



The Effect of Substituting Sulfur for
the Imide Group in a Dye of the Indanthrene Series.

Thesis,

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Course V.

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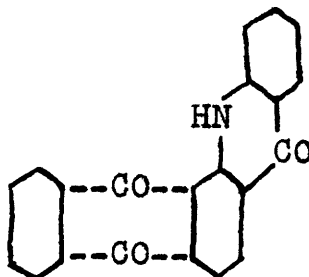
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Introduction.

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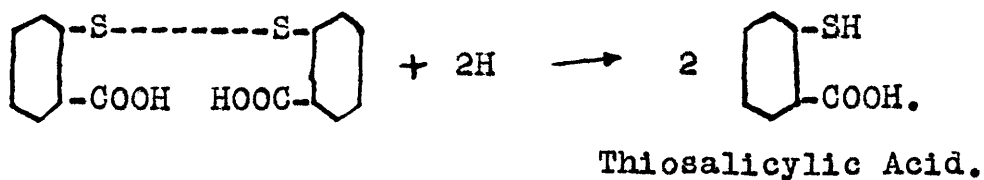
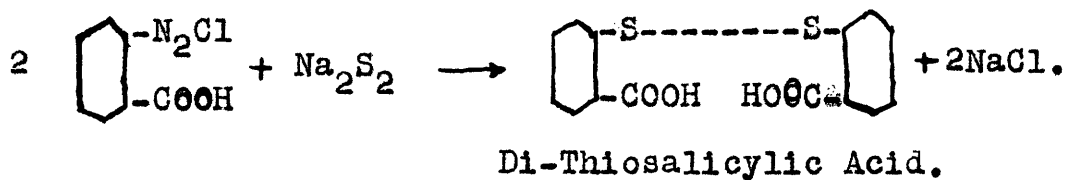
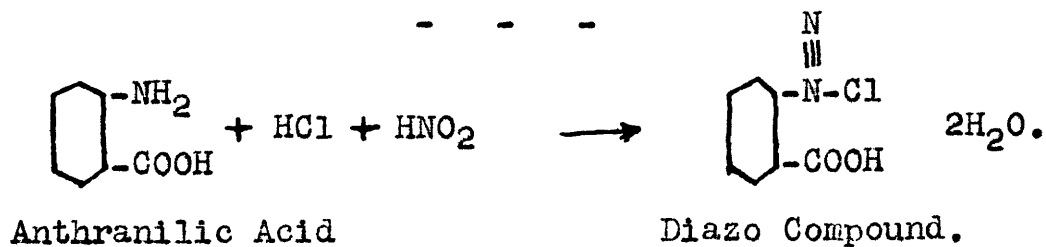
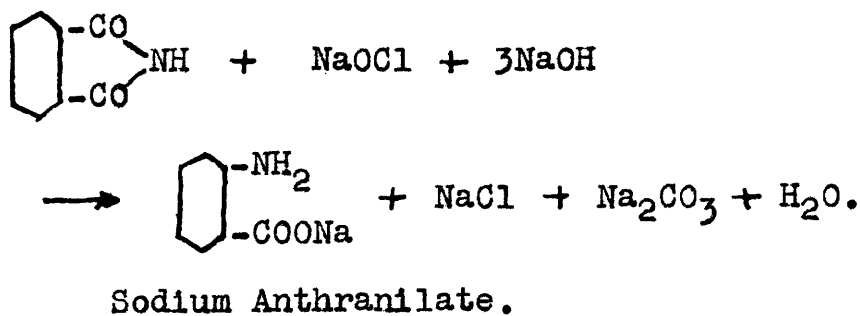
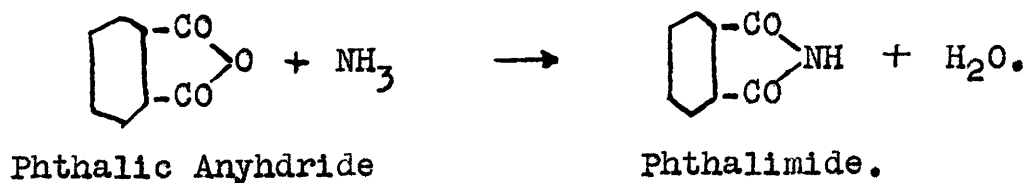
The object of this thesis was to determine how the color and fastness of certain dyes of the indanthrene series are affected by the substitution of a sulfur atom for the -NH- or -CO- group. The indanthrene dyes form very good vat colors, and sulfur, which is present in many intermediates, frequently increases the fastness and makes dyes more valuable.

A very fast dye of the indanthrene series, which produces a red-violet color, has the following formula:

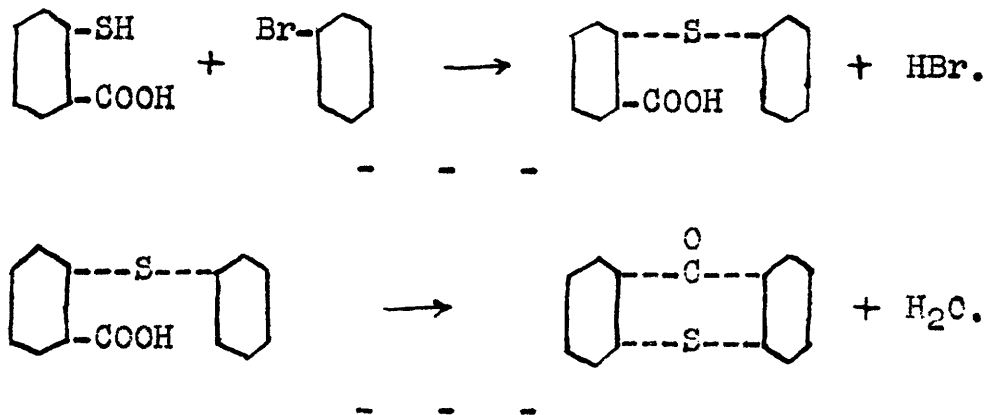


It was planned to substitute an atom of sulfur for either a carbonyl or imide group in this particular dye and observe the result.

It was desired to start from phthalic anhydride and run through the syntheses given below, in order to determine the yields and best methods and operation-factors which are not very well described in the literature.

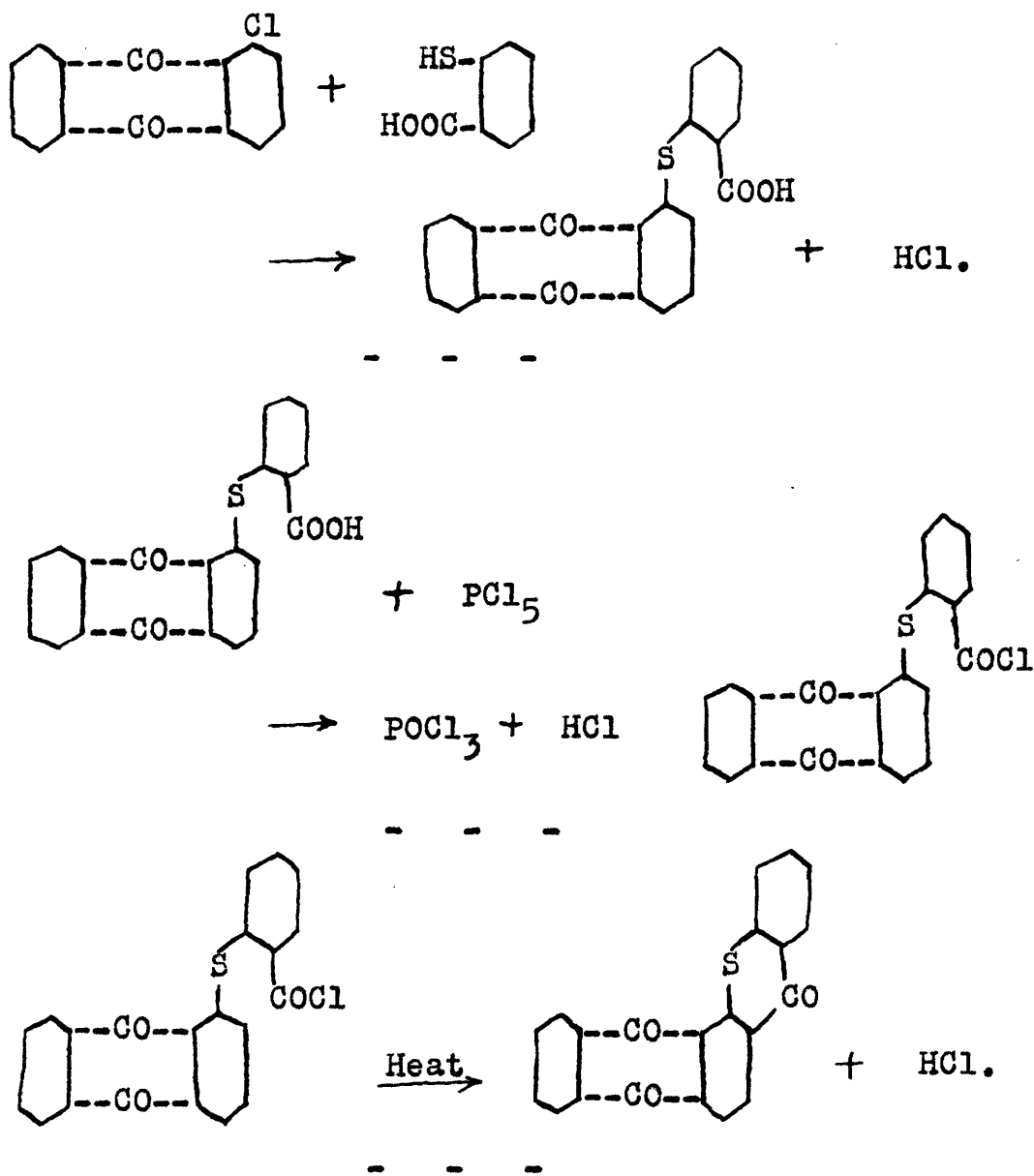


The first mode of attack was the condensation of thiosalicylic acid with brombenzene, as has already been done by E.G. Marsden and Samuel Smiles. This gives Thio-xanthone, as illustrated below:



If this synthesis could be carried out, a compound would be obtained with sulfur in place of one carbonyl group of the anthraquinone molecule. The yield of this product was too small to warrant further experimentation, and the process was abandoned.

The method finally used, was the condensation of alpha-chlor-anthraquinone with thiosalicylic acid; the formation of the acid chloride; and the closing of the ring with the elimination of hydrochloric acid. These operations are clearly outlined below:

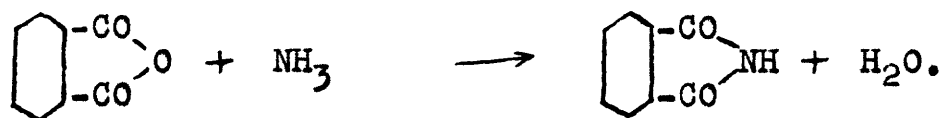


These syntheses were successfully carried out, as described in the following pages. The method was also made more promising by the fact that both alpha-chlor-anthraquinone and thiosalicylic acid are readily available as dyestuff intermediates.

Experimental Part.

The Preparation of Phthalimide.¹

- - -



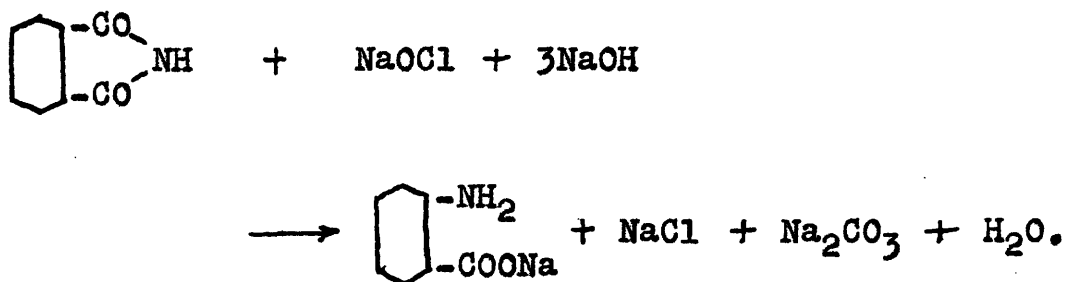
50 gms. Phthalic Anhydride.
60 " . Ammonium Carbonate.

These materials are mixed in a one liter round bottom flask, and heated to two hundred and twenty-five degrees centigrade on the oil bath for about twelve hours. At one hundred degrees, water and carbon dioxide are evolved, the mass then fuses, and finally solidifies. The fused mass is broken up into small lumps and extracted by boiling with water, the solution is decanted off through a fluted filter in a steam funnel, and allowed to cool. The small white needles of phthalimide then crystallize out, and may best be filtered off by means of a Büchner funnel. The results of this work are given below.

Run No.	Multiple of above quantities used.	Grams.	Yield.	
				Percent of theoretical.
1	2	54.0		54.0 %
2	2	69.5		69.5 %
3	4	178.0		89.0 %

This seems to show that a higher percentage yield can be obtained when larger quantities are used, than when only small amounts are used. Better results are also obtained if the fused mass is powdered, instead of being broken into small lumps.

The Preparation of Anthranilic Acid.²



30 gms. Phthalimide.
 60 " Caustic Soda.
 300 " Sodium Hypochlorite Soln., (5.06%).

Thirty grams of finely powdered phthalimide are dissolved, together with sixty grams of caustic soda, in two hundred and ten cubic centimeters of water, the solution being cooled by surrounding it with ice. Three hundred grams of a five and six hundredths per cent sodium hypochlorite solution are added with stirring, and the mixture warmed for a few minutes to about eighty degrees, at which temperature the reaction is soon completed. After cooling, the liquid is neutralised with hydrochloric or sulfuric acid, and then acetic acid is added to precipitate the anthranilic acid, which is filtered off and washed with cold water.

The results are tabulated on the next page.

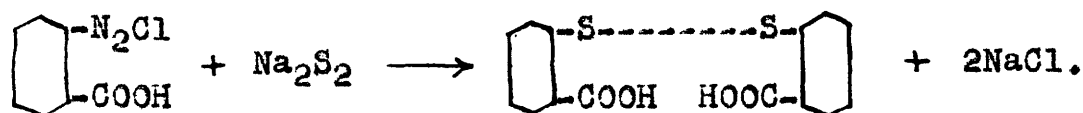
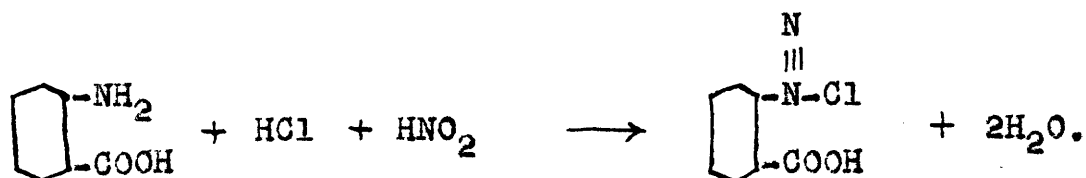
Results:

Run No.	1 st Ppt.	Extracted.	Total.	Yield %.
1	15.75 gms.	3.70 gms.	19.45 gms.	72.0%
2	12.50 "	2.20 "	14.70 "	55.0%
3	13.20 "	1.80 "	15.00 "	55.5%
4	13.70 "	1.80 "	15.50 "	57.3%
5	18.50 "	-----	18.50 "	69.0%
6	20.00 "	-----	20.00 "	74.0%

A Note on the Preparation of
Anthranilic Acid.

Although the literature does not so state, it is very important in the preparation of this acid that the solutions should be freshly prepared. When phthalimide is allowed to stand in contact with a solution of alkali, it decomposes with the evolution of ammonia. If this precaution is not observed closely, the yields obtained will be very poor, while if all the solutions are prepared just before being used, the yields may be increased by twelve to seventeen percent. The observance of these conditions is responsible for the increased yields in runs five and six.

The Preparation of Dithiosalicylic ³
Acid.



28 gms.	Anthranilic Acid.
48 "	Hydrochloric Acid (1.19 Sp, Gr.).
14 "	Sodium Nitrite, Pure.
52 "	Sodium Sulfide Crystals.
7 "	Sulfur.
24 "	Aqueous Caustic Soda (1.38 Sp. Gr.)
	Ice.

Anthranilic acid is mixed with one hundred cubic centimeters of water and forty-eight grams of concentrated hydrochloric acid, and then diazotized by the addition of a concentrated aqueous solution of fourteen grams of sodium nitrite, ice being added and the usual precautions observed. The diazo solution is then slowly run, with constant stirring, into a solution containing seven grams of sulfur and fifty-two grams of sodium sulfide in fifty-eight cubic centimeters of water, to which seventeen cubic centimeters of aqueous caustic soda has been previously added, the whole being cooled by the addition of sixty

grams of ice. It is necessary to regulate the temperature throughout the addition of the nitrite solution so that it does not rise above five degrees. After a short time nitrogen is evolved in large quantities, and the temperature rises 15 - 25°, due to the formation of dithiosalicylic acid. After two hours, hydrochloric acid is added until the solution is acid to Congo paper, and the precipitated dithiosalicylic acid is filtered and washed with one liter of water. The dithiosalicylic acid was used without weighing, for the next synthesis.

The Preparation of Thiosalicylic Acid.⁴



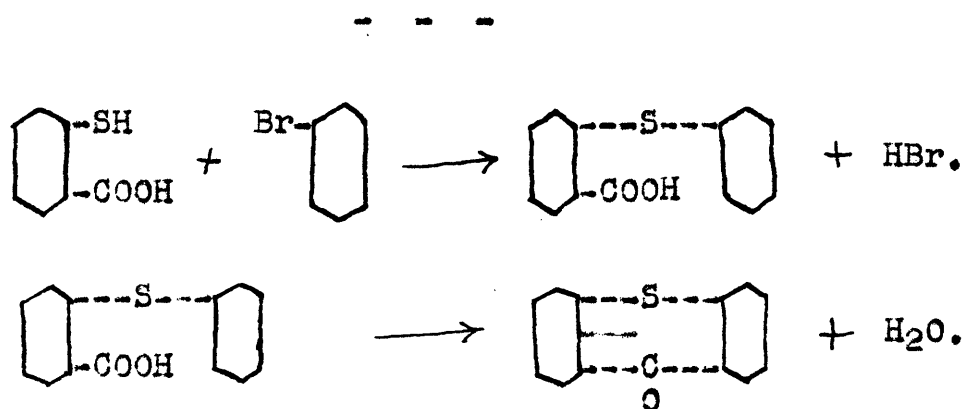
12 gms. Anhydrous Sodium Carbonate.
 20 " : Iron Powder.
 24 " : Aqueous Caustic Soda (1.38 Sp. Gr.).

The filtered and washed dithiosalicylic acid obtained in the previous experiment is brought into solution as sodium salt by boiling it with an aqueous solution containing twelve grams of anhydrous sodium carbonate, the solution being filtered from any undissolved sulfur. The liquid is then mixed with the iron powder, and the whole boiled for some hours, until a test portion on being treated with aqueous caustic alkali and filtered, yields a filtrate which does not smell of hydrogen sulfide when acidified. When this stage has been reached the iron powder is precipitated by the addition of seventeen cubic centimeters of aqueous caustic soda, the mixture boiled and filtered. The addition of acid to the filtrate causes the separation of thiosalicylic acid as a colorless or pale yellow precipitate melting at 165°, which is filtered and washed.

The results are tabulated on the next page.

Run No.	Yield.	
	Grams.	Percent of theoretical.
1	11.00	36.50 %
2	17.00	55.00 %
3	19.00	61.50 %

Condensation of Thiosalicylic Acid
with Brombenzene,⁵



Marsden and Smiles used the dithiosalicylic acid with brombenzene, instead of the thiosalicylic acid itself. Their method is as follows: the acid in quantities of about ten grams at a time, was mixed with fifty cubic centimeters of concentrated sulfuric acid and excess of brombenzene. Interaction immediately began with evolution of sulfurous acid, but it was hastened to completion by warming the mixture on the water bath at fifty degrees for three quarters of an hour. During the process the mixture was constantly shaken. The precipitate which separated out on pouring the mixture into water, was collected, and washed with water; finally, it was treated with aqueous alkali hydroxide to remove any dithio-acid. The solid residue was again collected, and washed with water until free from alkali. Recrystallization of the

dried substance from boiling alcohol gave minute, yellow needles, which melted at 141° C.

It was decided to ^{use} the thio-acid with brombenzene.

The following quantities were used:

7 gms. Thiosalicylic Acid.
10 " Brombenzene.
70 c.c. Conc. Sulfuric Acid.

About forty percent excess of the brombenzene was used. The reaction mixture was heated on the water bath for three quarters of an hour and then poured on cracked ice, after which, the excess brombenzene was distilled off with steam. As the actual ^{Yield} was only one and seven tenths grams, or three and two tenths percent, no more time was spent upon this reaction.

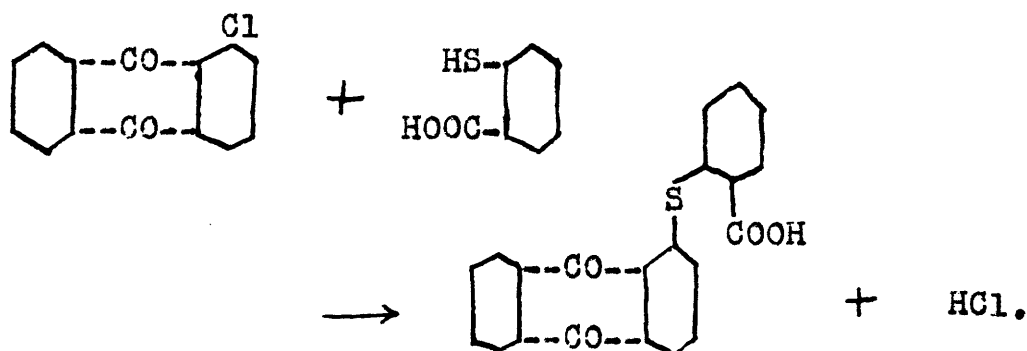
The next and successful method of attack was the condensation of thiosalicylic acid with alph-chlor-anthraquinone. The experiments on this reaction will be described in the following pages.

Purification of Alpha-Chlor-Anthraquinone.⁶

This compound is said to be purified by crystallization from toluene, in which it is readily soluble. It forms lustrous needles with a brown-yellow color when it is dissolved in sulfuric acid. In nitrobenzene and glacial acetic acid it is soluble. In alcohol it is only difficultly soluble.

The crude material used in the work of this thesis, originally melted at 149-152°, but upon recrystallization from glacial acetic acid three times, the melting point was raised to 162°. Further recrystallization did not improve the product. The use of toluene seemed to do no good whatever.

Condensation of Alpha-Chloro-Anthraquinone
with Thiosalicylic Acid.



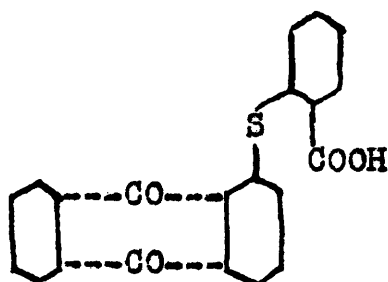
10 gms.	Thiosalicylic Acid.
16 "	Chloranthraquinone.
10 "	Sodium Acetate.
.4 "	Copper "
.4 "	Fine Copper Powder.
240 "	Amyl Alcohol.

All of the solids are thoroughly mixed on a piece of paper and placed in a five hundred cubic centimeter round bottomed flask. The amyl alcohol is then poured in, and the whole heated with the use of a reflux condenser, to one hundred and fifty degrees centigrade for a long time.

The reaction product is then filtered off, washed with alcohol, and dissolved so far as possible in sodium hydroxide solution, filtered to remove any foreign material, and the filtrate acidified with hydrochloric acid. The precipitated acid is then filtered off and dried. It is purified by dissolving out the unchanged thiosalicylic acid with ethyl alcohol.

The first time the reaction was carried out in eight hours, but the yield obtained was only seven and nine tenths grams or thirty-five and six tanths percent. The yield was finally improved however, until upon sixteen hours heating at one hundred and fifty degrees, a yield of eighty-seven percent was obtained.

The final melting point after three extractions with ethyl alcohol, was two hundred and fifty degrees. The apparent structure of the condensation product is given below:



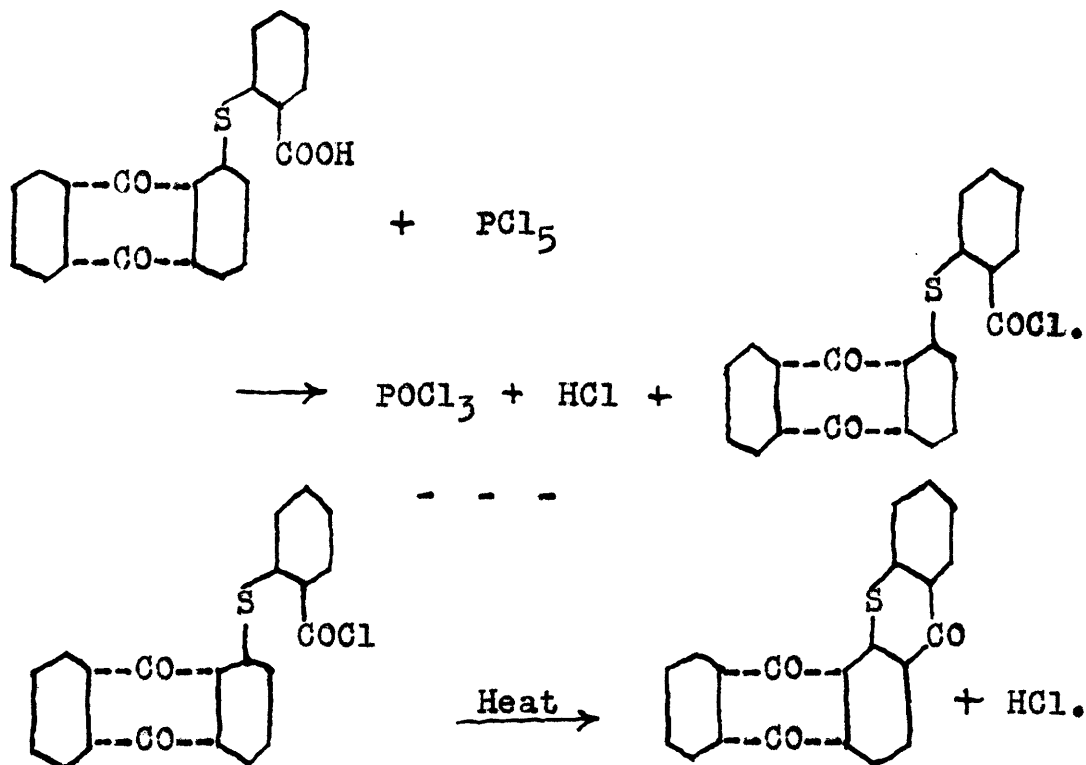
The presence of the carboxyl group is proven as the substance is readily soluble in either sodium carbonate or hydroxide, yielding a dark red solution in both cases. The acid is easily recovered unchanged upon treating this solution with either a mineral acid or acetic acid. The acid chloride is formed upon treatment with phosphorous pentachloride.

The absence of chlorine was determined by means of the qualitative test described by A.A. Noyes and S.P. Mulliken.

The amount of sulfur present was determined ^{by} the method of Carius. The results of three determinations were as follows: 8.70%, 8.65%, and 8.60%, an average of 8.65%, as against a theoretical value 8.90%, this seems to substantiate the structure given above very well indeed. Also the condensation product gives a vat with alkaline hydrosulfite. This phenomenon was interpreted as indicative of the presence of the anthraquinone residue.

Closing the Ring.

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3 gms. Phosphorous Pentachloride.
 5 " Intermediate Acid.
 150 c.c. Anhydrous Nitrobenzene.

The well mixed materials were placed in a five hundred cubic centimeter round bottomed flask with a reflux condenser, and heated to boiling on the air bath for seven hours. The product, which is dark red-brown in color, was filtered off, washed with ethyl alcohol and dried. The yield was seventy-two and one half percent.

This substance apparently has the structure given above, and has been checked up by a determination of the

sulfur content, which came out as 9.25%, as against 9.36% theoretically.

This closed ring compound is insoluble in alkalies, and is only slightly soluble in alcohol. The substance does not melt, but decomposes between 294 and 300° C., and is a non-crystalline material.

Value as a Dye.

In a basic solution of hydrosulfite this substance dyes both cotton and wool a fairly bright orange color, as might be expected. That this dye is very fast is shown by the fact that it is not affected by either acid nor alkali, nor by light as far as can be determined.

Summary and Conclusion.

It has been shown that the synthesis of thiosalicylic acid from phthalic anhydride can be carried out without a very great loss of material, the yields being from 70% to 90%, except in the case of thiosalicylic acid where the yield dropped off to 61.50%. Also it is possible to condense this acid with alpha-chlor-anthraquinone and then to close the ring with great efficiency, the yields^{being} 87% and 72.5% respectively.

In conclusion it may be stated that the effect of substituting a sulfur atom for the imide group increases the fastness of the dye, and gives an orange color instead of the red-violet color of the other compound containing the imide group in place of the sulfur.

References.

1. Cain and Thorpe, The Synthetic Dyestuffs and Intermediate Products. P. 295.
2. Same as above.
3. Cain and Thorpe. P. 297.
4. Same as 3.
5. E.G. Marsden and Samuel Smiles, The Synthesis of Derivatives of Thioxanthone from Aromatic Disulfides. Jour. Chem. Soc. London, Vol. 99. Pp. 1353 - 1358.
6. Friedländer: Fortschritte der Theerfarbenfabrikation. 1900 - 1902. Page 322.
Ger. Pat. No. 131538.