from benzene. Fine red needles resulted, m. p. 239.2° (corr.); yield, 30%. A benzene solution of the compound possessed a greenish fluorescence.

Anal. Calcd. for $C_{14}H_{10}O_4N_4S$: C, 50.90; H, 3.03. Found: C, 51.03; H, 3.12.

2-(*o*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—The 2-(*o*-nitrophenyl)-5-methyl-6-aminobenzothiazole (4 g.) was dissolved in concentrated hydrochloric acid (25 cc.) and refluxed for two hours with tin (10 g.), after which the excess of tin was filtered out, the filtrate diluted with an equal volume of water, then made strongly alkaline with sodium hydroxide solution and allowed to cool. The precipitate was removed and rubbed to a paste with strong sodium hydroxide solution, to liberate the amine, which was purified by crystallization from 65% alcohol. Fine yellowish or reddish-violet needles were obtained, m. p. 251° (corr.); yield 70%; bluish-violet fluorescence in alcoholic solution.

Anal. Calcd. for $C_{14}H_{13}N_3S$: C, 65.88; H, 5.13. Found: C, 65.47, 65.63; H, 5.25, 5.21.

2-(*m*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—Attempts to prepare this by reduction of the 2-(*m*-nitrophenyl) derivative, in the same way as the *o*-aminophenyl isomer, were unsuccessful, for no product of satisfactory purity could be isolated.

2-(*p*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—When the 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzalamino)-benzothiazole was similarly reduced with tin and hydrochloric acid, and the crude amine crystallized from 50% alcohol, orange-yellow or greenish-yellow needles were obtained, m. p. 255.5° (corr.); purplish fluorescence in alcoholic solution.

Anal. Calcd. for $C_{14}H_{13}N_3S$: C, 65.88; H, 5.09. Found: C, 65.98; H, 5.22.

In the course of the reaction, therefore, the *p*-nitrobenzalamino group was hydrolyzed.

Preparation of a Columbia Yellow Dye from 2-(*o*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—Some of this thiazole was sulfonated and an aqueous solution of the sodium sulfonate was oxidized with a freshly prepared sodium hypochlorite solution, to obtain a dye of Columbia Yellow (Colour Index No. 814) type. Analysis of the black amorphous product gave figures which indicated that it was probably a mixture of the di- and tetra-sulfo acids.

Anal. Calcd. for $C_{28}H_{20}N_6S_2(SO_3H)_2$: C, 50.45; H, 3.34. For $C_{28}H_{18}N_6S_2(SO_3H)_4$: C, 40.67; H, 2.66. Found: C, 46.02; H, 3.33.

It dyed un mordanted unbleached cotton a deep orange-tan, of approximately the same fastness as other dyes of this type. Diazotizing and coupling experiments with β -naphthol led to the conclusion that the dye still retained free amino groups and that probably only the amino groups on the 2-phenyl participated in the formation of the Columbia Yellow dye. The azo dyes so produced were likewise direct dyes for cotton.

Preparation of a Columbia Yellow Dye from 2-(*p*-Aminophenyl)-6-aminotoluthiazole.—The thiazole (2.5 g.) was heated for fifteen hours at 75–85° with a mixture of 20 cc. of concentrated and 25 g. of fuming (50%) sulfuric acid. The solution was poured upon cracked ice, the precipitate collected, dissolved in ammonium hydroxide solution,

the solution reprecipitated by hydrochloric acid, this solution and precipitation repeated once or twice and the product dried at 120°.

Anal. Calcd. for $C_{14}H_{12}N_2S(SO_3H)$: C, 50.14; H, 3.88; S, 19.16. For $C_{14}H_{11}N_2S(SO_3H)_2$: C, 40.48; H, 3.13; S, 23.13. Found: C, 41.10, 40.83; H, 3.82, 3.94; S, 19.16, 20.5.

The product is hence a mixture of the mono- and di-sulfonic acids.

It was dissolved in sodium carbonate solution, and mixed with a freshly prepared sodium hypochlorite solution. The solution rapidly turned dark red and, after standing for twenty-four hours, was precipitated by the addition of concentrated hydrochloric acid. The precipitate was collected, dissolved in ammonium hydroxide solution and reprecipitated with hydrochloric acid, then dissolved in water and reprecipitated with concentrated hydrochloric acid, and finally dissolved in water and the solution evaporated on the water-bath. The dye was left as a lustrous black solid.

Anal. Calcd. for $C_{24}H_{20}N_6S_2(SO_3H)_2$: C, 50.45; H, 3.34. For $C_{24}H_{18}N_6S_2(SO_3H)_4$: C, 40.67; H, 2.66. Found: C, 44.90; H, 2.63.

The product was therefore a mixture of di- and tetra-sulfo acids. Its tinctorial properties, as well as its behavior when diazotized and coupled with β -naphthol, were much the same as those stated for the dye from the 2-(*o*-aminophenyl) isomer, except that the dyeings with the latter were of lighter shade.

2-(*o,p*-Diaminophenyl)-5-methyl-6-aminobenzothiazole, secured by reduction of the dinitrophenyl compound in similar manner, crystallized from 50% alcohol in fine orange needles, m. p. 285.5°; yield, 70%; sky-blue fluorescence in alcoholic solution.

Anal. Calcd. for $C_{14}H_{14}N_4S$: C, 62.22; H, 5.18. Found: C, 62.11; H, 5.36.

An attempt to prepare a thiosulfuric acid of **2,4-diaminotoluene**, by the process used for the preparation of the 2,5-diaminotoluene-4-thiosulfuric acid, proved unsuccessful.

Summary

1. A method for the preparation of 2,5-diaminotoluene-4-thiosulfuric acid is described. A potentiometric titration of this acid shows its ionization constant to be 5.56×10^{-6} at 25°.

2. Condensation of this acid with nitrobenzaldehydes gives the corresponding 2-nitrophenylaminotoluthiazole, except in the case of the *p*-nitrobenzaldehyde, when the thiazole obtained carries also a *p*-nitrobenzal group on the 6-amino.

3. Certain of these nitro derivatives were reduced to the corresponding amines, and with some of the latter preliminary studies were made of their conversion into dyes of Columbia Yellow type.

NEW YORK, N. Y.