

Papers presented for Degree of Doctorate of Science

by R. S. Wishart, M.A., B.Sc.

1. Thesis - Studies in the Azine Series.

Additional Papers in support of Thesis -

1. Synthesis of Naturally Occurring Inosite. An account of work done by H. Wieland and R.S.Wishart at Munich University, 1914.
2. Notes on the Action of Para-Toluidine on Meta Toluylene Di Amine. by R. S. Wishart.
3. On the Constitution of Colouring Matters derived from Quinoline, in particular on the Constitution of the Isocyanines, by R. S. Wishart. An Account of work done at Cambridge University Laboratories under the supervision of Sir W.J.Pope and Dr. W.H.Mills, 1919.



W. Wishart

SYNTHESIS OF NATURALLY OCCURRING INOSITE.

BY.- R. S. WISHART.

AN ACCOUNT OF WORK DONE BY.-

H WIELAND & R.S. WISHART.

AT

MUNICH UNIVERSITY. 1914.

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still more simple would it be from carbon monoxide which can be transformed by potassium into the potassium salt of hexa-oxybenzene $(COK)_6$.

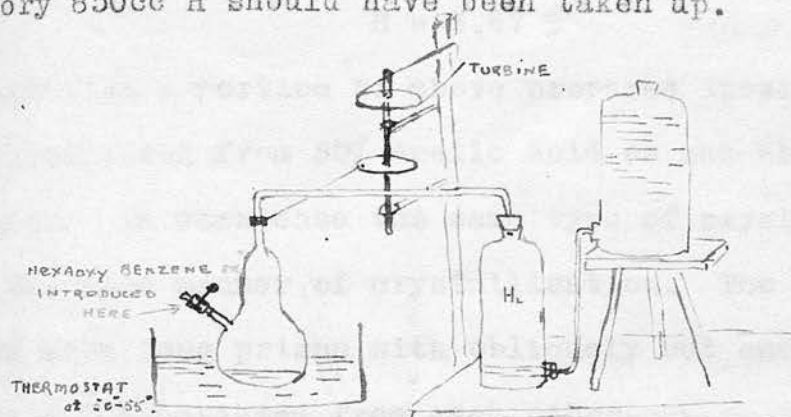
As catalyser in the hydration Palladium Black was used.

Hexa-Oxy benzene was prepared by the method given by Von Nietzki and Benckiser (Ber 18,499 (1885) and as the reaction with hydrogen and Palladium Black is only successful with very pure material, this was recrystallised several times by the method given by the above authors.

During preliminary experiments considerable difficulty had to be overcome, until it was found that the slightest trace of impurity and especially trace of HCl - which adhered to the hexa-oxybenzene and had to be freed from it by washing with water - caused the hydration to cease completely. The reaction was brought about in a pear shaped shaking flask of the Willstater pattern (Ber. 45,1472, (1912) & Ber 46,3330 (1913)) at a temperature of 50° - 55° and owing to the insolubility of hexa-oxybenzene this latter was used in suspension. 2 grams hexa-oxybenzene in 30 grams of water were shaken with 1 gram of Palladium Black. In 4 hours 820cc hydrogen were absorbed, and all organic substance was then in solution. As a test portion became coloured on exposure to air there was still some oxidisable substance present.

During the next three hours it was shaken until a total of 970cc hydrogen was absorbed and the action had come to an end. Then the flask was shaken at a temperature of 80° for 1 hour

during which only a few ccs hydrogen were absorbed. By theory 850cc H should have been taken up.



The contents of the flask were filtered and brought to dryness in vacuum over H_2SO_4 & solid KOH . After standing some time crystallisation began in the syrup. The residue was then twice rubbed well with 15cc alcohol each time, in which inosite is difficultly soluble. The alcohol was poured off and the hard syrupy mass rubbed with a very little water. The inosite was in this way partly crystallised. Then just so much alcohol was added as not to bring down a precipitate and after standing .3 grams Inosite was obtained in a crystalline state. This was purified by dissolving in a very little hot water, adding a drop of alcohol, and allowing to crystallise in the cold. These crystals were dried to constant weight and had a melting point of $218^\circ-219^\circ$, the same as given by Maquenne (A ch (6) 12,570 (1887) and the same as given by a preparation of natural Inosite. The melting point of the mixed substances was not altered.

Micro analysis by ^{Pregl's} ~~Pugh's~~ method.

		17.26	
11.715 mg. substance	gave	28.58 mg CO_2	& 7.20 mg H_2O .
13.330 mg	"	19.55 mg CO_2	& 8.01 mg H_2O .
C = 40.18 %		H = 6.83%	
40.00 %		6.68%	

$C_6H_{12}O_6$ requires C = 40.00%

H = 6.67 %

In addition a portion of above prepared Inosite was recrystallised from 50% Acetic Acid as was also the natural inosite. In each case the same type of crystals were observed and the same manner of crystallisation. The crystals in both cases were long prisms with obliquely cut ends, and were not to be differentiated from each other.

The solubility **and** other properties of the above synthetic inosite were the same as those of the naturally occurring substance. To make quite sure of the identity of the synthetic inosite it was acetylated with acetic anhydride and a little zinc chloride, and the hexa acetyl body obtained recrystallised from alcohol. This gave a melting point $210^\circ - 211^\circ$. That from natural inosite 211° , and a mixture of the two had a melting point of $210^\circ - 211^\circ$.

In the above research the total yield was not determined, but this would certainly be much greater than the .3 grams indicated, as without working up the mother liquors more than 1 gram inosite was obtained. This synthesis of Inosite forms a conclusion to the fine work of Mietzki & Benckisser on hexa-oxybenzene.

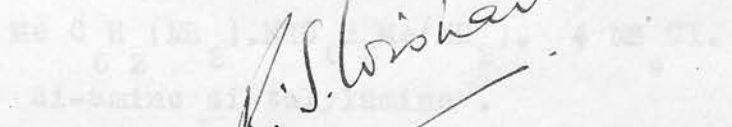
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R. J. Wisheart

According to the literature on the subject, when p-toluidine
p-toluidine hydrochloride, and meta toluylene di-amine are heated
together in sealed tubes at 200-275°C the product is p-tolyl-m-tolylisno-



NOTES ON THE ACTION OF PARA-TOLUIDINE
ON META TOLUYLENE DI AMINE.



K. S. Wiseman



Fawley.

Hault

(2) Use of open vessels (allowing HCl to escape for autocatalysis)

(retention of NH_2 .)

3.

(3) Variation in time of heating , to obtain if possible an indication of the rates of reaction of the three reactions

(4) Variation in the amount of HCl required .

(5) Use of catalysts .

(6) Effect of the addition of NH_4Cl to the reaction mixture .

4

(7) Effect of increasing the pressure without retaining the ~~ammonia~~ ammonia .

(I) Of the three products of the reaction , di-tolylamine hydrochloride is very easily hydrolysed by water , and can thus be easily separated from the hydrochlorides of the other two products which, having free NH_2 groups, are not easily hydrolysed. At the same time the hydrochlorides of di-amino di- tollylamine and p-tolyl m-toluylene di-amine have about the same solubility in water -100 c.c. cold water dissolve 1.2 grams of the former hydrochloride and 1.0 grams of the latter , whilst the bases themselves show greater differences in solubility in water at 100°C , di-amino di-tolylamine being more soluble in water at 100°C than p-tolyl m- toluylene di- amine , which is practically insoluble .

It was found that by increasing the proportion of m-diamine to to p-toluidine there was, of course , a greater yield of di-amino di-tolylamine, which was evidenced by the greater impurity of the product obtained , as shown by the lowering of its melting point. The most suitable proportions found were 7molecular proportions of toluidine to 1 of toluidine hydrochloride to 1 of m-diamine. The product from this mixture allowed of the separation of the separate substances without undue loss of p-tolyl m-toluylene di-amine.

as two . The presence of hydrochloric acid is thus

essential to the reaction.

3.

(2). Use of open and closed vessels.

Experiments in an autoclave at 260° - 270° C showed that all three reactions were reversible, that equilibrium was attained in about 20 hours. After that time the proportions of unchanged diamine was always about 23%.

In an open vessel fitted with an air reflux condenser a continuous evolution of ammonia was observed. The temperature rose steadily from 200° C to 216° C (with a mixture of the above proportions) and thereafter remained steady. The escape of ammonia, due to the partial dissociation of ammonium chloride at 216° C, allowed the reaction to proceed to completion in 20 - 24 hours. The p-tolyl m-toluylene di-amine and di-amino di-tolylamine were obtained in about the same proportions as in the autoclave experiments, but the amount of di-tolylamine was much increased, which made the separation somewhat more difficult.

(3) Rate of formation.- Time of heating.

As the rate of each of the three reactions taking place probably varied, experiments were carried out varying the time of heating, and these, as shown in Table I, established the fact that the rate of formation of p-tolyl m-toluylene di-amine was greater than those of the other two products. After 16 hours the yield of ~~this~~ this base, calculated on the amount of diamine used up, decreases indicating that the rates of formation of the other two substances have increased.

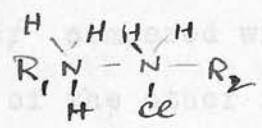
(4) Variation in the amount of hydrochloric acid. (Table II.)

When no hydrochloric acid was used (in the form of hydrochloride) no reaction occurred. One molecule was found to be as efficient as two. The presence of hydrochloric acid is thus essential to the reaction.

The reaction does not then consist in a simple splitting off of ammonia from ~~two~~ two molecules of the amino substances as -



but probably some unstable intermediate is first formed in which hydrochloric acid plays an essential part such as -



from which ~~then~~ ammonium chloride is then split off, this unstable intermediate being only possible ^{as a} ~~in the state of~~ its hydrochloride and not as a base.

(5) Catalysts . (Table III.)

Addition of iodine or of benzoic acid had no appreciable effect on the yields . Bucherer's sulphite reaction was tried without success , only a small amount of diamine being used up . In an open vessel with ammonium sulphite no reaction occurred . With sodium bisulphite in open vessels none of the desired product was obtained ; most of the m-toluylene diamine appeared to have been converted into sulphonic acids . Some sulphonation product was isolated , but was not further examined .

In an iron autoclave the results were very poor , and the pressure rose to 60 atmos . owing to liberation of hydrogen . With a lead lining normal reaction occurred , but some lead was found in the end-product , especially in the ammonium chloride experiments .

(6) . Effect of ammonium chloride addition .

AS the reactions in closed vessels were all balanced actions, it was thought that

was thought that the formation of diaminoditolylamine and ditolylamine might be retarded by adding excess of these byproducts to the reacting mixture and that the yield of p-tolyl-m-toluylene - diamine might be thus increased. The results, however, were unsatisfactory, the yield of product being smaller (41.6%) and the melting point lower (230° - 233° C \downarrow). The reverse reaction is ~~evia~~ evidently slower compared with the direct reaction.

The addition of the other reaction product, namely, ammonium chloride, was then tried in the hope that the main reaction would be less retarded than the other two. This hope was realised. In an autoclave the addition of one molecular proportion of NH_4Cl raised the yield of p-tolyl m-toluylene diamine from 52.5% to 55.3% on the diamine unrecovered, and two molecular proportions gave a further increase to 66.2%. The rate of reaction was not appreciably slower with two molecules than with one molecule NH_4Cl .

In an open vessel the reaction was practically complete in 24 hours in the presence of one mol. proportion NH_4Cl , the yield of p-tolyl-m-toluylene diamine being 69.0%. No further increase in yield resulted when larger proportions of NH_4Cl were added.

(7) Effect of increased pressure.

By increasing the pressure on the reacting mass, and at the same time allowing the ammonia to escape, it was hoped to obtain a greater yield. This was not attained, the only result being to decrease the time of reaction considerably. Acting on this, the escaping gasses, passing through the reflux, were led into a trough of mercury $4\frac{1}{2}$ " deep. Using $7/5$ g.mol. p-toluidine, $2/5$ g.mol. NH_4Cl , and $1/5$ g.mol. m-toluylene diamine, the boiling point was raised fairly rapidly to 216° - 217° C. After 24 hours 1.7 grams m-

1.7 grams m-toluylyene diamine remained unchanged , and the yield of p-tolyl m-toluylyene diamine hydrochloride on the m-toluylyene diamine used was 67.2 % . (m.p, 232° C) . Using $\frac{1}{2}$ " more mercury and boiling rapidly for 15 hours , the following results were obtained ; viz.

Unchanged diamine - 0.75 grams .

Yield of tolyl-m-toluylyene diamine hydrochloride on diamine used

- 65.6 % . (m.p. 236 C.)

Raising the pressure by more than 6" mercury had no effect in increasing the yield . The temperature of the boiling mixture at 6" mercury additional pressure was 220° C and after boiling for 15 hrs a good ^{product} was obtained in 68.6 % yield . (m.p. 238° - 240° C .).

Similar experiments were carried out using p-toluidine , p-toluidine hydrochloride , ammonium chloride and m-toluylyene diamine in the proportion of 7:1;1:1 , in order to ascertain if the additional pressure and consequent higher temperature would reduce the time of reaction . It was found that using 6" mercury additional pressure reduced the time of reaction from 24 hours to 15 hours. The yields in the two experiments after boiling rapidly for 15 hrs were 66.7 % and 68.6 % respectively (m.p. 236° C) . and the amount of unchanged m-toluylyene diamine was in both cases about 4% of that used . Thus the yield of p-tolyl m-toluylyene diamine and the amount of diamine unchanged were not appreciably altered by the substitution of one mol. NH Cl for two mols.

(8). Isolation of the products ⁴

The reaction mixture was made faintly alkaline with caustic soda and excess of p-toluidine was steamed off . There remained (1) /

(1) an alkaline aqueous

(i) an alkaline aqueous layer containing unchanged diamine in solution, together with a certain amount of diaminoditolyamine and p-tolyl-m-toluylene diamine, and (ii) an oily layer consisting of p-tolyl-m-toluylene diamine, diaminoditolyamine, and ditolyamine.

The separation of ditolyamine was easy on account of the ready hydrolysis of its hydrochloride. The other two bases contain free NH_2 groups and their hydrochlorides are therefore less easily hydrolysed by water.

The separation of p-tolyl-m-toluylene diamine from diaminoditolyamine presented considerable difficulty. The hydrochlorides have about the same solubility in water - 100 c.c. of cold water dissolving 1.2 grams diaminoditolyamine hydrochloride, or 1.0 grams of p-tolyl-m-toluylene diamine hydrochloride. On adding salt to saturation the p-tolyl compound was more completely salted out; in 100 c.c. there remained 0.2 grams diaminoditolyamine hydrochloride or 0.05 grams p-tolyl m-toluylene diamine hydrochloride, as shown by titration with normal diazo benzene solution.

Crystallisation from hot solution gave a fairly pure product, but involved ^{a certain} ~~the~~ loss of product. Complete salting out resulted in a product melting at about 220°C instead of at 240°C . The best results were obtained by a partial salting out. A good product, (marked "(a)" in the tables), and a further quantity, much less pure and melting at about 190°C - 210°C , was obtained by completely salting out the mother liquor. (This product is marked "(b)" in the tables). Further recrystallisation or re-salting did not improve the quality of the "(b)" product; the limit of separation had apparently been reached.

Separation of p-tolyl-m-toluylene diamine hydrochloride from a

mixture containing more than 20% of diaminoditolyamine hydrochloride was found to be unsatisfactory. With smaller proportions of the latter, however the partial salting out worked very well. Pure diamino ditolyamine melts at 154-155°C (Ullman and Schmidt) and its acetyl derivative at 247°C (ibid). Good specimens of p-tolyl-m-toluylene diamine hydrochloride had a melting point of 240-241°C. The effect of adding 10% of diaminoditolyamine hydrochloride was to lower this to 233°C, with previous softening at 220-225°C. A further 10% addition gave a mixture which softened at 215°C and was completely melted at 228-230°C. The melting point of the product as hydrochloride thus provides a good indication of its purity.

The melting point of the p-tolyl-m-toluylene diamine prepared ~~from~~ from a specimen of the hydrochloride melting at 240-241°C was 56-61°C, which was raised to 66-67°C by recrystallisation from ~~the~~ ligroin. From this a specimen of hydrochloride was prepared which melted at 245°C.

Experimental

300 g. p-toluidine - 2.8 g.mols.

57.4 g. p-toluidine hydrochloride - 0.4g.mols.

48.8 g. m-toluylene diamine - 0.4 g.mols.

21.4 g ammonium chloride - 0.4 g.mols.

were mixed and heated under air reflux condenser. The liquid ~~was~~ ^{220-222°} began to boil at 200°C and the temperature rose to 216°C during 6-8 hours. Heating was continued for a period of 15 hours, the escaping gases being passed through a trough of mercury 6" deep. The mixture must be rapidly boiled throughout. Sufficient NaOH is then added to neutralise

is then added to neutralise the HCl present , and the excess p-toluidine is steam distilled off . The alkaline layer is separated from the oily layer in the bottom of the flask , ~~one~~^{two} litres of hot water ~~is~~^{are} added to the oil and boiled for $\frac{1}{2}$ hour . The aqueous ~~lay~~ layer is again separated from the oil . This aqueous layer deposits diaminoditolylamine on cooling (2.75g) This was very impure (m.p. 125° C instead of 154° C - 155° C) and was found to contain a about 20 - 25 % of p-tolyl-m-toluylene diamine . The alkaline ~~mother~~^{liquor} and the aqueous mother liquor contained all the unchanged m-toluylene diamine , which was estimated by titration with diazo benzene solution and found to be 2.05 and 1.4 grams respectively. From the ready solubility of the m-diamine only a portion of the 1.4 grams is m-toluylene diamine , the bulk being the sparingly soluble diaminoditolylamine , which gives a red chrysoidine . At least 93% of the diamine has entered into the reaction .

The heavy oil was transferred to a flask and 50 c.c. conc . HCl added . The liquid was made up to $2\frac{1}{2}$ litres and boiled for 15 mins A considerable amount of oil was produced (hydrolysis of ditolylamine hydrochloride). The liquid was then filtered through a tripple layer of filter paper and a plug of glass wool to retain the oil . The amount of ditolylamine thus separated was 23 . gram ($2\frac{1}{2}$ litres)

The hot filtrate ~~was~~^{is} then treated with 200 g. NaCl , which precipitated 64.5 grams (a) of p-tolyl-m-toluylene diamine hydrochloride (m.p. 235°-238° C.) From the mother liquor by saturating with NaCl a further 3.4 grams (b) were obtained , (m.p. 190°-200° C) The liquor was then made alkaline with ammonia and yielded 3.5 g (c) of a substance which softened and darkened at 125°-130° C . From ~~this~~ this latter there was obtained by crystallisation from benzene about 1. gram of diamino ditolylamine hydrochloride (m.p. 151°-152° C)

The mother liquors of (c) still contained some m-diamine which ~~gave~~ gave chrysoidine with diazo benzene .

Yield of p-tolyl-m-toluylene hydrochloride (a) - 69 % on the amount of unrecovered m-toluylene diamine .

Of the 341 grams of p-toluidine used (base and hydrochloride)

278 .g. - 81.7 % are recovered (as base)

25.0 g. - 7.3 % form ditolylamine .

25,5 g. - 7.5 % form p-tolylm-toluylene diamine .

11.8 g. - 3.5 % are unaccounted for .

341 . grams , 100 %.

Of the 48.8 g . m-toluylene diamine used

32.72 g. - 67.5 % form p-tolylm-toluylene diamine .

3.45 g. - 7.0 % ~~form~~ are unchanged .

2.75 g. - 5.6% form diamino ditolylamine .

7,5 g. - 15.4 % are estimated to form the bases in (b) ,(c)
and mother liquor .

2.3 g. are unaccounted for . - 4.5 %.

48.8 g. - 100 %.

TABLE I. VARIATION IN TIME OF HEATING.

Open vessel : 149.8 g. p-toluidine; 28.7 g. p-toluidine hydrochloride; 24.5 g. m-toluylenediamine. NoNH_4HCl

Time hours.	Temp. °C	Recovered p-toluidine. gms	p-Toluidine in aq. distillate. gms	Unchanged m-diamine. gms	Diamino-ditolylamine. cryst. gms	Tolyl-m-tol: diamine HClide. gms	M.P. °C	Purity %	m-diamine used up. gms	% diamine used up gms	% yield of tol: m-tol: diamine on diamine used
4	205-210	190.5	6.4	14.26	0.7	6.02	226-232	70-80	10.24	41.8	30.22
8	205-215	169	10.7	11.77	0.19	14.17	226-231	70-80	12.73	51.95	54.6
12	200-215	166	10.2	9.45	0.75	19.0	230-232	90	15.05	61.5	61.9
16	200-216	159	9.9	6.88	0.42	22.5	235-236	94	17.62	71.9	62.7
20	200-216	145	16.7	5.39	-	22.5	233	90	19.11	78.0	57.8
24	200-216	118	13.6	3.0	-	25.6	237	96	21.5	87.8	58.4

TABLE II. VARYING AMOUNT OF HCl PRESENT OPEN VESSEL.

Time : 24 hours; amount of m-toluylenediamine = 24.5 grams.

Temp. °C	p-toluidine. g.	p-Tol: HClide. g.	Recovered p-toluidine. g.	Recovered Toluylene diamine. g.	Diamino-di-tol: amine. g.	Tolyl-m-tol: diamine (a) (b) Gms	% Yield on diamine used up.	Purity of Yield. %	% Yield of pure substance.	
211	171.2	nil	170.4	24.16	nil	nil	nil	nil	nil	
216	149.8	28.7	131.6	3.0	nil	25.6 (M.P. 237°)	2.8 (185°-200°)	58.4	96	55.7
216	128.5	57.4	130.0	4.65	trace	25.1 (M.P. 230-232°)	2.2 (210°C)	61.3	85	52.1

TABLE III. CATALYSTS.

Method.	Time, hrs	p-toluidine. g	p-tol. HClide. g	m-tol: diamine. g	Catalyst.	Diamino-di-Tol: amine.	Tolyl-m-tol. diamine hClide.	M.P. °C
Open.	6	21.4	28.6	24.4	1% Iodine	1 gm.	6.3 g.	225
Open.	6	21.4	28.6	24.4	1 g. Benzoic.	1.1 g	3.7	232-5°C
Autoclave.	24	299.6	57.4	49.0	4 g. Iodine.	trace	25.5	238-242

TABLE IV. VARYING PROPORTION OF p-TOLUIDINE.

Open Vessel.

Time. hrs	Temp. °C	p-toluidine. g.	p-Tol-HClide. g.	m-Tol- diamine. g.	Recovered p-toluidine g.	Recovered m-Tol.diamine g.	Diamino- di-Tolyl- amine.	Tolyl-m- tol:diamine HClide.gms.	% Yield.	M.P. °C
6	221	42.8	57.2	48.8	47	-	2.35	13.5	13	243-6°
6	215	288.9	43.1	36.6	283.4	26.1	0.65	(a) 5.3 (b) 3.2	23	248-50 225-8
24	215	144.5	43.05	26.6	94.0	2.4	0.3	29.0	38.9	242
35	216	240.75	71.75	61.0	181.0	4.9	1.0	(a) 48.0 (b) 13.3	43.0	240 140-8°

Note: (a). . . allowed to crystallise from hot solution.

(b). further yield on complete salting-out.

TABLE V. AUTOCLAVE.

Temperature 260-270°C.

Time. hrs	Pressure atm.	p-Tolu- idine. g	p-Tol: HClide. g	m-Tol: diamine. g	Recovd m- Tol.diamine g	Recovd p- toluidine. g	Diamino di-tolyl amine. g	Tolyl-m- Tolylene diamine HClide.	% Yield.	M.P. °C	Method of obtaining hydrochloride.
20	22-23	200	-	50 as HClide	-	117	-	32.4	44.3	-	crystallising.
20	31	225	-	75	-	124	1.1	56.2	51.3	210-213	complete salted
20	17-18	288.9	43.05	36.6	13.1	254.7	2.37	(a) 13.8 (b) 9.5	50.0	243-5 228-230	Crystals. salted.
24	22-23	288.9	86.2	73.2	18.32	283	2.0	59.0		220-222	Salted.
24	17-18	299.6	57.4	49.0	12.2	-	2.3	(a) 36.5 (b) 6.5	48.6	235-238 195-205	(a) Partial (b) Complete.
36	17-18	299.6	57.4	49.0	11.5	285.3	3.8	(a) 40.0 (b) 10.75	52.5	239-240 210-214	(a) Partial (b) Complete.

TABLE VI. . . WITH ADDITION OF NH_4Cl .

PARA TOLUIDINE = 299.6 g.
 p-Toluidine hydrochloride = 57.4 g.
 m-Toluylenediamine = 49 g.

Time. hrs	Pressure atmos:	NH_4Cl g	Method.	Recov'd p-Tolu- idine. g	Recov'd m-Tol: diamine. g	Diamino di-Tolyl- amine. g	Tolyl- m-Tol: diamine. g	% Yield on dia- mine used.	M.P. °C	% m-Tol- diamine recov'd.	Di-Tolyl amine. g
24	17	21.4	Autoclave	306	16.99	4.75	(a) 36 (b) 4	55.3	237-8 120-30	34.5	11
24	17	42.8	do	-	15.24	2.15	(a) 46.7 (b) 4.9	66.2	232-5 v.low.	31.1	-
24	-	21.4	Open	-	3.45	4.1	(a) 64.5 (b) 3.4	69.0	235-8 190- 200	7.0	23
24	-	42.8	Open	-	3.32	-	(a) 64.0 (b) 4.5	68.8	236-7 203-7	6.6	-
24	-	21.4	Open	-	5.24	-	(a) 60.9 (b) 5.9	68.7	238-40	10.0	-

ON THE CONSTITUTION OF COLOURING MATTERS DERIVED
FROM QUINOLINE, IN PARTICULAR ON THE CONSTITUTION
OF THE ISOCYANINES.

BY.- R.S. WISHART. M.A., B.Sc.

An account of work done at Cambridge University
Laboratories under the supervision of Sir. W.J.Pope,
and Dr. W. H. Mills, 1919.

CAMBRIDGE, 1919.



ON THE STRUCTURE OF COLOURING MATTERS DERIVED FROM
QUINOLINE, IN PARTICULAR OF DI-METHYL ISOCYANINE.

RICAL.

In 1856 Greville Williams obtained a blue dye by the action of *caustic alkali* on the Amyl Oxide of Quinoline, though Coal Tar Leucoline gave no such dye. (Trans Ry Soc. 1856, 21, 377)

In 1882 Hoogewerf & Van Dorp (Rec. Trav, chim 1882, I, 1, 107) established the identity of quinoline & Leucoline and proved that pure quinoline alkyl iodides gave no blue dye with potassium hydroxide, though quinoline alkyl iodide ~~was~~ and Lepidine alkyl iodide gave the dye. Lepidine alkyl iodide was thus necessary to produce the blue dye.

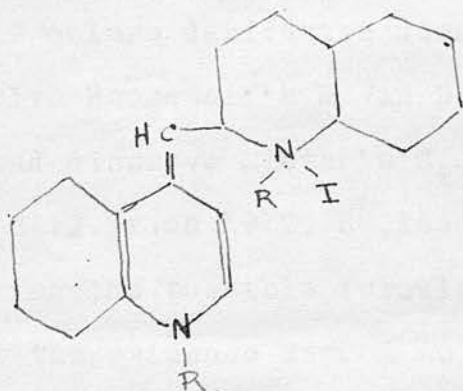
In 1883 Spaltholz (Ber. 1883, 1847) obtained a bluish red colouring matter from one part quinaldine ethyl iodide and 1.9 parts quinoline ethyl iodide in alcoholic solution by treatment with potassium hydroxide. To this the name of Ethyl Red was given, or di-ethyl Isocyanine iodide and the generic name of Isocyanines applied. Spaltholtz gave to this substance the formula $C_{23}H_{25}N_2I$, while Hoogewerf and Van Dorp regarded it as having the formula $C_{23}H_{23}N_2I$ (Rec Trav. Chim, 1883 II, 28, 41, & 1884 III. 337).

The former assumed that 1 Mol. of Hydriodic Acid was eliminated from 1 Mol. quinoline ethiodide and 1. Mol. quinaldine ethiodide. The latter believed that oxidation took place by removal of two atoms of hydrogen at the same time, as well as elimination of 1. Mol. of Hydriodic Acid. This was the commencement of the controversy on the constitution of the Isocyanines.

(Chemische Industrie 1903. 26. 54) (J.S.B. Ind.)

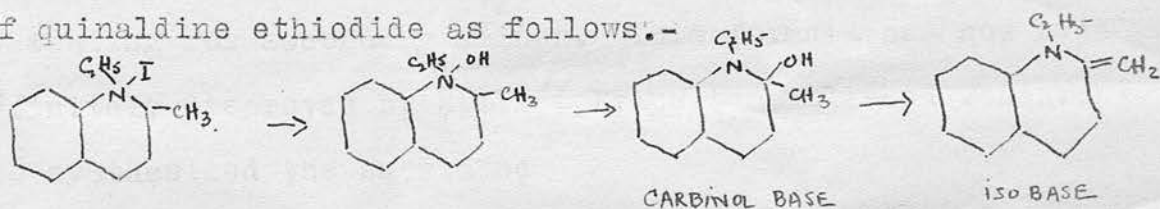
The question received little attention until Miethe (1903 p. 318) discovered that the Cyanines and Isocyanines when used on a photographic plate ~~produced a fog~~ *acted as a sensitizer.* This sensitising action, especially that of Ethyl Red, upon a gelatine bromide photographic plate greatly exceeded that of any previously known dye. This at once gave importance to this class of dye.

Miethe & Book (Ber. 37, 2008, (1904)) investigated the



He supported this by analogy with dyes from secondary Amino Pyridinium Halogenides. The Chromophore in the case of the Isocyanine is a chain of 5 carbon atoms with 2 conjugated linkages and in the case of the Cyanine 7 carbon atoms with three conjugated linkages, the latter being thus deeper in colour than the former.

In 1908 Vongerichten & Höfchen (Ber. 1908, 41, 3054) showed that the Methyl group of the quinaldine residue entered into the reaction by demonstrating that no Isocyanine was formed by using methiodides of di-methyl-quinaldine or Benzylidene quinaldine instead of quinaldine methiodide itself. They also endeavoured to show that the mechanism of the reaction was through the carbinol base & isobase of quinaldine ethiodide as follows. -

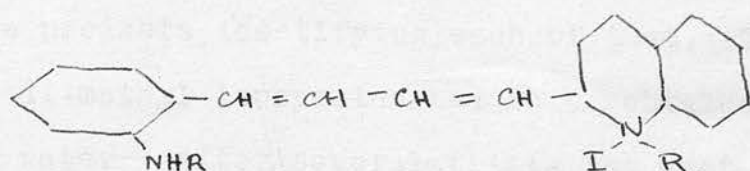


They showed also that this last can also be brought into reaction with N.Methyl γ quinaldone by Phosphorous pentachloride in benzene solution, giving dyes which possess the properties of isocyanines.

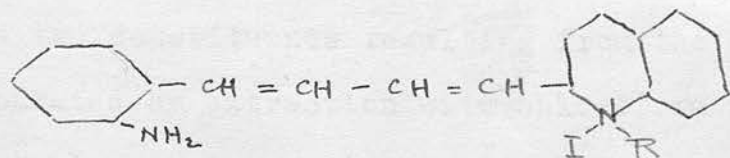
By oxidation of the isocyanine with potassium ferricyanide in the cold they obtained N ethyl α quinolone, *but could not trace the other products of oxidation.*

In 1912 Kaufmann & Vonderwahl (Ber. 1912 45, 1404) obtained further evidence to support König's view by showing that 4 substituted quinolines did not give the isocyanine reaction except with substituents like chlorine, which are readily removed. e.g. - 4 Phenyl derivative does not give

isocyanine but 4 chloro derivative does. This would definitely involve Hoogewerf's & Van Dorp's formula $C_{23} H_{23} N_2$ 1. and disprove Miethe's $C_{23} H_{25} N_2$ 1. W. König in 1912 (J.pr.ch 1912, 86,166) revoked his view of 1906 and reviewing the possible formulae came to the conclusion that the evidence seemed to prove that isocyanines were normal condensation products of Ortho Amino Aldehydes with quinaldinium salts of the formula.



He held that this open chain formula, rupture of the ring having taken place, explained all the properties of the isocyanines, bringing in as evidence that Hofmann obtained isocyanines from a mixture of Halogen alkylates of Benzo-thiazoles & μ methyl benzo thiazoles in which γ condensation cannot occur. This open chain formula seemed to be favoured until Otto Fischer (J.pr.ch.1918,(11) 98,204) stated that he could find no evidence of a ruptured ring by testing for secondary amines. This formula has now been definitely disproved by Mills & Evans (unpublished research) who synthesised the substance



starting ~~that~~ from ortho nitro cinnamaldehyde and found that it was not a sensitiser and was not an isocyanine.

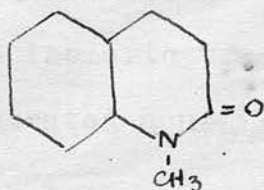
Before commencing on the work of oxidising the isocyanines with Potassium Permanganate, assuming the open chain formula, I attempted to eliminate methyl iodide from di-methyl-isocyanine iodide by heating to a high temperature in vacuum and so obtain the base as Kaufmann had done, and also by heating with quinoline for several hours, the latter method

gave a yellow substance which did not contain halogen, would not crystallise and which did not melt at 300°. This substance was probably the base. As it would not benzoylate or acetylate, its further investigation was discontinued.

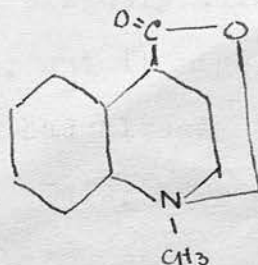
The only satisfactory method of establishing the constitution of the isocyanines was to carry through a complete oxidation with aqueous potassium permanganate at 0°, and to isolate all the products, identifying each of them. To do this a salt of di-methyl isocyanine had to be obtained which was soluble in water. After several trials the acetate was selected as the best suited to the purpose of oxidation, both because of its solubility and because in subsequent treatment the acetate radical would lend itself to easy displacement by the chlorine radical. The acetate was easily obtained from the iodide by boiling with silver acetate in alcoholic solution. In the first place the oxidation was carried through with 3% potassium permanganate. Owing to the colour of the sensitiser it was somewhat difficult to determine the point at which the oxidation was complete, and this had to be done by judging the change of colour from sensitiser colour to the pink of slight excess of potassium permanganate using filter paper.

The two constituents resulting from the oxidation were separated by extraction with chloroform and were found to be, on replacing the acetate radical by chlorine in the aqueous portion, 1 Methyl 2 quinolone and Methyl chloride of cinchoninic acid, eliminating hydrochloric acid from the latter I obtained 1 Methyl cinchoninic betaine.

The formula of these two substances, the first and third are established as follows.-

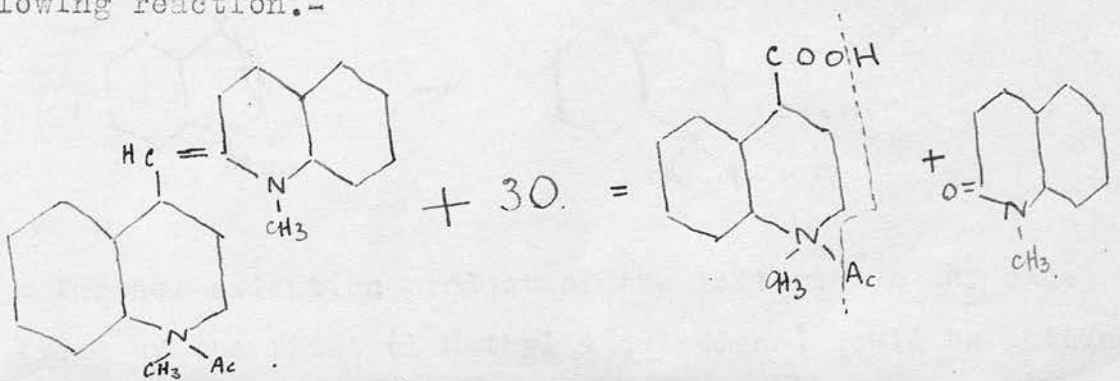


1st. METHYL 2 QUINOLONE



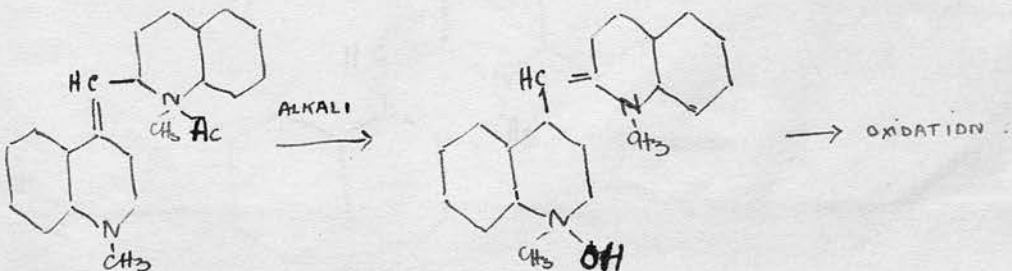
3rd. METHYL CINCHONINIC BETAINÉ

The yields obtained of each of these substances from oxidation established the fact that these are the main products of oxidation and that only a very small amount of an unidentified substance was obtained in addition. The amount of oxygen used up from the potassium permanganate confirmed the view that three atoms of oxygen were used in oxidising the sensitiser and this agreed with the theory of the structure as will be shown. From the two oxidation products the only conclusion one can come to with regard to the structure of the isocyanine is as set forth in the following reaction.-



The splitting up of the body taking place as usual at a double bond.

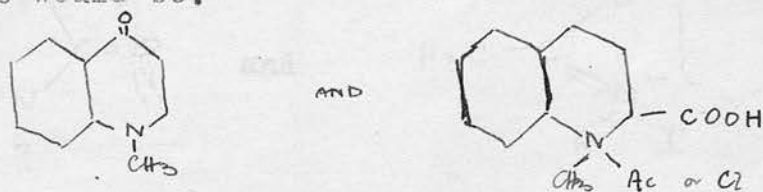
It might be contended that using a three percent potassium permanganate solution would immediately cause the solution to become alkaline with the formation of ~~the~~ potassium hydroxide, and that the first formula of König & of Kaufmann might still hold, the effect of the alkali being to cause the Molecule to assume an isomeric structure more liable to attack as follows.-



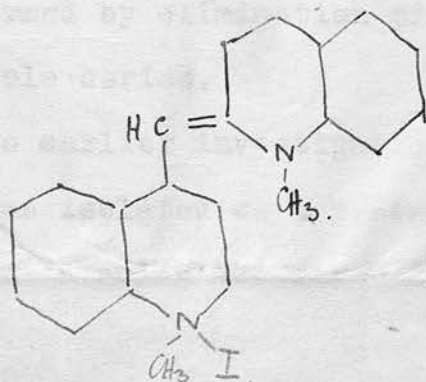
Again it was noticed that the concentrated solution of the isocyanine acetate in water had a slightly duller or browner colour than an alcoholic solution, and it might be contended that this isomeric transformation had already taken place in concentrated aqueous solution. This, however, was not

likely to happen as on slight dilution or on adding a small quantity of acetone the true colour of the sensitiser was immediately restored.

In order to counteract any effect of alkali during the oxidation sufficient glacial acetic acid was added to the 3% potassium permanganate to neutralise the end products, and the oxidation was carried out in strictly neutral solution. Again the same products were isolated. If Kaufmann's formula was the true formula of isocyanine then oxidation would take place at the double bond and the products would be.-

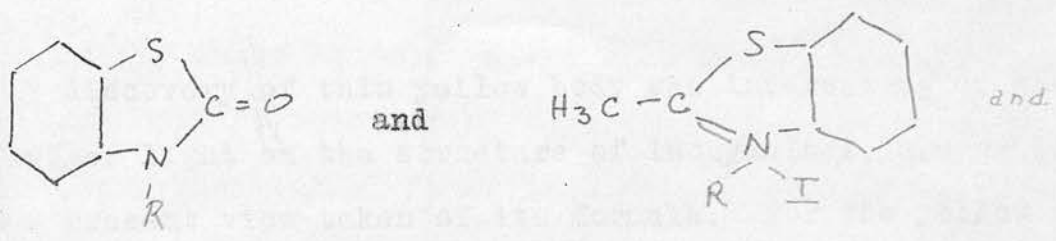


or a further oxidation product of the latter. In any case no trace of the first (1 Methyl 4 quinolone) could be obtained at all. This shows, I think, that an aqueous solution of the isocyanine acetate, being a true solution of the isocyanine salt, is oxidised normally by the aqueous potassium permanganate and that alkalies do not first transform it into a tautomeric form such as that of Kaufmann's formula. We must assume that oxidation would take place at the double bond and the structure of di-methyl isocyanine is thus represented as follows.-

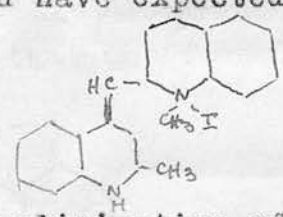


It occurred to me that the iodine atom in the above mol. might possibly oscillate between the two nitrogen atoms in the mol. In order to obtain information on this point I attempted to bring about the condensation of 2 Methyl kynurin

and Quinaldine Methiodide by means of piperidine. A bluish green sensitiser of poor quality was formed but the same sensitiser was also formed by the action of piperidine on Quinaldine Methiodide alone. The kynurin does not in this case enter in the reaction, so that the oscillatory nature of the iodine seems to be disproved though this does not at the same time rule out of court the possibility of the presence of a residual valency between the iodine and the two nitrogens. There is an interesting analogy in this case with the benzo thiazole series. Mills and Amies condensed



obtained a mixture of yellow body and sensitiser, the yellow body being the same as that referred to on page 10, and the sensitiser having the formula given on that page. Of course one cannot draw strict analogies in the two cases, but the failure to form the sensitiser in the isocyanine series tends to confirm the view that the iodine is in position indicated in this paper and not as given by Kaufmann, for if the latter had been the case one would have expected the sensitiser of formula

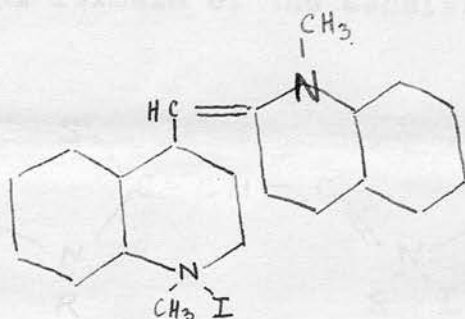


to have been formed by elimination of water by analogy from the Benzo Thiazole series.

Again during the earlier investigations on the Isocyanines a yellow body was isolated as a product from the boiling of the isocyanine with quinoline for a short time(as I pointed out previously if isocyanine is boiled with quinoline for several hours a brown yellow product can

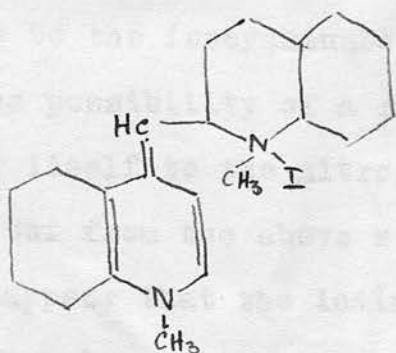
be isolated which is non crystalline and does not contain iodine). The yellow body obtained by boiling isocyanine iodide with quinoline for a short time was obtained in only 10% yield. It was an iodide and its melting point was much higher than that of the sensitiser. It was difficult to obtain this yellow body pure, or to test its purity, owing to its very high melting point, and this accounts probably for the slight inexactitude of the results of analysis. These, however, are sufficient to prove it to be an isomer of the isocyanine iodide.

The discovery of this yellow body was interesting as shedding further light on the structure of isocyanine, and confirming the present view taken of its formula. For the yellow body I would suggest the following formula.-

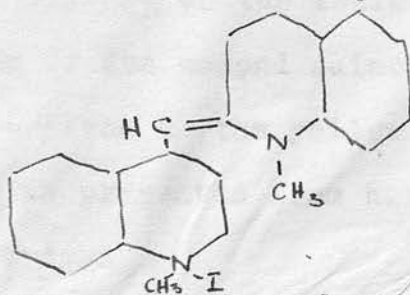


This is then the trans form of the isocyanine iodide which itself would have the cis formation.

It may be suggested that the formula of the yellow body might be as follows.-



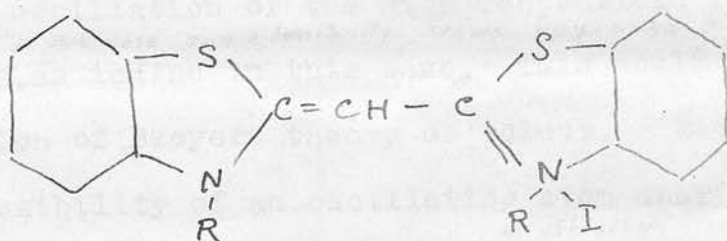
and that of isocyanine



i.e give to the yellow body Kaufmann's formula and reserve for the isocyanine itself the formula advocated in this paper.

If this were so then one would have expected that the corresponding yellow body would have been formed by condensation from kynurin and quinaldine methiodide. In this reaction no trace of yellow body was found.

The only other structure possible for the yellow isomer is as I have suggested viz.- the trans modification of the formula for the isocyanine. In this connection it is interesting to observe that recently Mills & Amies (unpublished research) working in the Benzothiazole series prepared isomers of the sensitisers which were yellow in colour. These isomers indeed were formed at the same time as the sensitisers in the same reaction, and both were desposited together, being separated by their difference in specific gravity. The Benzothiazole sensitiser was also transformed into a yellow substance by means of Aniline and this yellow isomer had a very high melting point, being over 300°. These two yellow bodies were identical. There is a strong analogy between the benzothiazole series and isocyanine series. Mills & Amies give the structural formula of the sensitiser in the Benzothiazole series as -

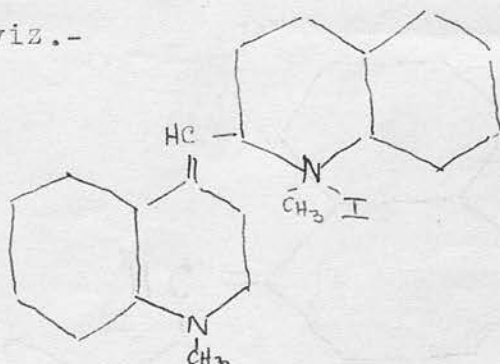


and the trans form is given as the structure of the yellow isomer.

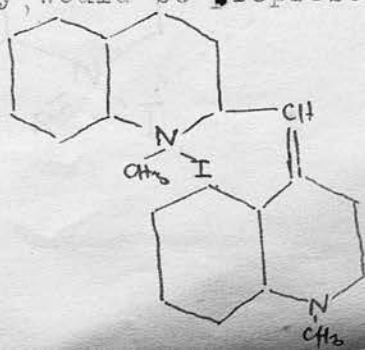
Referring to the isocyanine series again the cis configuration allows the possibility of a residual valence of the iodine atom attaching itself to the nitrogen atom of the second quinoline nucleus, but from the above structure given to the yellow body it would appear that the iodine atom is prevented from having a residual valence with the other nitrogen

with the other nitrogen. At the same time there is still the chain of five carbon atoms & three conjugated linkages usually considered the chromophore and yet in this case the colour of the body is yellow. In the case of the isocyanine we have a chain of five carbon atoms with three conjugated linkages together with ^{the possibility of a} a residual valency closing the whole chain, and this appears to be the only difference in structure between the isocyanine and its isomer, the yellow body. The striking fact is the intensity of colour in the isocyanine and the lack of it in the trans form. I would suggest that this might lead to a theory of colour depending not only on the presence of a chain of conjugated linkages, but also on the presence of the possibility of a residual valency closing the whole chain which might give rise to vibration in the chain of carbon atoms if one considers the possibility of the oscillation of the atom responsible for the residual *(though in this case such a possibility seems disproved by the Kynuriv experiment)* valency, as iodine in this case. This would suggest an extension of Baeyer's theory of colour. But even leaving the possibility of an oscillating atom apart altogether the presence of a residual valency ^{or affinity} closing the chain of conjugated linkages in carbon atoms might be sufficient to produce intensity of colour.

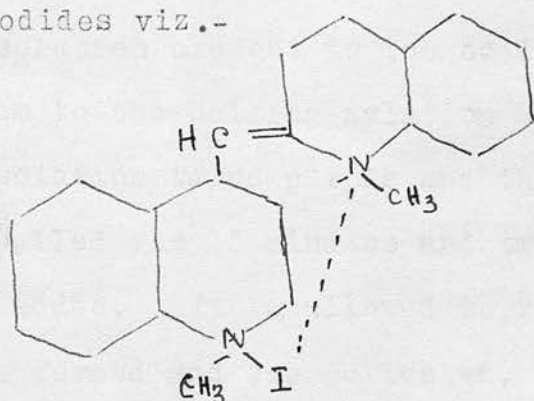
Again, assuming Kaufmann's formula to be the formula for isocyanine viz.-



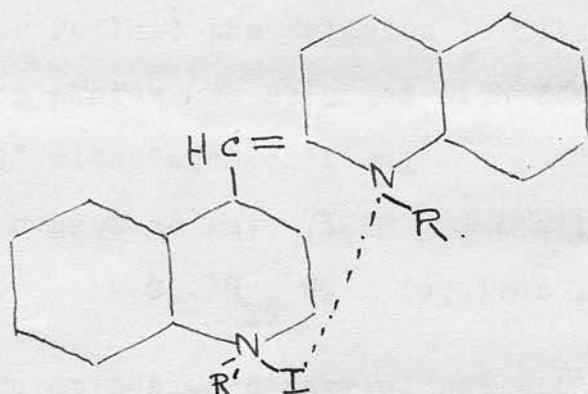
Then the isomeric form of this formula, which would be that of the yellow body, would be represented by.-



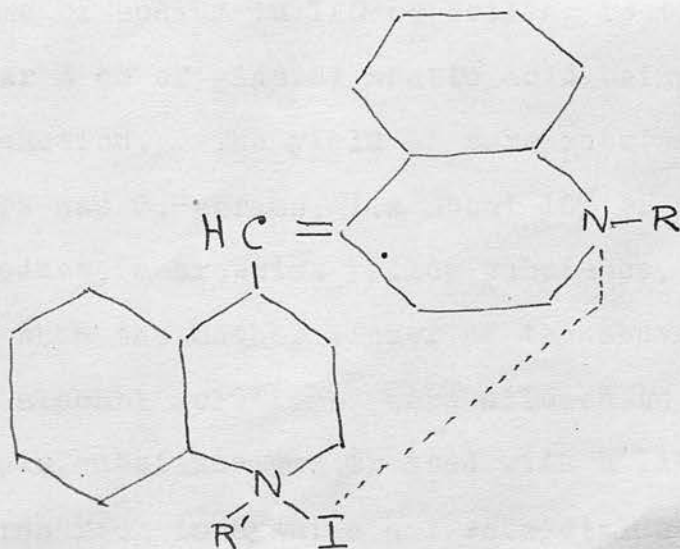
This seems improbable as the molecule would be too ~~much~~ *greatly* loaded on one side and steric hindrance would probably come into play and prevent the formation of such a body. Steric Hindrance does play a part in the formation or rather non-formation of certain isocyanines. Quinoline methiodides substituted in the 5 position, also β Naphthoquinoline will not condense to form sensitizers. This again would tend to confirm the view put forward as to the structure of di-methyl-isocyanine iodides viz.-



Isocyanines then have the general structural formula,-



by Analogy Cyanines obtained by using lepidines instead of quinaldine alkyl iodides would have the formula.-



EXPERIMENTAL.

Preparation of 1 - 1' Di methyl isocyanine iodide.

(Pope & Mills T. 1920, 17)

11.56 grams quinoline methiodide and 5.70 grams quinaldine methiodide are dissolved in 200 cc absolute alcohol and brought to the boil under reflux, the solution kept boiling slowly. .54 grams Sodium are dissolved in 60 cc rectified spirit and solution brought to the boil. This is added in a slow stream to the boiling solution of the methiodides. The yellow solution turns purple and the colour darkens. It is then boiled for 15 minutes and two cc of glacial acetic acid added. It is allowed to remain overnight, crystals are formed and are collected. The substance is recrystallised from 120 cc methyl alcohol boiling for half an hour under reflux; the solution is filtered hot. On cooling green plates are obtained with fine lustre. Melting point is 268° with decomposition.

.2369 grams substance gave .1298 grams silver iodide.

I = 29.62 %. $C_{21}H_{19}N_2I$ requires I = 29.78%.

Similar preparations were carried out with twice the above quantities, 23.12 grams quinoline methiodide, 11.40 grams quinaldine methiodide in 400 cc absolute alcohol and 1.08 grams of sodium in 120 cc boiling rectified spirit added, ~~for~~ 4 cc of glacial acetic acid being added at the end of reaction. The yield of pure substance from above quantities was 3.3 grams, i.e about 10% of mixed methiodides. A bye product, a brownish yellow substance, was also obtained when the Mother liquor of the above, i.e, the absolute alcohol solutions, were allowed to stand for some days. This substance was treated with a little dilute HCl to free from isocyanine and recrystallised from Aniline. It was difficult to free completely from Isocyanine and required treatment several times with HCl

and several recrystallisations from Aniline. Finally they were fine elongated yellowish brown needles, an iodide with melting point approximately 340° . The yellow body, isomer of isocyanine referred to in the theory had approximately the same melting point and the mixed melt of these two yellow bodies did not appreciably change from that temperature, being $342^{\circ} - 345^{\circ}$.

A Kaufmann and P. Strüben (Ber. 1911, 44, 690-701) discovered the erythroapocyanines and xanthoapocyanines. These were prepared from quinoline methiodide alone with KOH. The latter are Reddish Yellow bodies which melt over 300° . They suggest that erythroapocyanines which are Reddish bodies are probably Mono acid Salts of 2-2 Diquinolenyls but they do not suggest a formula for the xanthoapocyanines. It is possible that this byproduct may be xanthoapocyanine, yet it has the same melting point as the trans form of the isocyanine viz. - 340° approx. and the melting point of a mixture of these two substances is the same as for each separately; so that on the other hand it is possible that this byproduct is the trans form of the isocyanine. It is highly probable that this latter is the case, and this would tend to confirm the view taken of the formula of the trans form, the isocyanine and the trans isocyanine being formed at the same time by the action of sodium ethoxide on the methiodides of quinoline and quinaldine. Beyond determining the melting point and mixed melting point this yellow body " Bye product" was not further investigated.

Preparation of 1-1' Di-methylisocyanine acetate

In order to carry out the experiments it was necessary to obtain a salt of isocyanine which would be fairly soluble in water. The iodide bromide and chloride, as well as the nitrate, were found to be fairly insoluble in water and unsuitable for our purpose. The iodide was then

transformed into the acetate as follows.-

5 grams isocyanine iodide were added to a flask in which was placed 250 cc rectified spirit, the flask was then heated under reflux until all the iodide was in solution. Then to the boiling solution 10 grams silver acetate, made into a milky paste with 30 cc rectified spirit were added. The mixture was boiled for half an hour, a portion of the liquid filtered and tested for halogen. It was found at the end of that time that the whole of the isocyanine iodide had been transformed into the acetate. The solution was filtered hot and the spirit removed on the water bath, the last traces of spirit being removed by blowing a current of hot air through the flask. The acetate was dissolved in 250 cc water and allowed to cool. The acetate was found to be much more soluble in aqueous solution than any of the former salts, and was then used for oxidation purposes. As stated above, the solution had a slight duller or browner colour than that of an alcoholic solution of isocyanine but the true colour was restored on adding a little acetone. Acetone was not added to the solution to be oxidised. The isocyanine acetate was oxidised with 3% aqueous potassium permanganate solution in the cold (0°) with efficient stirring.

During the preliminary oxidations the colour of the isocyanine was observed to give place to a brown colour gradually, and the completion of the oxidation could be gauged by spotting a drop of the liquid on filter paper and stopping the action on the first signs of a permanganate coloured ring round the moistened spot.

1.45 grams isocyanine acetate dissolved in 100 c water required 45.7 cc 3% KMnO_4 and this was just sufficient to discharge all sensitiser colour and render faintly red by permanganate. Taking the molecular weight of the acetate as 390 this amount of permanganate represents 59 grams oxygen, i.e., between 3 & 4 atoms of oxygen.

In subsequent operations the amount of permanganate solution to supply 3 atoms of oxygen was calculated and this amount plus 15% was added to the acetate.

5 grams of isocyanine iodide were made into the acetate as described above. The aqueous solution of 250 cc was divided into two parts, and each part was oxidised separately. To each was added gradually in the cold, and with efficient stirring, 67.5 cc 3% potassium permanganate solution. The addition took half an hour. After standing for half an hour in the cold the manganese di-oxide was filtered off. The MnO_2 precipitate was extracted with pyridine, filtered and the pyridine removed. No substance could be traced in this precipitate except traces of unchanged isocyanine. The filtrates from the oxidation were then extracted 6 times with its own volume of chloroform each time, the chloroform extract dried over potassium carbonate, the chloroform removed and the residue dried in a vacuum dessicator for several days. The residue was a brownish mass which became solid after about 7 days, standing over H_2SO_4 and paraffin wax. This solid was then placed in a flask and extracted several times with boiling ligroin (b.p $40^\circ-60^\circ$) under reflux. A light yellow solution was obtained from which long white needle shaped crystals separated on cooling. 5 grams isocyanine iodide gave 1.38 grams crude product, which represents a yield of ⁷⁹~~20~~% 1 Methyl 2 Quinolone. The pure substance recrystallised from ligroin had a melting point of $73^\circ-74^\circ$. It formed a hydrochloride when a few drops of HCl were added to the substance, this Hydrochloride was recrystallised from 50% HCl and had a melting point of $110^\circ-113^\circ$. This again formed a double salt with mercuric chloride of melting point 189° , after recrystallisation from hot water.

A specimen of 1 Methyl 2 Quinolone was prepared from quinoline methiodide and potassium ferricyanide in alkali (Decner, J. pr. Chem, 1893, ii ^{47, 31.} ~~22, 2005~~); from this the Hydrochloride and mercuric chloride double salt were prepared. Their

titrated against $\frac{N}{20}$ Sodium Hydroxide solution. 8 ccs of this solution were required to neutralise. This neutral solution was again titrated against $\frac{N}{20}$ Silver Nitrate solution, using potassium chromate as indicator. 8.1 cc Silver Nitrate solution were required to replace all the Chlorine. A second experiment was carried out using .1010 grams substance and 7.9 cc alkali and 8cc Silver Nitrate were the amounts required. The molecular weight of the substance would then be $\frac{20,000}{3} \times .103 = 257.5$ approximately. This went to prove that one Hydrogen atom was replaceable and that one chlorine atom was also replaceable. It was then an acid and a salt. This experiment was used merely to act as a guide in determining its probable constitution, it showed at least that the quinoline nucleus was probably intact, and gave a guide as to the number of carbon atoms in the molecule.

From 5 grams of isocyanine iodide 1.7 grams of this hydrochloride was obtained, which represents a yield of 70% of theory, taking this as subsequently proved to be, as the methyl ~~hydro~~chloride of cinchon~~ic~~ acid. A specimen of cinchon~~ic~~ acid manufactured by Schuchardt was converted into the methyl iodide by heating with the theoretical quantity of methyl iodide and sodium carbonate for 10 hours at 45° - 50°. Hans Meyer (Monatshefte 1903, 24, 201).

On treatment with acid the methiodide of cinchon~~ic~~ acid was precipitated. This was recrystallised twice from rectified spirit and was obtained as fine yellow needles. An aqueous solution of this iodide was then shaken up with excess of freshly precipitated silver oxide in the cold. The solution became colourless, was filtered, and the filtrate evaporated to dryness in a vacuum dessicator. The solid was taken up in spirit and precipitated by addition of Ether. The substance

obtained was the betaine. The ~~hydrochloride~~ chloride was made by the addition of a few drops HCl to an aqueous solution of this betaine and the solution evaporated to dryness on the water ^{bath} ~~water~~. It was obtained pure by taking up in alcohol and precipitation by Ether. On addition of Picric acid solution to the concentrated solution of ~~hydrochloride~~ chloride or Betaine long yellow needles of the picrate were deposited which were purified by recrystallisation from hot water.

Returning to the ~~hydrochloride~~ chloride obtained from the isocyanine, this was then converted into the iodide by adding to the concentrated solution to which three drops HCl was added 1 cc concentrated solution of potassium iodide. A yellow precipitate was immediately formed which was filtered and recrystallised from rectified spirit. If allowed to stand in contact with excess of KI solution the solution also deposited dark brown hair like crystals which were probably periodides as they disappeared on saturation with sulphur di-oxide. The formation of these was avoided by filtering at once. The yield on transforming to the iodide was poor, 1.5 grams ~~hydrochloride~~ chloride gave 1 gram iodide but the ~~hydrochloride~~ chloride could be recovered from the Mother liquor by boiling up with freshly precipitated silver chloride, evaporation of the filtrate to dryness, taking up the residue in spirit and precipitation by Ether. If the iodide solution containing excess of KI was evaporated to dryness the product was black and tarry due to excess of iodine. The first few attempts to convert the hydrochloride into the betaine direct by shaking with freshly precipitated silver oxide resulted in a more or less coloured product being obtained when the solution was evaporated to dryness. This colour was subsequently got rid of by first converting the ~~hydrochloride~~ chloride into the iodide as described above, recrystallising the iodide

from rectified spirit and transforming ^{the} ~~and~~ aqueous solution of the iodide into the betaine by shaking with silver oxide. The only disadvantage was that the iodide being much less soluble than the ~~chloride~~ required a considerably greater volume of water to keep it in solution during the action of the silver ~~iodide~~ ^{oxide}, and a consequently longer time to evaporate to dryness in vacuum. The chloride or betaine gave with Picric acid long yellow needles of the picrate.

The following is a table of melting points obtained, the synthesised product from cinchon~~ic~~ acid being termed for conciseness "Schuchar~~dt's~~" & the substances obtained from the Isocyanine "Sensitiser".

	<u>Sensitiser.</u>	<u>Schuchardt's.</u>	<u>Mixed.</u>
<u>Betaine.</u> *	Darkens at 170° becomes softish, then hardens at 207°, becomes very dark, brown	Darkens at 170° respect as "sensitiser"	Behaves exactly as "sensitiser" and "Schuchar dt's "
	melts 219°-221° with decomposition.	Melts at 222°-223° with decomp.	Melts 222°-223° with decompn.
<u>Chloride.</u>	233°-234° with decompn.	235° with decompn.	234°-235° with decompn.
<u>Picrate.</u>	228°	228°	228°-230°
<u>Iodide.</u> †	222° decomp 225°-227°	222° Decomp 226°-228°	222°-223° decomp 225°-227°

RESULTS OF ANALYSIS.

"Sensitiser Iodide".

.0855 grams iodide gave .0585 grams silver iodide
I = 37.0%.

"Schuchar~~dt's~~" Iodide".

.1358 grams iodide gave .0938 grams silver iodide
I = 37.3%.

Both iodides were found to contain 1. Mol. water of

* Claus (Ann, 1892, 270 34) gives mp. as 222°, darkening 170°

† H. Meyer (Monatsh. 1903, 24, 201) " " 222°

crystallisation.

$C_{11}H_{10}NO_2, I H_2O$ requires

$$I = 38.1\%$$

Betaines and iodides were then dried at 110° at 10 m/ms pressure.

"Sensitiser Iodide".

.1391 grams substance gave .2117 grams CO_2 and .0443 grams H_2O

$$C = 41.51\% \quad H = 3.53\%$$

"Schuchardts" Iodide".

.1582 grams substance gave .2408 grams CO_2 and .0491 grams H_2O .

$$C = 41.5\% \quad H = 3.44\%$$

$C_{11}H_{10}NO_2, I$ requires $C = 41.88\%$

$$H = 3.18\%$$

"Sensitiser Betaine".

.1040 grams substance gave .2684 grams CO_2 and .0451 grams H_2O .

$$C = 70.39\% \quad H = 4.82\%$$

Schuchardt's Betaine".

.1412 grams substance gave .3656 grams CO_2 and .0617 grams H_2O .

$$C = 70.62\% \quad H = 4.85\%$$

$C_{11}H_9NO_2$ requires $C = 70.6\%$

$$H = 4.81\%$$

The alcoholic ether mother liquors after filtering off the methyl chloride of cinchoninic acid were then examined. The alcohol and ether were removed on the water bath. In the flask a small amount of yellow crystalline material remained. This was dissolved in hot alcohol and crystals were deposited on cooling again. Melting point was found to be $193^\circ-194^\circ$. It was a hydrochloride and formed a picrate from Picric Acid, also yellow needles of melting point $159^\circ-161^\circ$. A mercuric chloride double salt was also

formed but as the total substance present was merely a trace this could not be investigated further.

Oxidation of the Isocyanine in strictly
neutral solution.

5 grams isocyanine iodide were transformed into the acetate as described above and the acetate dissolved in 250 cc of water as before, this again was oxidised in two portions. The oxidising agent used was 3% potassium permanganate solution to which had been added one equivalent of glacial acetic acid, i.e., to every six grams potassium permanganate 1.14 grams glacial acetic acid were added. The oxidation was carried out as before at 0° with very efficient stirring, and the addition of the permanganate was carried out so slowly that the whole operation lasted a half to three quarters of an hour. At the end of the oxidation it was found on testing that the solution was strictly neutral. The manganese dioxide was filtered off, and again only traces of unchanged isocyanine were found on extracting it with pyridine. The mother liquor was then made alkaline by addition of small quantity of potassium carbonate & extracted with chloroform as before. The chloroform extract was dried and the chloroform removed. The residue was then extracted first with ligroin. This gave a mercuric chloride double salt of melting point 189°. Again the residue was extracted with benzene and this gave also a mercuric chloride double salt and a hydrochloride of melting point 112°-113°. If the ~~Y~~ γ quinolone had been present it would have been taken up with benzene but no trace of it could be found, the whole of the substance being the ~~a~~ quinolone already obtained and described.

The aqueous portion from the chloroform extraction

was cleaned with charcoal as previously described. On completing the process described above for obtaining the betaine or the methylchloride of cinchoninic acid only .17 grams could be traced from 5 grams isocyanine iodide. From the alcohol-ether mother liquors, however, .4 grams of the yellowish needle shaped crystalline body were obtained, which had a melting point of 193° - 194° as before. The charcoal used for cleaning the substance was then examined. It was boiled under reflux with rectified spirit six times. From the alcoholic extracts on evaporating down and treating with ether 1.55 grams of the methyl chloride of cinchoninic acid was obtained of melting point 236° . It formed as before the picrate and the iodide of melting points as previously indicated, the iodide decomposing 228° - 230° . The amount obtained from the charcoal together with the amount obtained direct accounted for the same proportion of methyl chloride of cinchoninic acid as in the previous oxidation.

It was thus found that the only difference was a slight increase in the quantity of the unknown substance of melting point 193° - 194° . This gave acid reactions and was a hydrochloride.

.107 grams of this unidentified substance was dissolved in 20 cc water and titrated against $\frac{N}{20}$ sodium hydroxide using phenolphthalein as indicator. 16.5 cc $\frac{N}{20}$ solution were required to neutralise. The n point was very clear and distinct. This neutral solution was titrated against $\frac{N}{20}$ silver nitrate solution and 19.1 cc were required to precipitate all the chlorine, using potassium chromate as indicator, but the n point was indistinct, & it was observed that a considerable quantity of silver chromate was precipitated on standing. This would give as the probable approximate molecular weight $\frac{20.000 \times .107}{16.5} = 130$

= 130 approximately, which would exclude any formula having the quinoline nucleus in its structure, and might lead to the conclusion that rupture of the ring had been effected to a small extent. This unidentified substance was not investigated further.

Preparation of the trans form of Di-Methyl
Isocyanine Iodide.

2 grams isocyanine iodide were placed in a small wide test tube or conical flask under air reflux and 6 grams

pure Quinoline (B.P 230° - 233°). added.

The Quinoline was then boiled on a sand bath, when the isocyanine gradually went into solution, the colour gradually changing to brown. In about 10-15 minutes there was no trace of Isocyanine colour left., the solution was boiled for a total of 20 minutes after which it was allowed to cool gradually. There was then a deposit of brown crystals which were collected, washed first with a small quantity of pure quinoline, then with ether. Yield was only 10%.

The substance was recrystallised from Aniline when a mass of brownish yellow needles were obtained. The yields of crude products were usually 10% but on one occasion as much as 30% was obtained. If the mixture of quinoline and isocyanine was not heated for a sufficiently long time either no yellow body was obtained at all or the yellow body was contaminated with unchanged isocyanine. If, on the other hand, the mixture was heated too long a solid pitch was obtained which yielded with difficulty on treatment with pyridine then with water or spirit, a brown non-crystalline substance which did not contain iodine.

This substance was not investigated further as it was found impossible to obtain it crystalline from any of the ordinary crystallising media.

The brownish yellow crystals obtained as above recrystallised from Aniline were found to darken at 320° - 325° and melt at 342° - 345° approximately. On account of the high melting point and the difficulty of correctly estimating it, it was also difficult to gauge the purity of the substance obtained.

.1252 grams substance gave .2732 grams CO_2 & .0477 grams H_2O .

C = 59.51%

H = 4.23%

$C_{21} H_{19} N_2 I$ requires C = 59.16%

H = 4.46%.

.1546 grams substance gave .0875 grams silver iodide. I = 30.6%.

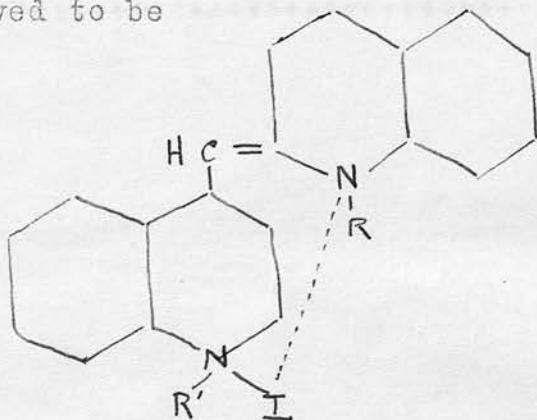
$C_{21} H_{19} N_2 I$ requires I = 29.8%

+++++

SUMMARY.

(1).

From the foregoing the structural form of Isocyanines has been proved to be



(2). The question of colour has also been touched upon.

The structure of the yellow isomer admits of only one interpretation, viz the trans form of the isocyanine. This precludes the possibility of a residual valency of the iodine atom attaching itself to the second nitrogen of this body. This would lead one to connect such a formation viz, a conjugated chain of carbon atoms, together with another atom having the possibility of a residual valency of this atom closing the chain, with intensity of colour. Many examples could be given of such structures where it is possible to give such an interpretation. For example.- the triphenyl methane dyes admit of such an interpretation. In the rosolic acid series ~~we have~~ and

and in the rosaniline series we have examples

On the other hand we have many loose molecular combinations with the possibility of a metal such as Na or Fe acting in this way.

But on the other hand again it is possible to point to many intensely coloured compounds which cannot be given a structure admitting this residual valency.

This question naturally must be left entirely open as it is far too complex to come within the limits of such a paper as this, and cannot, of course, be settled on such meagre evidence.

MANCHESTER. APRIL 10TH, 1920.

R. L. Wis hart

The Sect.

Thesis submitted for the Degree of D.Sc.

The Degree of D. Sc. conferred

18th December, 1925.

STUDIES IN THE AZINE SERIES.

PART I. ON THE NAPHTHOPHENOSAFRANINES.

PART II. ON THE NAPHTHOPHENOSAFRANINONES.

PART III. ON THE HYDROXY NAPHTHOPHENOSAFRANOLS.

by

R. S. WISHART.

Thesis for the Degree of D.Sc.

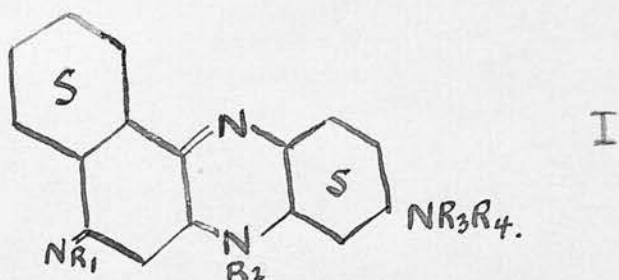


1.

INTRODUCTION.

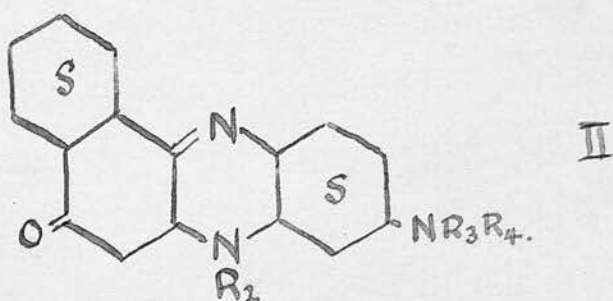
Dyestuffs of the Naphthopheno-safranine type, and especially their sulphonic acids, are of considerable importance. Numberless patents have been taken out claiming different methods of preparation of these dyes, and these will be referred to later.

In this paper it is proposed to describe a new method of synthesising substances of type I:-



in which the sulphonic groups may be either in the benzene nucleus or in the naphthalene nucleus, or in both, or in which the sulphonic acid groups may be absent altogether. Most patent literature claims are restricted to either non-sulphonated or mono-sulphonated substances. The process to be described is more general, and applies equally to non-sulphonated, mono-sulphonated and di-sulphonated substances.

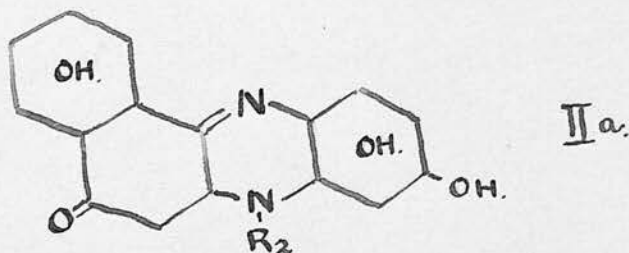
Secondly, it is proposed to describe a new method of preparing Naphthopheno-safraninones of type II:-



in which again the sulphonic acid groups may be in either the benzene or the naphthalene nucleus or in both.

The treatment of this type of substance has led to an interesting sidelight on the question of fluorescence which will be dealt with.

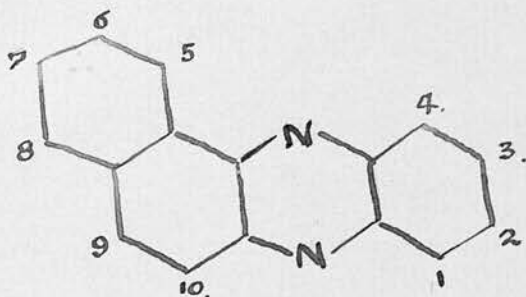
Thirdly, it is proposed to discuss the question of the products of scission of these substances with caustic soda, and other reagents, with the production of Poly- hydroxy- Naphthopheno-safranols of type IIa:-



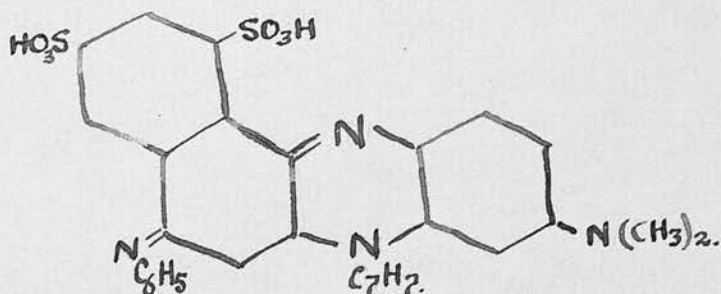
These substances and those of type II have been examined spectroscopically, which has led to interesting results.

Also a method of identifying a dyestuff of type I will be described, a method dependent on the products of scission, and the spectro-analysis of the safranin-ones and safranols. At the present time there is no satisfactory method of analysing a substance of type I, as, with drastic treatment the ring structure is completely disrupted and the products are usually unidentifiable.

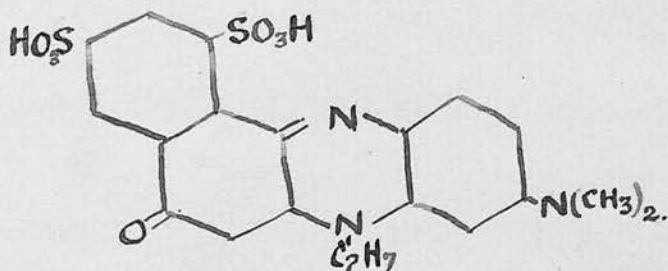
The nomenclature adopted in the following pages will be in accordance with the following numbered scheme.



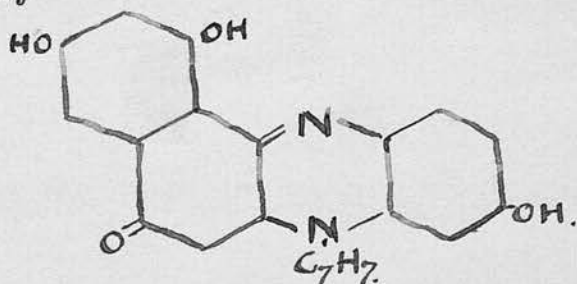
so that a substance with the following constitution



will be named 2 - di methyl 9- phenyl N-tolyl Naphtho-
pheno -safranine 5-7 disulphonic acid; a substance of
the following constitution.



2- di methyl N- tolyl Naphthopheno-safraninone 5-7
di-sulphonic acid; and a substance of the constitution
represented by



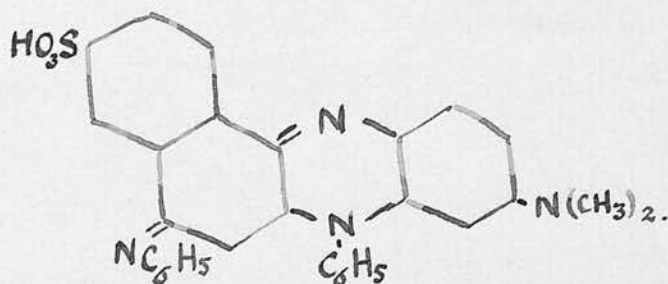
will be named 5-7 di hydroxy N - tolyl Naphthopheno-
safranol.

PART I.

ON NAPHTHOPHENO-SAFRANINES.

There exists in the Patent literature a number of methods of preparing a substance of type I.

Kehrmann and Herzbaum in 1917 (Ber. 1917, 50, 873, 882) obtained Naphthopheno-safranines of type I by the action of substituted 1-3 Naphthalene-diamines on nitroso derivatives; e.g. 1-3 di-phenyl naphthalene diamine 7-sulphonic acid and nitroso di methyl aniline hydrochloride gave 2-dimethyl 9- phenyl Naphthopheno safranine 7- sulphonic acid:-



Kehrmann and Herzbaum used the method described in D.R.P. 78497/1893.

This method is elaborated in another Patent, viz. that of Casella D.R.P. 185986/1904. Azo compounds are also used in place of nitroso derivatives.

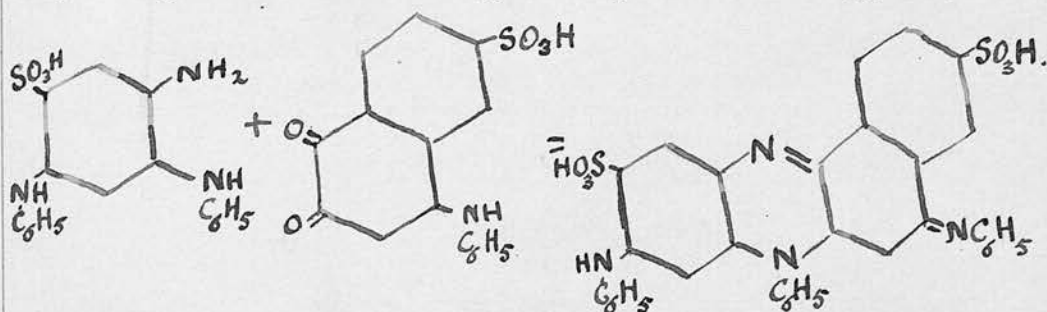
Para diamines having one free NH_2 group when oxidised with di substituted 1-3 naphthalene diamines or their sulphonic acids by means of Sodium Bichromate in acetic acid solution also give Naphtho-Pheno safranines, as is claimed in D.R.P. 184661/1906.

Again from the same type of intermediate with air oxidation, using a solution of copper sulphate in/

in ammonia as a catalyser, Naphthopheno-safranines are obtained. This is claimed in D.R.P. 206646/1907.

All these methods have as their starting point sulphonic acids of diphenyl 1-3 naphthalene diamines, which in themselves are difficult to obtain in the pure state.

Another method of arriving at these substances is from mono-substituted ortho phenylene diamines having one free NH_2 group and ortho Naphthoquinones, e.g. 4-amino 6-sulphonic acid of di-phenyl m-phenylene diamine and 4-phenyl amino 6-sulphonic acid of ortho-Naphthoquinone react to give a product of type I, viz.



i.e.,

(D.R.P. 205358/1907).

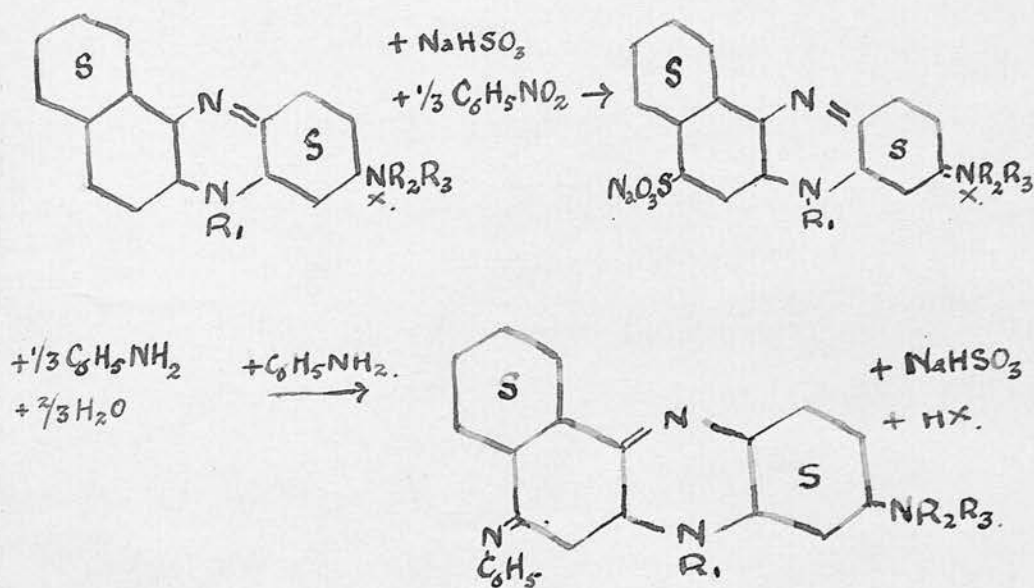
2-9 di-phenyl naphthopheno safranine 3-7 di sulphonic acid.

Naphthophenosafraanines can also be prepared from isorosindulines and arylamines by air oxidation in presence of alkalies, e.g. from di methyl isorosinduline and aniline, 2- di methyl 9-phenyl naphthopheno safranine is obtained. (D.R.P. 183,117. and other PATENTS).

The essence of the reaction lies in the absence of strong acids, and this probably accounts for the fact/

fact that unsulphonated derivatives of isorosindulines react well, but that mono-sulphonic acids give poorer results, whilst di-sulphonic acids do not react at all, the di-sulphonic acids of the isorosindulines being fairly strong acids. It was the fact that di-sulphonic acids failed to give this reaction that turned the writer's attention to another method of causing the anilido group to enter the nucleus in the 9-position. It had been found that sodium bisulphite reacted with isorosindulines, that the sulphonic acid group entered the nucleus in the 9-position, and that the hydrogen thus liberated formed the leuco compound. This reaction was utilised in the hope, that, by boiling the compound formed with aniline and an oxidising agent, the sulphonic acid group would be further displaced by the anilido group. This was found to be the case. When isorosindulines were heated with sodium bisulphite solution, aniline and an oxidising agent in water suspension Naphthophenosafranines were formed. After several comparative failures with other oxidising agents such as air, $Mn O_2$, $Fe Cl_3$, Iodine, etc., the oxidising agent found to give the best results was nitrobenzene. It was found that only a small quantity of bisulphite was necessary, as the sulphonic acid group was immediately replaced by the anilido group and the bisulphite regenerated. When no oxidising agent was present the yield of naphthophenosafranine was /

was very small, and the liquors would not oxidise to the naphthophenosafranine by air oxidation, showing that the leuco compound of the sulphonic acid intermediate does not react with aniline. It is therefore necessary to prevent the formation of the leuco compound so that the isorosinduline sulphonic acid itself may be oxidised to naphthophenosafranine. The amount of nitrobenzene required was found to be $1/3$ gram molecule, although excess of that amount was not deleterious to the reaction. Aniline was always used in excess. The reaction proceeds according to the following scheme:-



This reaction occurs at the boiling point of an aqueous mixture of aniline, sodium bisulphite solution, and either a suspension or a solution of the isorosinduline. It was carried out with numerous unsulphonated/

unsulphonated isorosindulines as well as mono- and di-sulphonic acids of the series, and was found to act in the above manner in every case except one, viz. when a sulphonic acid group occupied the 8- position in the isorosinduline nucleus, when no reaction took place. For example 2- phenyl naphthylamine 5- sulphonic acid reacts with para amino di-phenylamine ortho sulphonic acid under the influence of Sodium bichromate oxidation to form an isorosinduline, but this substance will not subsequently react with aniline in the presence of bisulphite and nitrobenzene to give a naphthopheno safranine. Evidently steric hindrance comes into play and prevents the reaction taking place, or if the bisulphite reacts and the $-SO_3H$ group enters the nucleus in the 9- position; the two SO_3H groups in the peri position form a very stable anhydride, which is not easily hydrolysed and will not therefore react with aniline.

It was also found that other aryl-amines, e.g. metanilic acid will also react in like manner to aniline. When phenyl isorosinduline mono-sulphonic acid, which is insoluble, was boiled up in aqueous suspension with metanilic acid, nitrobenzene, and sodium bisulphite, a soluble blue dyestuff, was formed, viz. 2- phenyl 9- m-sulpho phenyl naphthopheno safranine sulphonic acid.

The/

The times required for the completion of the reaction varied very considerably with different substances. In some cases the reaction was complete in $\frac{1}{2}$ to 1 hour, in others 12 hours were necessary.

EXPERIMENTAL.Preparation of β Naphthylamine sulphonic acids.

As starting points for the above synthesis the following intermediates were subjected to the Bücherer reaction with sodium bi-sulphite and toluidine, viz.

2 - Naphthol 6- sulphonic acid. (Schäfer's acid).

2 - Naphthylamine 6-8 di sulphonic acid.
(Amido G - acid).

2 - Naphthol 7 - sulphonic acid (Oxy F- acid.)

For example, 102 grams Potassium salt of Amido G acid were boiled under reflux with 1000 grams of 33% sodium bisulphite solution, 600 cc. of water, and 80 grams of para toluidine for 24 hours. After steam distilling, the liquors were acidified with HCl, and concentrated to 1500 cc. The precipitate obtained on cooling was redissolved in hot water and re-precipitated by acid.

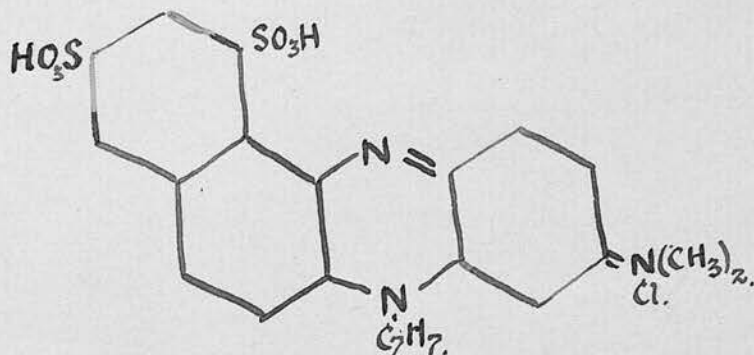
Proceeding in the same manner good results were also obtained of tolyl - Brünner and tolyl - F - acids.

Preparation of Isorosindulines.

These tolyl derivatives were then condensed with various nitroso compounds to give isorosindulines. Isorosindulines were also obtained from them, though in smaller yield, when they were oxidised with para amino di-phenylamine o- sulphonic acid by means of sodium bichromate.

(1) Preparation of 2-di methyl N-tolyl iso-rosinduline 5-7 di-sulphonic acid.

2-tolyl naphthylamine 6-8 di-sulphonic acid condensed with 1.5 gram molecules of nitrosodi-methyl aniline hydrochloride forming III. viz.-



III.

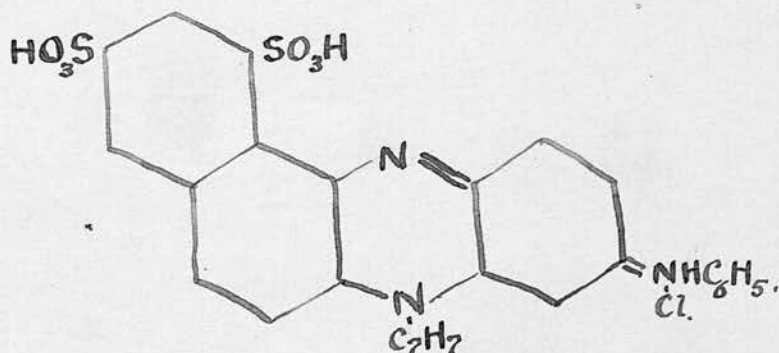
On mixing the components (the nitroso compound as hydrochloride) a blue paste was formed gradually in the cold, and after stirring overnight the reaction was completed by heating for three hours on a boiling water bath. Upon cooling the fairly concentrated solution, after partial salting out, crystals were deposited in 80% yield. This product was then re-crystallised from hot water.

In concentrated sulphuric acid it dissolved with a brown or dull green colour which on slight dilution with water, changed to blue and on further dilution to red violet. These colour changes are peculiar, and do not seem to conform to the general reactions of/

of isorosindulines, which usually give with sulphuric acid a blue or blue violet colour changing to red on dilution, but seem to indicate that oxidation has taken place and given rise to a hydroxyl group in the 4- position in the naphthalene nucleus. This was found not to be the case, so it was concluded that the product was in fact the isorosinduline indicated by III.

(2) Preparation of 2- Phenyl N- Tolyl Isorosinduline 5 - 7 di-sulphonic acid.

Tolyl amido G - acid in the same way condensed with nitroso di-phenylamine, but in this case no blue paste was formed initially and two products were always formed, one soluble in alcohol, giving with sulphuric acid a dull brownish green colour, changing to blue and then to red violet on dilution with water; the other insoluble in spirit or in water, and giving no definite colour reactions with H_2SO_4 . The former was the substance IV.

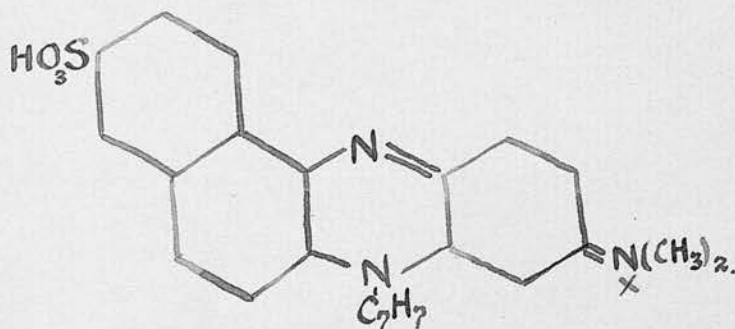


IV.

The yields in this case were poorer than in the case of substance III.

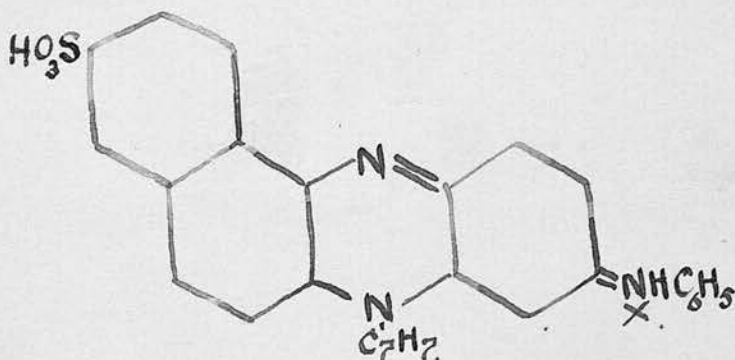
(3) Preparation of Isorosindulines from Tolyl Brünner acid and Tolyl F- acid.

When tolyl Brünner acid and nitroso di-methyl aniline were condensed in acetic acid solution at the temperature of a boiling water bath the product (V) obtained on pouring on to water consisted of fine brown crystals insoluble in water, alkalies or acids.



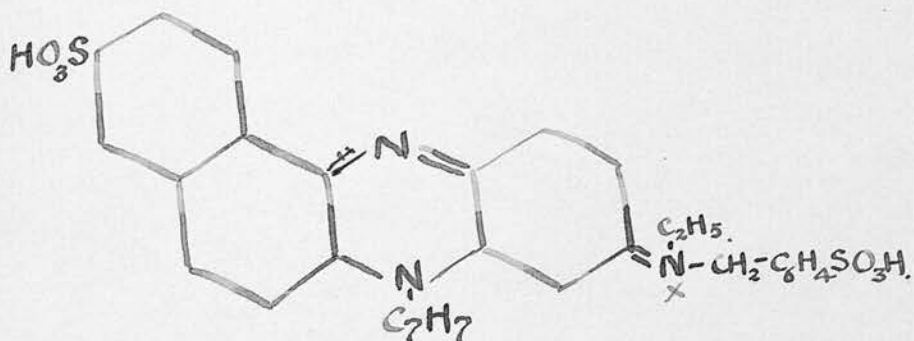
V.

Similarly tolyl Brünner acid and nitroso di phenyl-amine gave (VI).



VI.

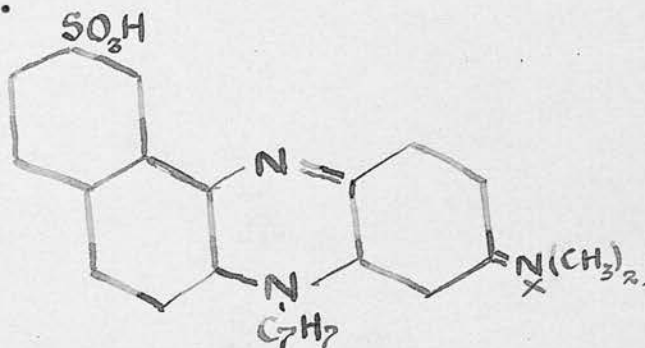
while tolyl Brünner acid and nitroso ethyl benzyl aniline sulphonic acid condensed to form VII.



VII.

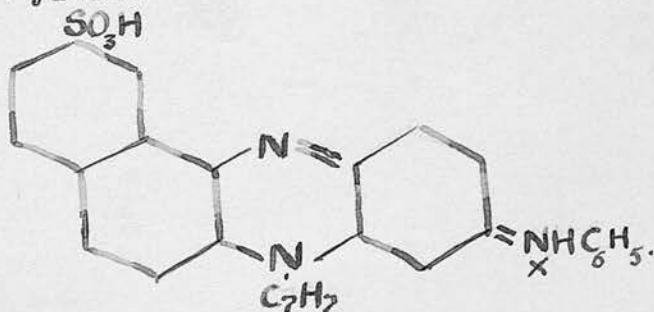
this substance, being soluble in water, was obtained as a sodium salt by salting out from solution.

In the same way tolyl F-acid and nitroso dimethyl aniline resulted in the formation of VIII in good yield.



VIII.

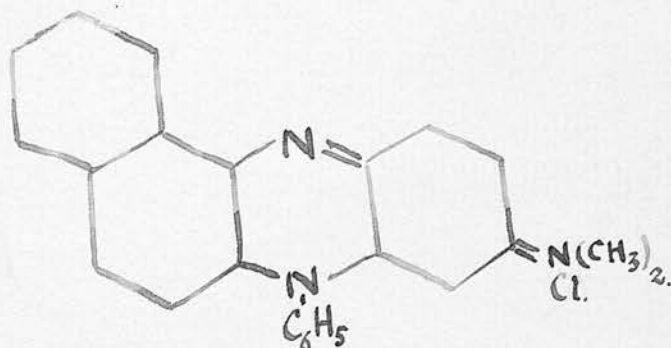
and tolyl F-acid and nitroso di-phenylamine in IX also in good yield.



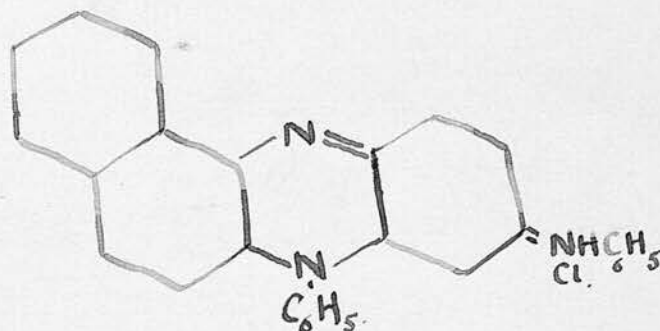
IX.

(4) Preparation of unsulphonated isorosindulines.

Unsulphonated isorosindulines, e.g. Neutral Blue (X) were obtained by the condensation of phenyl β naphthylamine and nitrosodi-methyl aniline in hot methylated spirit (Witt, Ber 1885, 21, 723)



and Phenyl isorosinduline (XI) similarly from phenyl β naphthylamine and nitroso di-phenylamine. (Fischer and Hepp. Ber 29, (1896) 2754.)



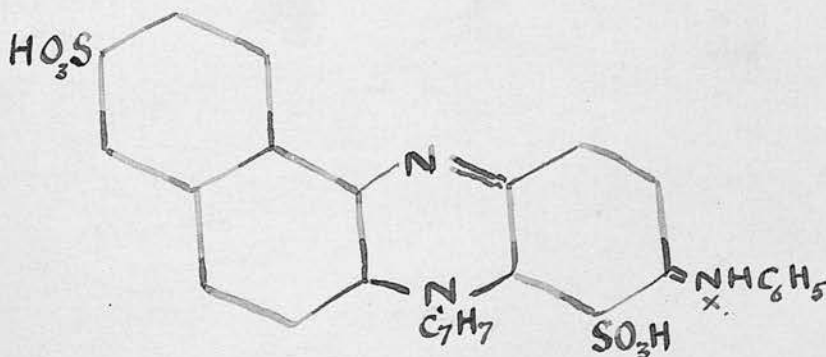
With regard to the colour reactions given by the condensation products in sulphuric acid, it was noticed that all the products obtained by condensating nitroso di-methyl aniline or nitroso-ethyl - benzylaniline sulphonic/

sulphonic acid with tolyl amido G- acid, with tolyl Br^unn^{er} acid and with tolyl F- acid, gave the same initial colour, viz. a dull greenish brown, while, on the other hand, the products obtained by condensing nitroso di-phenylamine with tolyl Br^unn^{er} acid or with tolyl F- acid gave either a blue or a blue violet, similar to that given by Neutral Blue, Phenylisrosinduline and their sulphonic acids. It is difficult to reconcile the reactions of the first named bodies with their constitution, and no explanation can be offered.

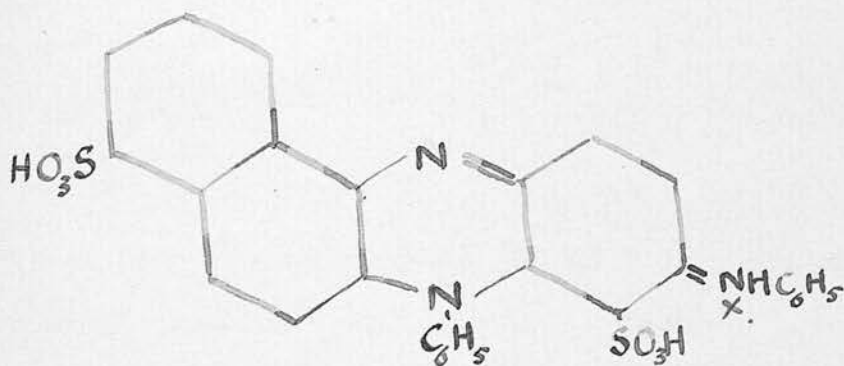
(5) Preparation of isorosindulines having one sulphonic acid group in the benzene nucleus.

These substances were obtained when phenyl or tolyl β naphthylamine (or a sulphonic acid of this substance) was oxidised with p-amino diphenylamine o- sulphonic acid by means of sodium bi-chromate in dilute acetic acid solution. The yields were not good.

Tolyl Br^unn^{er} acid and p-amino diphenylamine o-sulphonic acid when thus oxidised gave rise to XII, whilst phenyl β naphthylamine 5-sulphonic acid and the same second component yielded XIII.

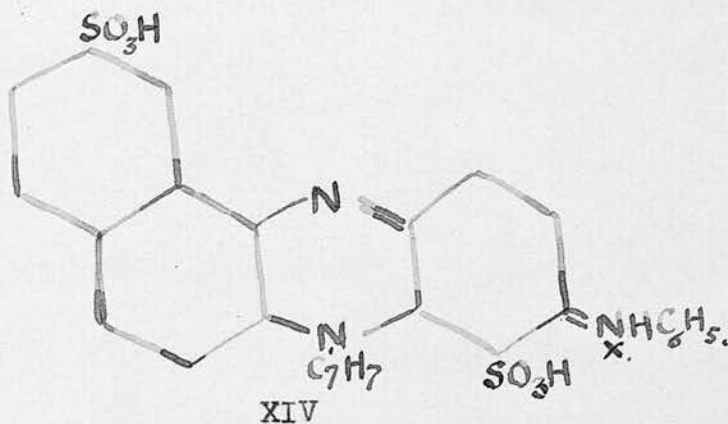


XII.

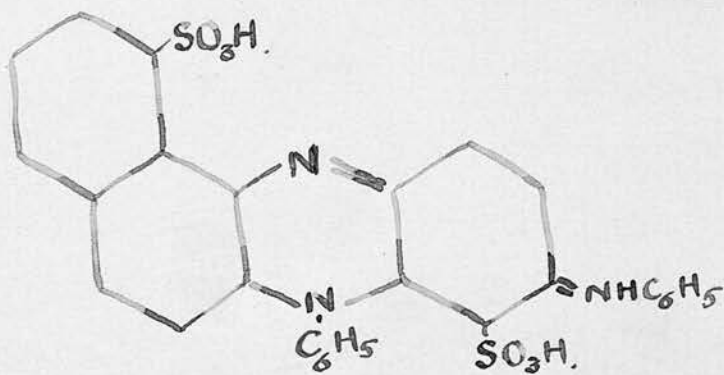


XIII.

In the same way tolyl β naphthylamine 7- sulphonic acid gave rise to XIV, and phenyl β naphthylamine 8- sulphonic acid to XV.



XIV



XV.

Preparation of Naphthopheno safranines from the isorosindulines.

These Isorosindulines III to XV inclusive were subjected to treatment with aniline, sodium bisulphite, and nitrobenzene in aqueous suspension or solution at the boiling point, the mono sulpho derivatives being insoluble in water and soluble in aniline, the disulpho derivatives being soluble in water and less soluble in aniline. Each substance was transformed into a derivative of Naphthophenosafraanine with the single exception of XIII.

(1) Preparation of 2- di-methyl 9- phenyl N- tolyl naphtho-pheno-safraanine 5-7 di-sulphonic acid.

Substance III was originally examined, and as this failed to react with aniline when air oxidised in presence of strong alkalies the above method was eventually evolved of transforming it into the safranine type.

Substance V, which is insoluble, was transformed into a soluble substance when boiled up with sodium bisulphite and subsequently air oxidised, a sulphonic acid group being introduced into the 9- position. It was found that when para toluidine was added to the weak bisulphite solution of substance V and this mixture boiled, that an insoluble substance was obtained which/

which was considerably bluer than the original substance itself in acetic acid solution. The same reaction applied to III gave a product in small yield of much bluer shade than III itself. Air oxidation in conjunction with bisulphite treatment did not produce much better results, but when the amount of bisulphite was cut down to a very small quantity the yields were increased to 40%. Various oxidising agents were used in conjunction with bisulphite; MnO_2 caused the yield to become practically theoretical, though the purity of the substance was not satisfactory. The same remark applied to the products obtained when $FeCl_3$ and Iodine were used, the colour reactions with sulphuric acid being olive green changing to dull blue or blue violet on dilution with water, whereas pure safranines give a very bright green with sulphuric acid. It was obvious that in no case had the reaction proceeded to completion. With nitrobenzene safranines were obtained of very much greater purity and in very much better yield.

20 grams of substance III in aqueous solution were boiled up for 16 hours with 3 grams nitrobenzene, 40 grams aniline and 8 cc. 40% sodium bisulphite solution. The resulting product, after removing excess aniline in steam, crystallised out from the concentrated aqueous solution in beautiful copper coloured plates sparingly soluble in water, slightly more so in alkalis, /

alkalies, and giving with sulphuric acid a very bright green colour changing to blue and blue violet on dilution. The yield was 22 grams of XVI, which contained 2 molecules of water of crystallisation. For analysis of C and H, the hydrated substance was used owing to the rapidity with which it absorbed water. For S. and N the dried substance was analysed.

Found C - 55.60%)
 H - 4.12%) on hydrated substance.
 S - 9.7 9.73 9.72%)
 N - 9.2 9.04 8.97%) on dried substance.

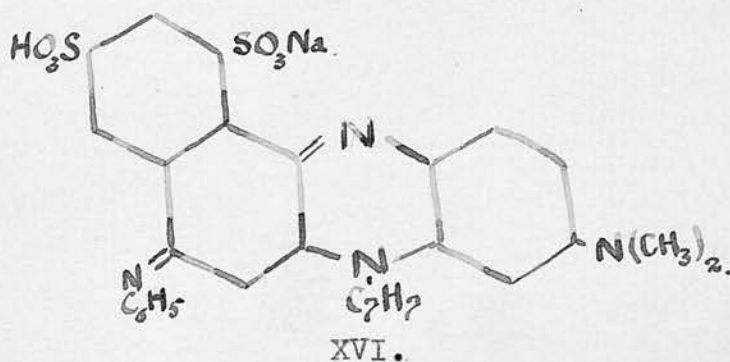
required for $C_{31}H_{25}N_4S_2O_6 Na$

S - 10.06%

N - 8.80%

required for $C_{31}H_{25}N_4S_2O_6 Na, 2H_2O$ - C = 55.36%

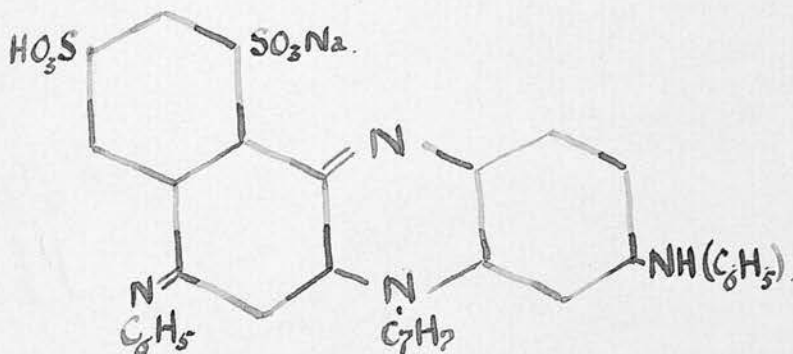
H = 4.30%



Further proof of its structure is given by the fact that, treated with NH_3 at $150^{\circ}C$, aniline is given off, and when treated with $NaOH$ solution at $220^{\circ}C$. both aniline and di-methylamine were isolated.

(2) Preparation of 2-9 di-phenyl N- tolyl naphtho-phenosafranine 5-7 di-sulphonic acid.

Substance IV was treated in the same way as described above and there resulted almost a theoretical yield of XVII.



XVII.

This substance also, on treatment with 10% NaOH solution at 200°C gave among the scission products sufficient aniline to account for two anilido groups in the structure.

(3) Preparation of 2- di methyl 9- phenyl N- *tolyl naphtho-phenosafranine 7- sulphonic acid.

In dealing with the mono sulphonated isorosindulines V and VI and with substance VII (di sulphonated, with one sulphonic acid group in the side chain) it was found that, when treated with aniline at 90°C in dilute caustic soda solution and air oxidised, naphtho-phenosafranines were obtained; though the products were not so pure as when the same safranines were formed by means/

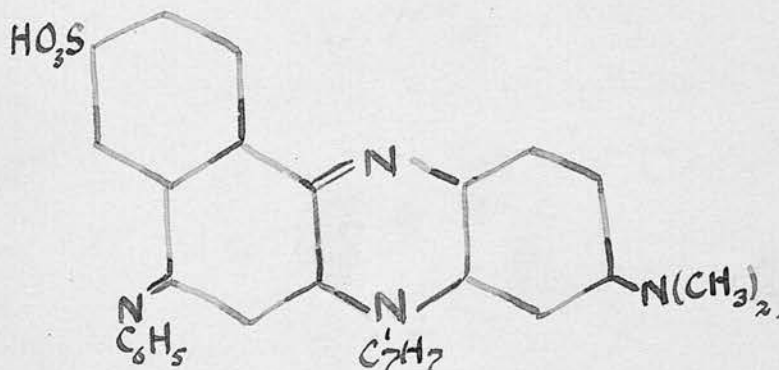
means of the above bisulphite reaction. The times of reaction were much shorter in the latter reaction than in the former and the colour reactions were much better.

In each case the product from the nitrobenzene, bisulphite process was obtained in crystalline bronze plates, which with H_2SO_4 gave a brilliant bright green colour, while the green ^{colour} given by the product of air oxidation was invariably duller.

To 5 grams of substance V was added 20 grams of aniline, 1.0 gram nitrobenzene, 80 cc. water, 2 cc. 40% sodium bisulphite solution and the mixture boiled for 12 hours. 2.6 grams of coppery lustrous plates were deposited, (XVIIa) which with sulphuric acid gave a bright green colour, changing to red and depositing a red violet precipitate on diluting with water.

Found S- 6.10% N - 10.59%.

Required for $C_{31}H_{26}N_4SO_3$ S - 5.99% N - 10.48%



XVIIa.

The mother liquors contained a bye-product which probably contained another sulphonic acid group in the nucleus.

The main product was sulphonated with monohydrate containing a slight amount of SO_3 , the sulphonic acid group entering the side chain in the para position.

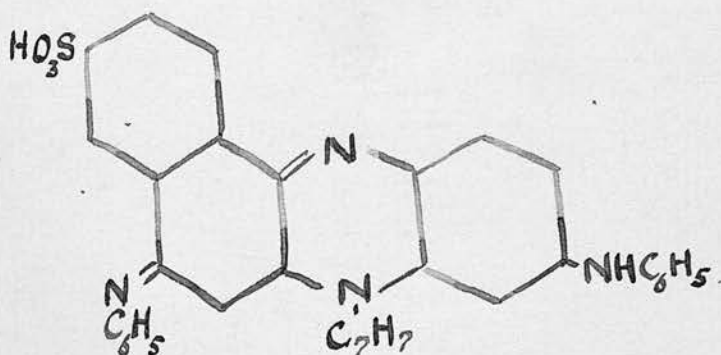
(4) Preparation of 2-9-di phenyl N-tolyl naphtho-phenosafranine 7- sulphonic acid.

With regard to substance VI the time of reaction was reduced to 5 hours. From 10 grams of substance a yield of 10.95 grams of a crystalline product was obtained, which with sulphuric acid gave a bright green colour changing to blue and depositing a blue precipitate on dilution with water. On drying at $100^\circ - 120^\circ \text{C}$. the substance lost one molecule of water of crystallisation.

Found S - 5.34%

N - 10.2%.

Required for $\text{C}_{35}\text{H}_{26}\text{N}_4\text{SO}_3$. N - 9.63% S - 5.5%.

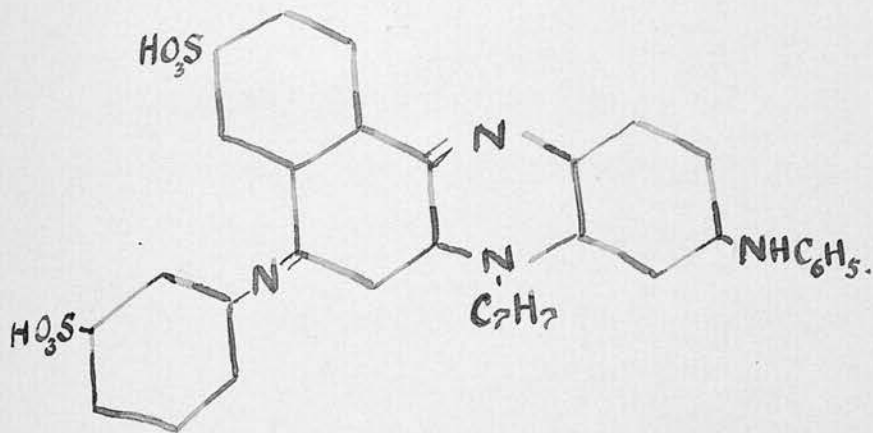


XVIII.

Again, on scission with 10% caustic soda, aniline was found in sufficient quantity among the products of the reaction to account for two anilido groups in the molecule. This substance (XVIII) was sulphonated by monohydrate at less than 30°C for 1½ hours, the product, on pouring on to water being a copper coloured powder, soluble in water to a blue solution. The SO₃H group again enters the side chain in the para position. Fischer and Hepp (A. 262. 237 - 264) note that, when phenyl isorosinduline was heated to 100°C with concentrated sulphuric acid, a sulphonic acid group was introduced into the side chain in the meta position, as metanilic acid was obtained when the product was heated to 200°C with water. The writer found that when the sulphonic acids of XVIIa and XVIII were subjected to treatment with 10% caustic soda solution at 200°C, sulphanilic acid was produced, which was in both cases isolated and identified.

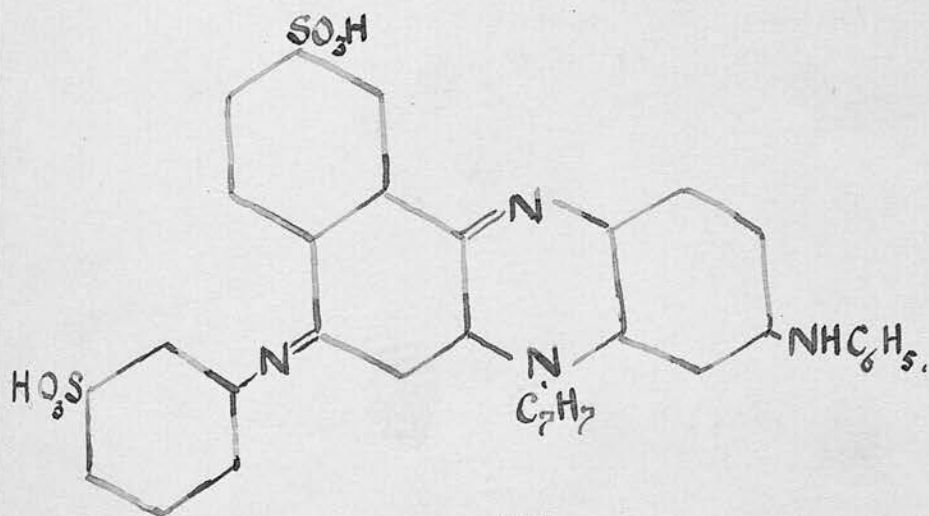
- (5) Preparation of 2- phenyl 9- m- sulpho- phenyl naphtho-pheno safranine 7- mono sulphonic acid, and 6- sulphonic acid.

Metanilic acid was also condensed with substance V, the reaction being carried out in 50% methylated spirit; the yield of soluble dyestuff of constitution XIX was very small, being about 25 - 30%, the remainder being unchanged substance.



XIX.

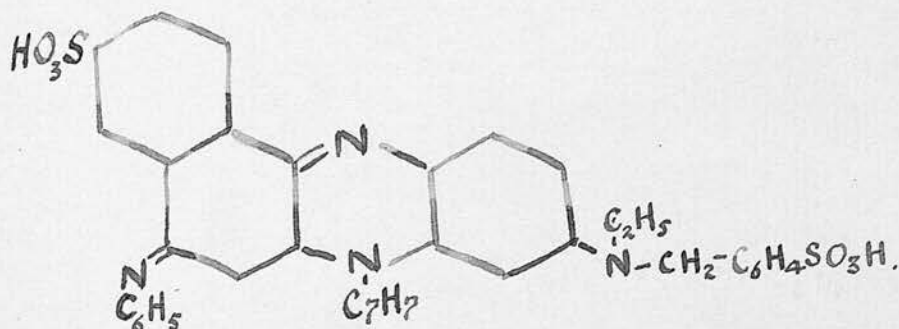
With IX (Tolyl F-compound) metanilic acid gave very good results. 3.0 grams of IX were boiled up with 3.0 grams metanilic acid in 50% spirit, 0.5 grams nitrobenzene and 2 cc. 40% NaHSO₃ solution. After 20 hours boiling and removal of the alcohol, 0.5 grams unchanged substance was recovered, and from the filtrate 2.8 grams dyestuff were obtained of constitution XX.



XX.

(6) Preparation of 2-ethyl p- sulpho- benzyl 9-phenyl N- tolyl naphthophenosafranine 7-sulphonic acid.

5.0 grams of substance VII were boiled up with 80 cc. water, 0.5 grams nitrobenzene, 20 cc. aniline, 2 cc. bisulphite solution for 45 minutes, when the reaction was complete. On steam distilling off excess aniline and nitrobenzene, and salting out the violet coloured filtered liquors 3.5 grams of a copper coloured powder were obtained which with concentrated sulphuric acid gave the safranine test of a bright green, changing to red and red violet on dilution.



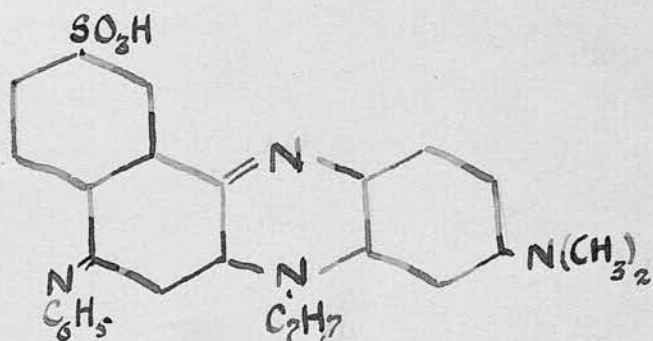
XXa.

(7) Preparation of 2- di methyl 9- phenyl N- tolyl naphtho phenosafranine 6- sulphonic acid.

In the case of substances V, VI, and VII the same products were obtained, though in a less pure state, when these substances were oxidised with aniline in presence/

presence of caustic alkalies at 90°C , but in each case the time required to complete the reaction was 8 - 12 hours. The dyestuffs were in most cases duller in shade than the corresponding substances made by the nitrobenzene process. However, when one turned to substance VIII it was found that the method of air oxidation with caustic soda and aniline gave excellent results and that the time taken was reduced to 45 minutes, the product being beautiful bronze coloured crystals.

5.0 grams of VIII, 0.3 cc. 35% caustic soda solution, 20 cc. aniline, 80 cc. water were mixed in suspension, violently stirred and air blown through whilst the mixture was maintained at 90°C . After 45 minutes the aniline was removed by steam distillation, and there remained 4.48 grams of beautiful bronze coloured crystals of the naphthophenosafraanine XXb.



XXb.

With bisulphite, nitrobenzene etc., from 5.0 grams of VIII the main product after 12 hours boiling was 3.45 grams of beautiful green crystals identical with above/

above, whilst a soluble bye-product probably having two sulphonic acid groups, was also isolated.

(8) Preparation of unsulphonated naphtho-
phenosafranines.

Both with Neutral Blue and with Phenyl isorosinduline very good results were obtained by the action of aniline and caustic soda on these substances in presence of air at 90°C. In both cases from 5 grams of substance, 20 cc. aniline, 3.0 cc. 35% caustic soda solution, heated on a boiling water bath and rapidly stirred in a stream of air (free from CO₂) a complete reaction was effected in from 50 to 75 minutes. After removing aniline, green lustrous crystals were obtained in both cases. Both substances gave the safranine test with sulphuric acid. By boiling up with aniline in small quantity, cooling, filtering, washing with spirit and ether the products were purified to a certain extent and obtained as beautiful lustrous green plates. Using the bisulphite, nitrobenzene process the reactions went equally well and in almost the same time.

The product in the case of phenyl isorosinduline, when basified with dilute caustic soda and crystallised first from pyridine and then from aniline, gave lustrous green plates which melted at 269°C - 272°C (d), similar/

similar to those obtained by the air oxidation process which melted at $270^{\circ}\text{C} - 273^{\circ}\text{C}$ (d). No difference could be noticed either in behaviour towards sulphuric acid, both products giving a bright green colour, changing to intense blue and precipitating on dilution. The main product in the two processes is thus the same.

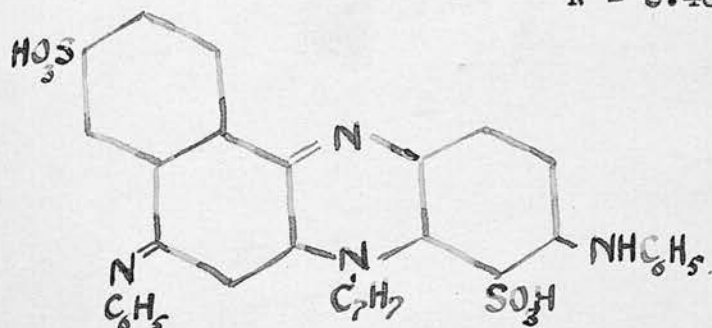
(9) Preparation of naphphenosafranines with a sulphonic acid group in the benzene nucleus.

These substances were formed in the same way as indicated above. 7.5 grams of the product of condensation of tolyl Brünner acid and para amino diphenylamine o- sulphonic acid were boiled up with 3.0 cc. 40% sodium bisulphite solution, 15 grams aniline, 1.2 grams nitrobenzene and 100 cc. water for 15 hours. After steaming off the aniline, the blue solution was salted out and yielded 4.2 g. of a substance which recrystallised well from 40 - 50% spirit to yield beautiful bronze crystals (XXI).

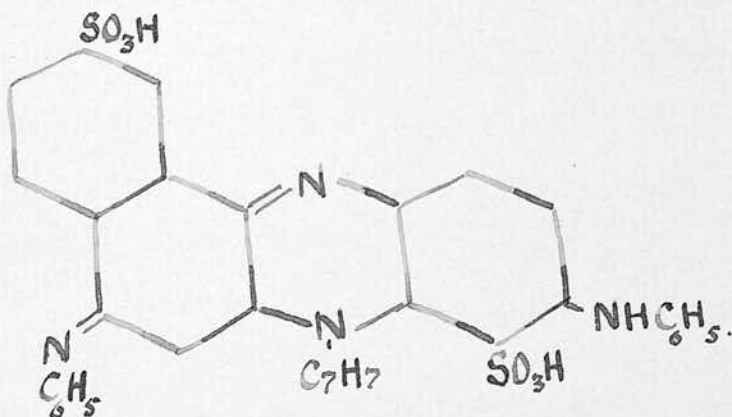
Found S = 9.80% N - 8.56%.

Required for $\text{C}_{35}\text{H}_{26}\text{N}_4\text{S}_2\text{O}_6$ S = 9.67%.

N - 8.46%



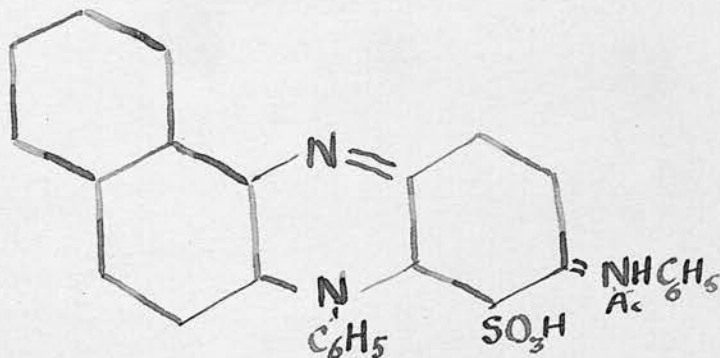
In the case of tolyl F - acid the time of reaction was only $\frac{1}{2}$ - 1 hour, the product being copper plates (XXII).



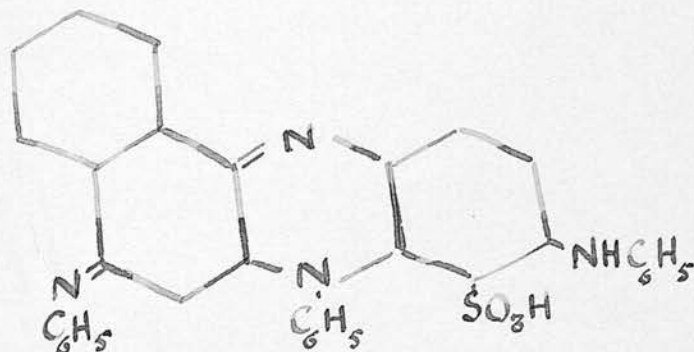
XXII.

(10) Preparation of 2-9 di-phenyl naphthopheno-
safranine I-sulphonic acid and 1-5 di-
sulphonic acid.

When 4.1 grams of phenyl β naphthylamine and 5.8 grams of p-amino di-phenylamine o-sulphonic acid were oxidised in 50% acetic acid solution by means of sodium bichromate at the temperature of a boiling water bath there was obtained 3.6 grams of an isorosinduline of constitution



and when this substance was boiled up for 18 hours with a trace of nitrobenzene, 1.5 cc. NaHSO_3 solution, 2 cc. aniline in aqueous suspension, there was obtained on steam distilling off excess aniline and nitrobenzene 2.0 grams of naphthophenosafranine of constitution (XXIIIa).

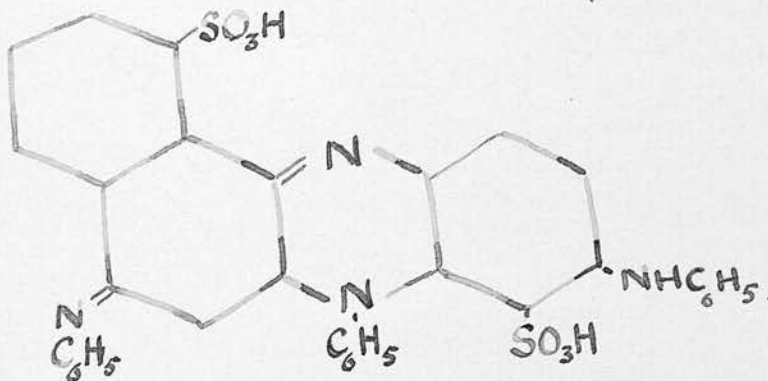


XXIIIa.

which was purified by washing with spirit and ether. With H_2SO_4 this substance gives a bright green colour which becomes blue on dilution with water and gives a blue precipitate on further dilution.

In a similar way when 9.0 grams of phenyl β naphthylamine *g*-sulphonic acid and 9.0 grams of *p*-amino di-phenylamine *o*-sulphonic acid were oxidised with sodium bichromate, there resulted 16.5 grams of the corresponding isorosinduline di-sulphonic acid. When this substance (11.0 grams) was boiled up with aniline, bisulphite, and nitro benzene in aqueous suspension for 2-3 hours, there was obtained on salting out/

out the blue liquors 8.65 grams of a naphthopheno-
safranine of the following constitution (~~XXIII~~).



(~~XXIII~~.)

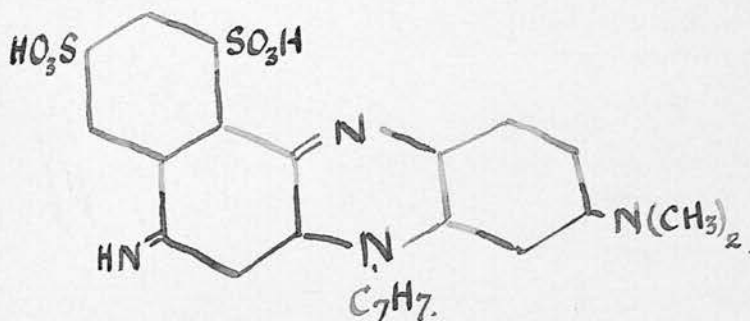
In the case of substance XIII as already stated no
reaction took place when this isorosinduline was
brought into contact with bisulphite, nitrobenzene,
etc.

PART II.

ON NAPHTHOPHENO-SAFRANINONE SULPHONIC ACIDS.

On Naphthophenosafraninone sulphonic acids.

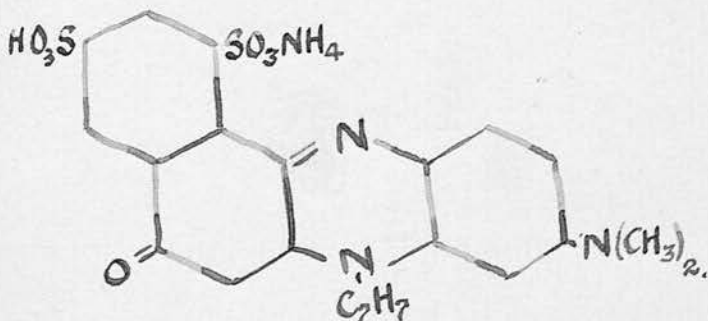
When substance III was subjected to treatment with ammonia, sodium bisulphite, and nitrobenzene in aqueous solution at 100°C for 6 hours in a bomb tube, the product of the condensation proved to be XXIV.-



XXIV.

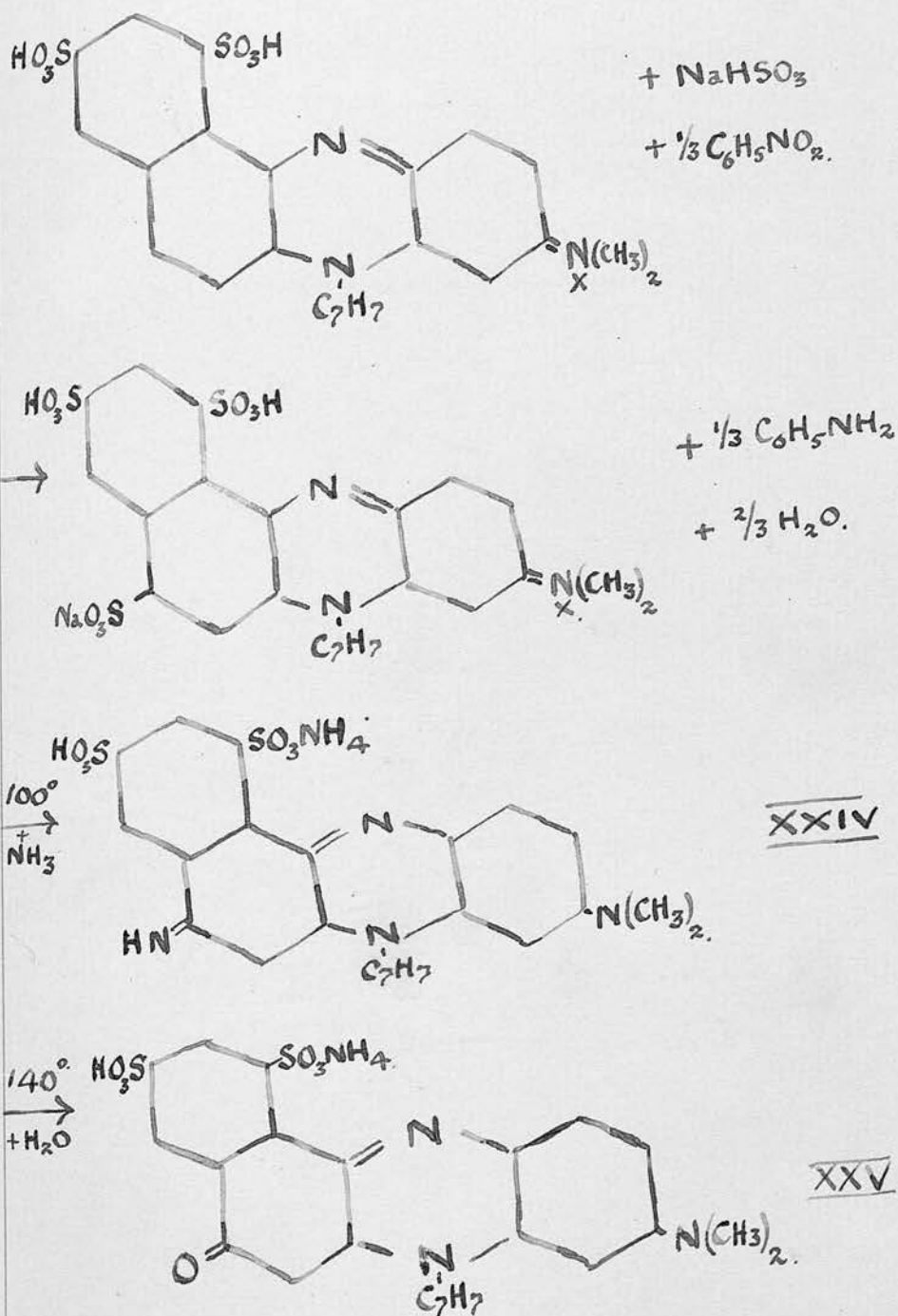
a safranin, giving a green colour with concentrated sulphuric acid, which on dilution turned blue then red, and dyed wool a red colour.

When however the temperature was maintained at 140°C for 12 hours the product from the reaction was a naphthophenosafraninone of the constitution XXV.-



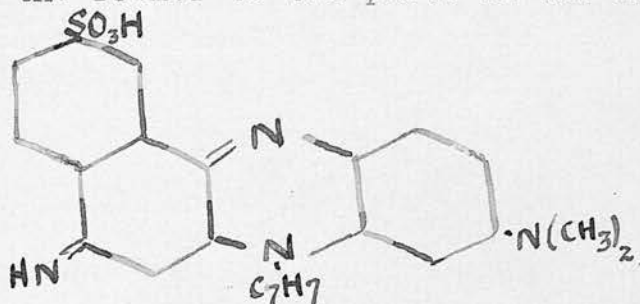
XXV.

i.e., mono ammonium salt of 2 di-methyl N- tolyl naphtho-phenosafraninone 5-7 disulphonic acid. No reaction took place when substance III was treated with ammonia alone, with bisulphite alone, with bisulphite and nitrobenzene, with ammonia and nitrobenzene, or with ammonia and bisulphite. The course of the reaction must then proceed as the following scheme indicates.--



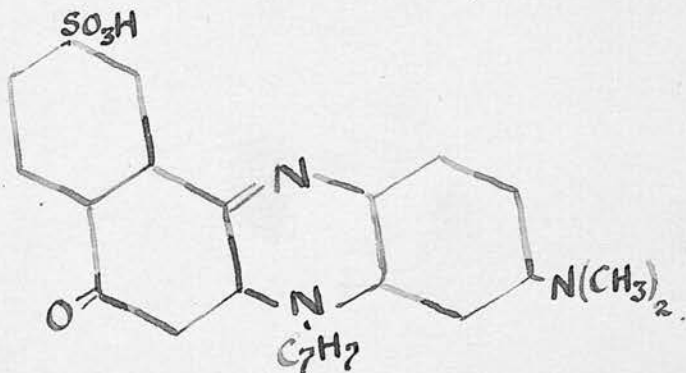
When substance XVI was heated at this temperature (140°C) with water, no reaction took place, but with dilute ammonia the same naphthophenosafraninone was obtained as was obtained with ammonia, bisulphite, nitrobenzene and substance III, i.e., XXV.

When 2-tolyl naphthylamine 7-sulphonic acid was condensed with nitroso di-methylaniline, and the product subsequently brought into reaction with ammonia, sodium bisulphite and nitrobenzene in aqueous suspension in a stirring autoclave, and the temperature maintained at 140°C for 12 hours, the product obtained consisted of two substances in the proportion of one part of the former to two parts of the latter, viz.-



XXVI.

and

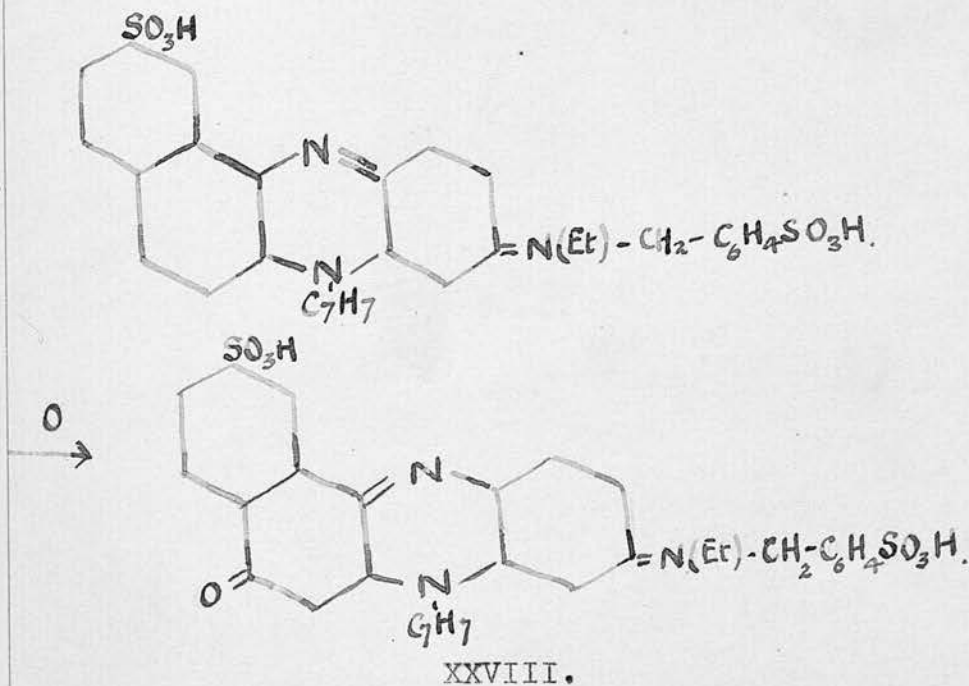


XXVII.

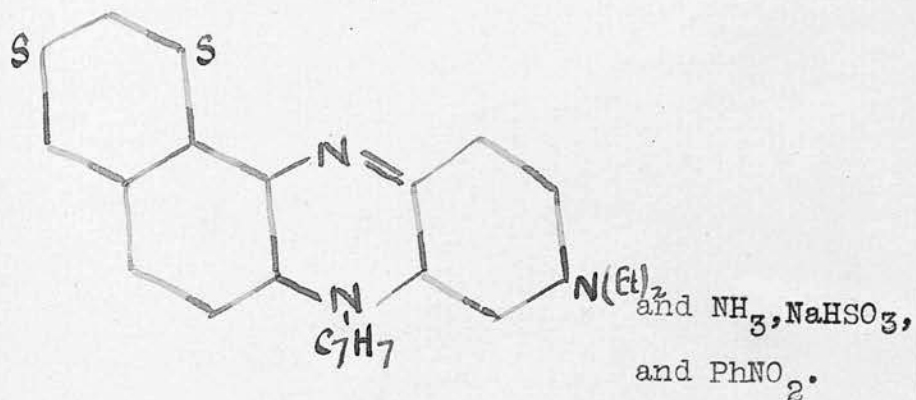
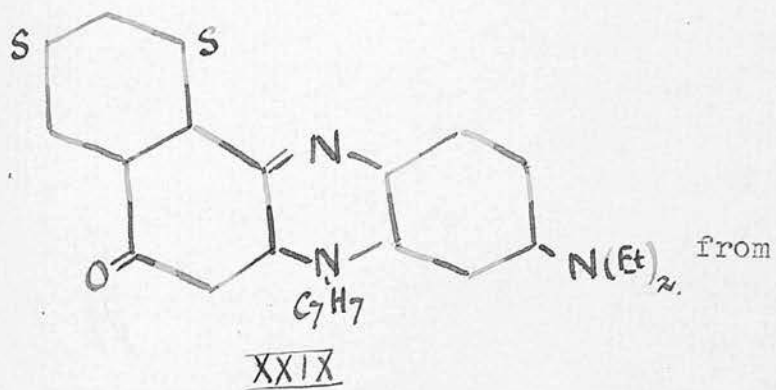
The former (XXVI) is insoluble in water, alkali or acid, and gives with concentrated sulphuric acid a green colour; whilst the latter (XXVII) is soluble in alkalies and gives with concentrated sulphuric acid a violet colouration. The same types of substances were obtained when other phenyl or tolyl naphthylamine sulphonic acids were used, except in the single case of the 5- sulphonic acid when no reaction took place.

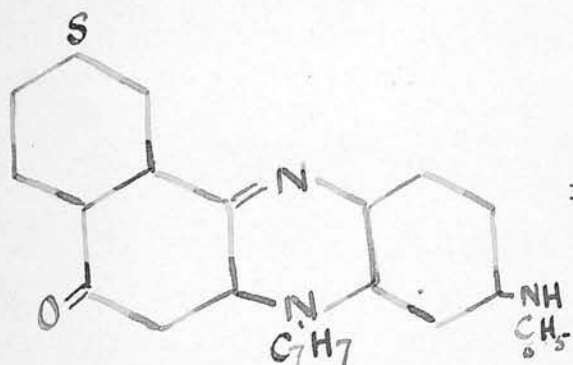
A considerable number of substances were treated in this fashion and the only exception was as stated with substance XIII.

The condensation of tolyl F- acid and nitroso-ethyl benzylaniline sulphonic acid resulted in the formation of 2- ethyl p-sulpho benzyl N- tolyl iso-rosinduline 6- sulphonic acid, which under this treatment was oxidised to the corresponding naphthopheno safraninone, the analysis of which for S and N gave conclusive proof of its structure, viz.-



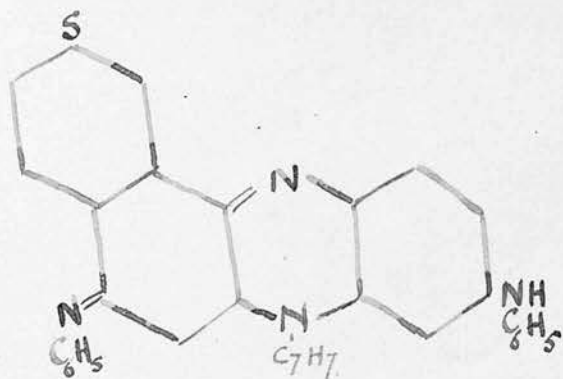
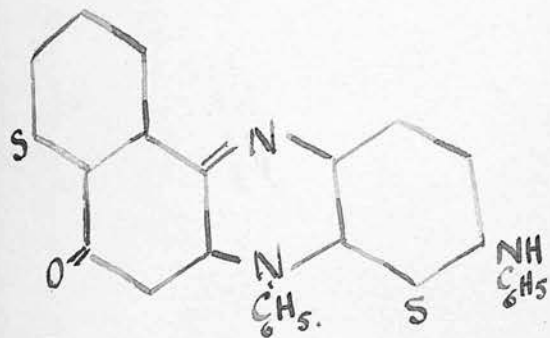
The following 2- N alkyl (aryl) naphthophenosafra-
 ninones were also prepared, viz.-





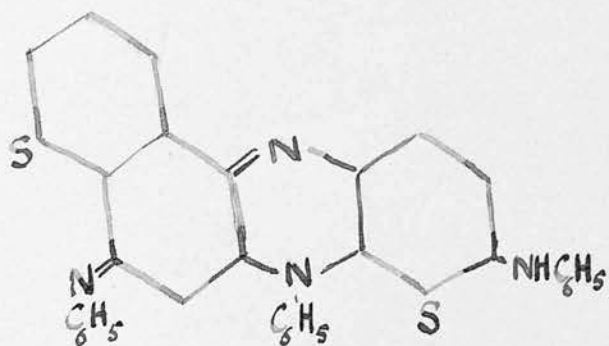
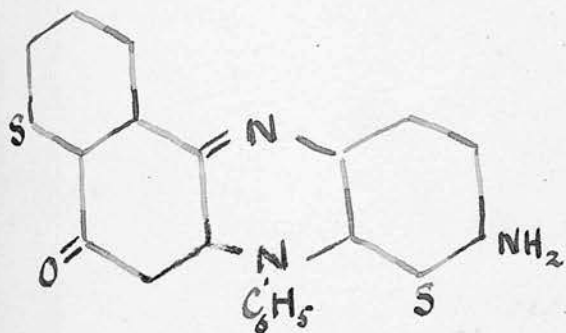
XXX.

from

and NH₃.

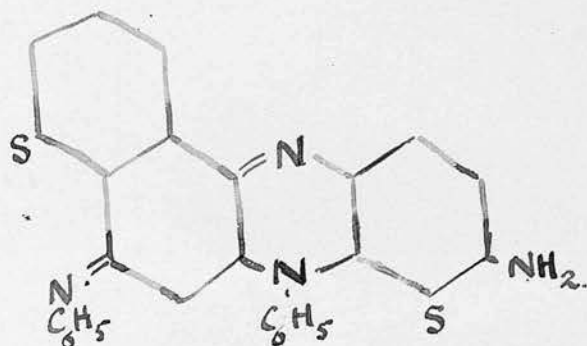
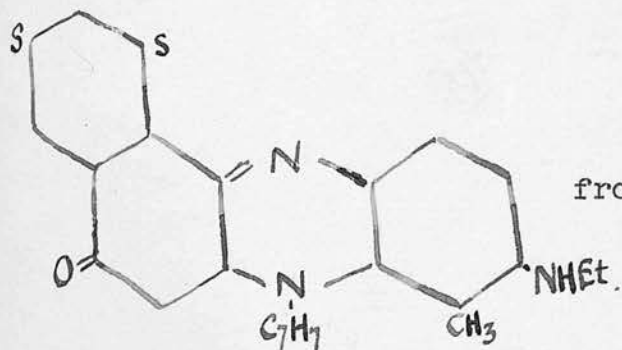
XXXI.

from

and NH₃.

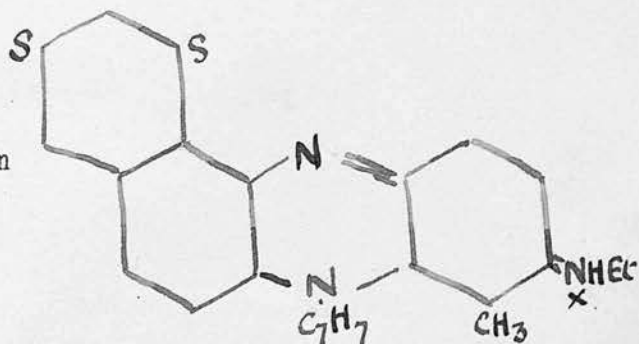
XXXII.

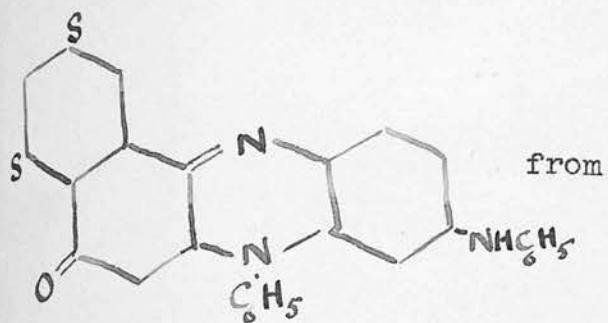
from

and NH₃.

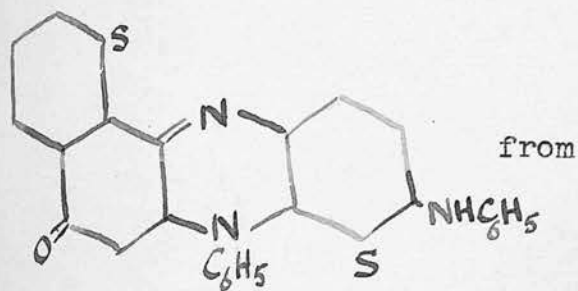
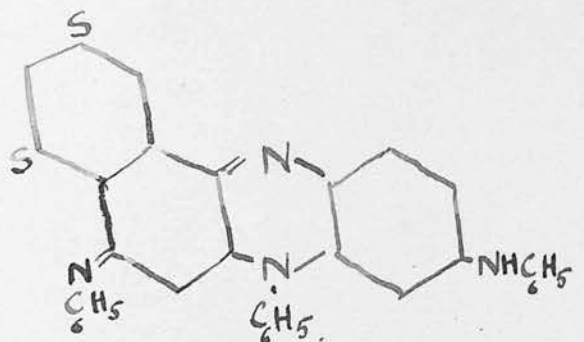
XXXIII.

from

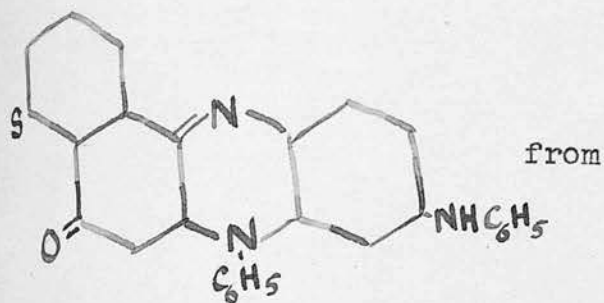
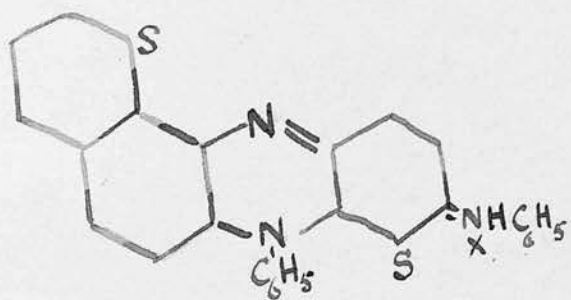
and NH₃, NaHSO₃ and PhNO₂



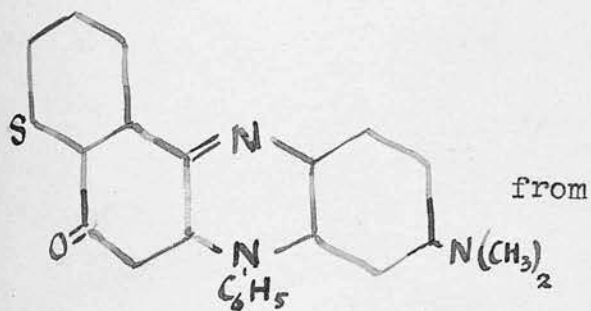
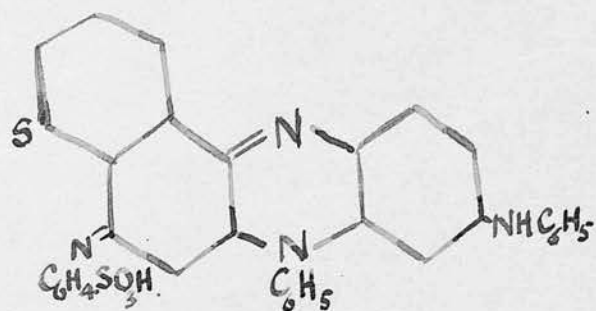
XXXIV.



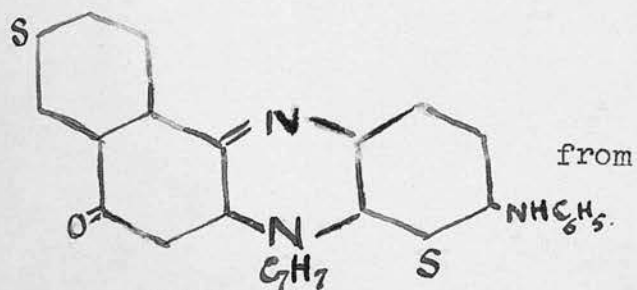
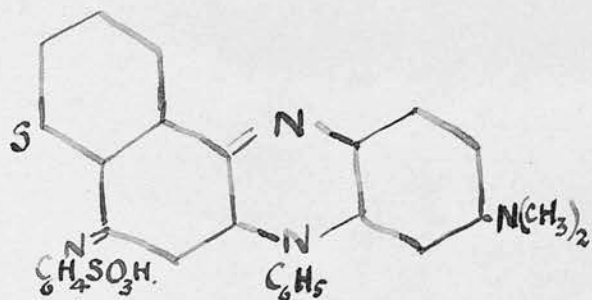
XXXV.



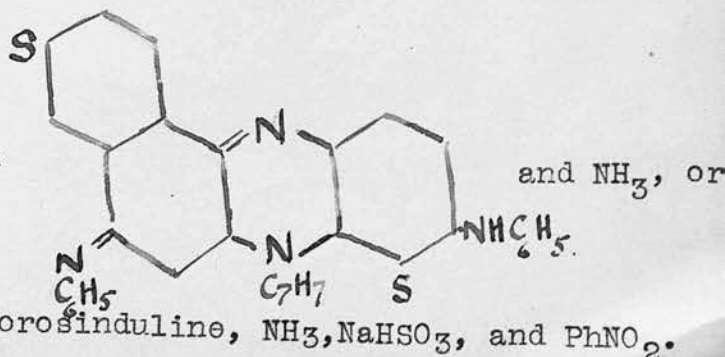
XXXVI.



XXXVII.



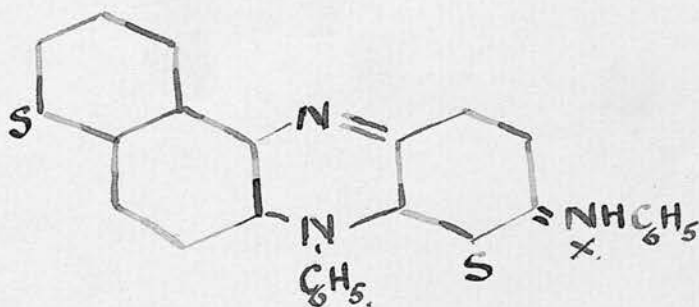
XXXVIII.



The safraninones having only one sulphonic acid group were only very slightly soluble in water, alkalies or spirit; those having two sulphonic acid groups were fairly soluble in these media.

The colour of these safraninones when soluble in aqueous solution is generally a bright red, some having a bluish tinge, and these solutions dye wool a very bright red colour, with a brilliant bluish tinge. It was however found that these dyes were extremely fugitive to light, but that fastness to light was considerably increased by having a sulphonic acid group in the 8- position. All other substituents had no effect on the fastness, substances having the 1- position substituted by $-SO_3H$ group or by $-CH_3$ being equally fugitive with substances having the 5-, 6-, or 7- positions substituted by SO_3H groups. Neither had the N- substituents any effect on increasing fastness to light.

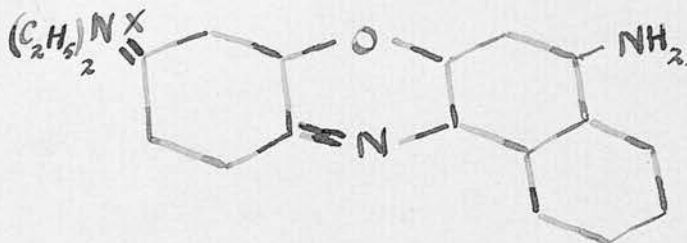
It was found too that when, e.g. phenyl (3 naphthylamine 5- sulphonic acid and p- amino di-phenylamine o- sulphonic acid were oxidised with sodium bichromate there resulted the isorosinduline



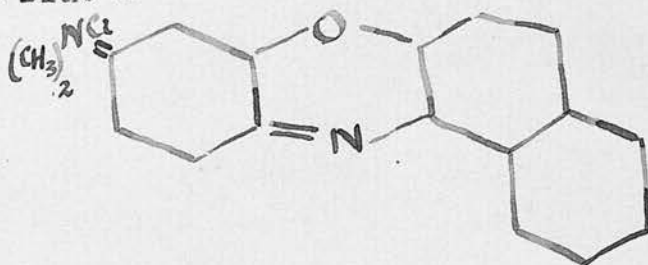
but that this substance gave no reaction with NaHSO_3 , PhNO_2 , etc.

In general when the 8- position of the iso-rosinduline nucleus was occupied by a sulphonic acid group, the only method of arriving at a naphthopheno-safraninone was through the naphthophenosafraanine and ammonia.

Thorpe (J.C.S. 1907, 324) found that some naphtho-phenoxazines e.g. Nile Blue A



and Meldola Blue -



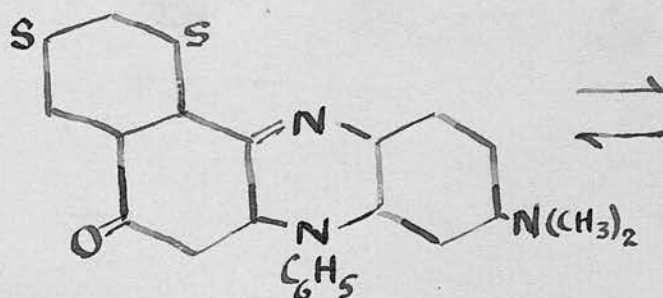
and other similar bodies were easily oxidised to the corresponding phenoxazones. This work arose out of observations made by Prof. Lorraine Smith that when certain tissues were stained by Nile Blue A and similar dyes, /

dyes, certain portions of the tissues were stained a red colour. This colour Thorpe found to be due to the presence of phenoxazones. It was thought that, there being a similarity between the phenoxazones and the naphthophenosafraninones here described, these new dyestuffs might be useful in microscopic work and act as selective stains. Naphthophenosafraninone XXV was used as a counter stain after haemotoxylin in the staining of sections. It was found that the tissues that usually stain with Eosin were stained a very bright pink, staining rather more intensely than Eosin. It does not decolourise with prolonged application of alcohol. When XXV and haematin were mixed together a precipitate was formed and a section was stained with the filtrate. The results were not so satisfactory. Using haematoxylin and XXV separately gave better results than when the solutions were mixed before use, and in this method of application the stain proved of use as a protoplasmic stain for tissues. I am indebted to Dr Arnold Renshaw, M.D., D.P.H. for his report on the use of this dyestuff as a microscopic stain.

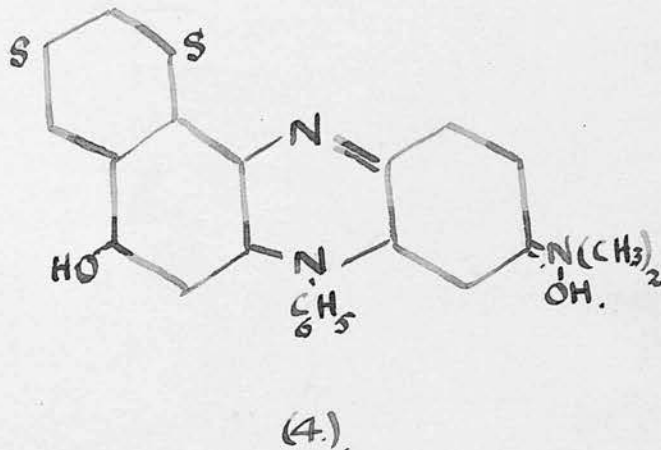
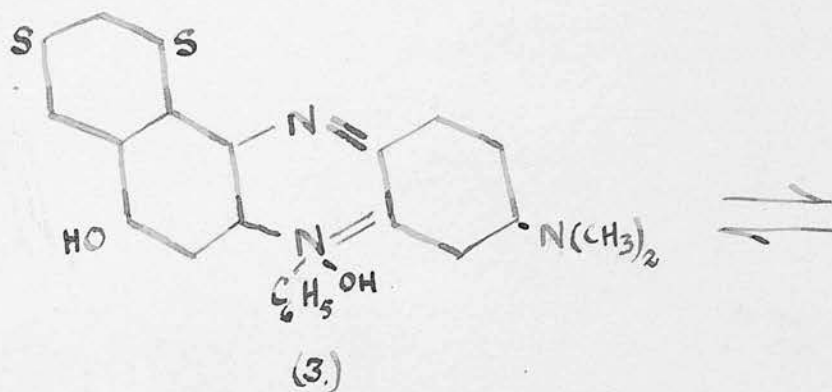
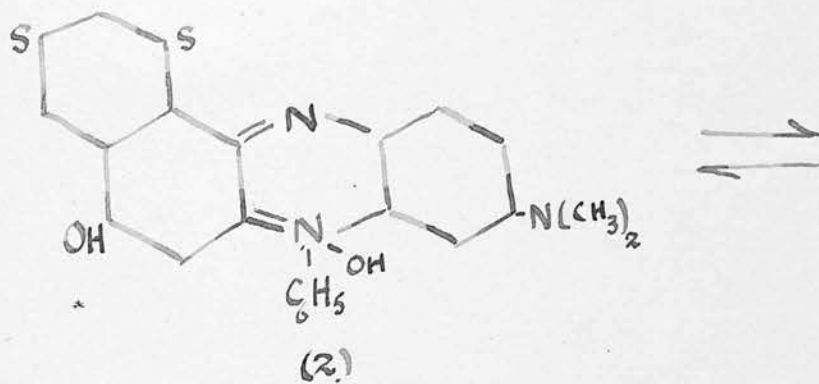
These safraninones were generally more or less soluble in ethyl alcohol. The solutions in this medium showed definite bands in the spectrum, and these bands differed in nearly all cases; in most cases the position of the SO_3H group, as well as the substituents in/

in the 2-N group having an effect on the spectrum. This is shown in the table of spectrum analysis at the end of the paper.

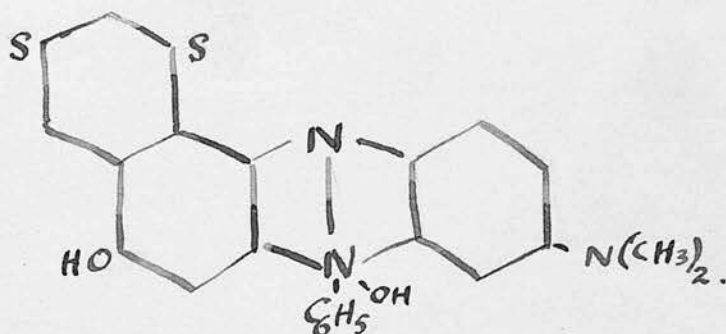
Also an interesting observation was made regarding the phenomenon of fluorescence of these alcoholic solutions of the safraninones. Fluorescence appeared when the position 2- was occupied by $-N(CH_3)_2$, $-N(Et)_2$, $-NH_2$, $-N(C_2H_5)(CH_2, C_6H_4SO_3H)$, and $-NH(C_2H_5)$, but not when the group was $-NHC_6H_5$, or when the $-NH_2$ group was acetylated. When the group was $-N(C_2H_5)(C_6H_5)$ fluorescence was observed in slight degree. The position of the SO_3H groups had no effect on fluorescence. It is difficult to see how these observations can be fitted into Hewitt's theory of fluorescence. Double symmetrical tautomerism of these compounds does not seem to be possible, as the intermediate phase in the oscillation between the two possible isomeric forms does not present a symmetrical complex. Take for example 2- dimethyl naphthopheno safraninone 5-7 di sulphonic acid the various stages of the oscillatory period would be represented by the following scheme.-



(L)



or phases 2 and 3 might be written as a single phase
thus.-



There is no symmetrical complex in any of these phases, all we can say from observations is that if the basicity of the aryl or alkyl-amino group in the 2- position is reduced as by introducing an anilido group there, or by acetylating a free NH_2 group, we may prevent the last phase (4) from forming at all, and so having no oscillatory motion in the molecule we have no fluorescence: or by introducing $\text{N}(\text{Et})(\text{Ph})$ instead of $\text{N}(\text{H})(\text{Ph})$ we increase the basicity and tend to produce fluorescence. If phase 4 does not form in the case of a less basic 2- group, but does form in the case first cited, then in phase 1 and phase 4 energy is alternately absorbed and emitted, and this will give rise to fluorescence in those bodies in which phase 4 is possible.

Fischer and Hepp in an admirable series of papers in the Annalen discuss various reactions of the rosindulines, safranines and similar substances. They confine themselves practically to unsulphonated derivatives, except in two isolated examples (A, 286 187) in which they treat phenyl isorosinduline sulphonic acids with caustic soda solution and obtain oxyrosindones. In a previous paper (A. 272, 306-354) in dealing with the action of a mixture of HCl and acetic acid on naphthopheno safranines they state that the substance 9-phenyl naphthophenosafraanine when so treated at 200°C gives rise to a safraninone, the anilido/

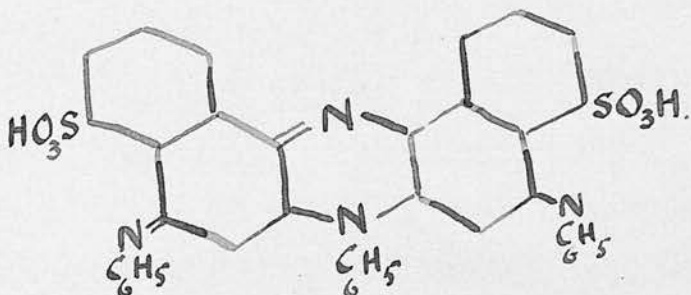
anilido group being replaced by a hydroxy group, whilst at 225°C the product was a naphthophenosafranols, the NH_2 group being also replaced by OH.

This was not the experience of the writer, who found that, when a naphthophenosafranin was treated with a mixture of hydrochloric and acetic acids a naphthophenosafranols was formed, there being no intermediate stage in this case. This will be further discussed under Part III.

Fischer and Hepp state also that these safraninones when dissolved in concentrated sulphuric acid show a dirty green colour, changing to brown and to red on dilution, whilst the corresponding safranols produce a green colour with sulphuric acid. The writer, however, found that safraninones having a di-methyl group in the 2- position gave with sulphuric acid a violet colour, changing to blue and further to red on dilution, that safraninones having a phenyl group in this position gave blue with sulphuric acid, again changing to red on dilution, whilst a free NH_2 group in the 2- position gave rise to a green colour with sulphuric acid changing to red on dilution. With naphthophenosafranols, which will be discussed in the next part, the colour given on dissolving in sulphuric acid was red violet if there was no hydroxyl group in the 8- position, and blue if a hydroxy group occupied that position.

All naphthophenosafranines gave a bright green colour with sulphuric acid.

Fischer and Hepp prefer the para quinoid form for the naphthopheno safranines and naphthophenosafranines. Evidence seems to point in this direction as, no matter what the side chains were in any naphthophenosafranine, the action of ammonia was to split off the side chain in the 9- position, and not that in the 2- position, which required a stronger alkali (NaOH) to remove. This was true in the case of a completely symmetrical substance, viz.-



which on treatment with ammonia at 180°C gave rise to only one molecule of aniline and not to two molecules.

When an attempt was made to methylate substance XXV by means of di-methyl sulphate it was found that di-methyl sulphate added on to the N of the ring but that methylation of the $-\text{C}=\text{O}$ group did not take place, as would have been expected if tautomeric change to ortho-quinoid form had taken place. For these reasons I have preferred to write the formulae in the para quinoid form in every case.

EXPERIMENTAL.

Preparation of mono-ammonium salt of 2- di- methyl
N- tolyl-Naphthophenosafraninone 5-7 di-sulphonic acid.

(XXV)

20 grams of 2- di-methyl N- tolyl isorosinduline 5-7 di-sulphonic acid, 8 cc. of a 40% solution of sodium bisulphite, 50 cc. of 88 ammonia, 2.25 grams of nitrobenzene, 200 cc. water were heated in an autoclave to 140°C for 5 hours. From the resulting intense red solution the excess nitrobenzene was steamed distilled off, and the alkaline liquors after filtering were carefully acidified with hydrochloric acid.

14.5 grams of a very fine copper coloured crystalline product were obtained, which was recrystallised from 75% spirit and obtained in fine greenish lustrous plates. The substance crystallised with two molecules of water of crystallisation, which were only removed at 130° - 140°C. It was analysed for S and N in the anhydrous state, but in the hydrated state for C and H, owing to its great hygroscopic tendency.

Found for S - 11.39, 11.75%

N - 10.17%

Required for $C_{25}H_{24}N_4S_2O_7$, S - 11.51% N - 10.07%

Found for C - 50.85%, H - 4.98%

Required for $C_{25}H_{24}N_4S_2O_7, 2 H_2O$, C - 50.84%,

H - 4.73%

With/



With concentrated sulphuric acid a violet colouration was obtained, changing to blue and brilliant red on dilution. This product was soluble in water to a brilliant red solution, also in absolute ethyl alcohol to a brilliant red solution showing a yellow fluorescence. When the ammonium salt was boiled with 7% NaOH solution, ammonia was given off, and the mono sodium salt was precipitated in fine copper plates on acidifying the solution. This too crystallised from 75% spirit, fine copper coloured plates being obtained.

Found N - 7.87% S - 11.29%

Required for $C_{25}H_{20}N_3O_7Na$. N - 7.5% S - 11.23%.

When 4.0 grams of 2- di-methyl 9-phenyl N- tolyl naphthophenosafranine 5-7 di-sulphonic acid were treated with 15 cc. 88 ammonia, 10 cc. water at 150°C for 5 hours in a bomb tube, the product was 3.6 grams of a substance which proved to be identical with XXV, the product obtained from the previous reaction.

Preparation of 2- ethyl p- sulphobenzyl N-tolyl naphthophenosafraninone 6- sulphonic acid. (XXVIII).

30 grams of 2- ethyl p-sulphobenzyl N-tolyl isorosinduline 6-sulphonic acid, 90 cc. 88 ammonia, 3.5 grams nitrobenzene, 12 cc. 40% sodium bisulphite solution, and 300 cc. water were mixed and heated for

5 hours at 140°C . On steam distilling and acidifying 14.0 grams of copper coloured plates were obtained, which on recrystallisation from 80% spirit gave 4.2 grams of beautiful bronze lustrous plates of the ammonium salt.

Found N = 8.4%. 8.66%.

S = 10.06%

Required for $\text{C}_{32}\text{H}_{30}\text{N}_4\text{S}_2\text{O}_7$. N = 8.66%. S = 10.00%

This substance was converted into the sodium salt by boiling with 3% caustic soda for some time, and acidifying the liquors. The sodium salt was also recrystallised from spirit. It was soluble in spirit to a red solution, showing a yellow fluorescence, it was also of course soluble in water.

Found S = 9.7%. Required S = 9.83%.

Preparation of 2-diethyl N-tolyl naphthopheno-safraninone 5-7 di-sulphonic acid. (XXIX).

10 grams of 2-di-ethyl N-tolyl isorosinduline 5-7 di-sulphonic acid, 33 cc. 88 ammonia, 75 cc. water, 1.2 grams nitrobenzene and 4 cc. of sodium bisulphite solution were heated together in an autoclave for 5 hours at 140°C and the liquors acidified. 5.9 grams of product were obtained, which yielded 1.2 grams of fine crystals ^{when} ~~which~~ recrystallised from 80% spirit.

Found/

Found N = 7.72%.

S = 11.57%. N/S = 3/2

Required for $C_{27}H_{25}N_3S_2O_7$ - N = 7.40% S = 11.29%

In this case the acid was obtained, the acid being probably less soluble than the ammonium salt. It is soluble in water and spirit to a red solution, the latter showing a yellow fluorescence.

Preparation of 2- phenyl naphtho pheno safraninone
1-8 disulphonic acid. (XXXI)

20 grms of the corresponding naphthophenosafraanine, 60 cc. 88 ammonia and 200 cc. water were heated together in an autoclave for 5 hours at $140^{\circ}C$. The reaction mixture was intensely red and completely in solution. On steam distilling 1.26 grams of aniline were obtained, and, on acidifying the liquors 13.85 grams of beautiful copper crystals were thrown out of solution. With sulphuric acid a blue colour was obtained, changing to red on dilution. This product recrystallised from 80% spirit in beautiful plates.

Found N = 9.91%. S = 11.22%.

Required for $C_{28}H_{22}N_4S_2O_7$, N = 9.50%. S = 10.85%.

This product was also soluble in water and spirit, the latter however showing no fluorescence.

If in the above, instead of using the safranin there named a homologue having a phenyl-ethyl amino group/

group in the 2- position was used, a similar reaction took place and there was isolated a copper coloured powder which with sulphuric acid gave a violet colour (not blue as in the previous case), changing to red on dilution. This product was 2- phenyl ethyl naphthophenosafraninone 1-8 di-sulphonic acid, soluble in water and spirit to a red solution, the latter in this case showing a yellow fluorescence, which was more marked in slightly alkaline solution than in neutral.

Preparation of 2- di-methyl N- tolyl naphthopheno-
safranine 6-sulphonic acid and 7- sulphonic acid, and
their corresponding safraninones. (XXVI and XXVII).

25 grams of di-methyl N-tolyl isorosinduline 6-sulphonic acid 75 cc. 88 ammonia, 8 cc. of 40% bisulphite solution, 2.5 cc. nitrobenzene with 300 cc. water were stirred in an autoclave, and heated for 12 hours at 140°C. The excess nitrobenzene was removed by steam distillation, and the alkaline liquors filtered. The residue consisted of 8.4 grams of 2-di-methyl N- tolyl naphthophenosafranine 6-sulphonic acid, which was then washed with spirit and ether. With sulphuric acid this substance gave the usual green colour, changing to violet and precipitating on dilution.

Found/

Found N - 12.06%. S - 6.85%

C - 65.71%. H - 4.90%

Required for $C_{25}H_{22}N_4SO_3$. C - 65.50%. H - 4.80%

N - 12.22% S - 6.98%

The alkaline liquors were acidified and 17.5 grams of a copper coloured precipitate were obtained, which proved to be 2- di-methyl N-tolyl naphthopheno safraninone 6-sulphonic acid.

Found N - 9.23%.

Required for $C_{25}H_{21}N_3SO_4$ - N - 9.15%

Similarly the corresponding 7-sulphonic acid was prepared from the corresponding tolyl Brünner acid compound. From 26 grams of the isorosinduline there was obtained 7.4 grams of the safranine and 16.1 grams of the naphthophenosafrafinone.

Preparation of 1-methyl 2-ethyl N-tolyl naphthopheno-safranine 5-7 di-sulphonic acid, and the corresponding 1-methyl 2-ethyl N-tolyl naphthophenosafrafinone 5-7 di-sulphonic acid. (XXXIII).

To 8.3 grams of tolyl amido G- acid, in glacial acetic acid at the boil, 6.0 grams of nitroso mono-ethyl o-toluidine hydrochloride were added. After 1 hour's boiling a fine amorphous powder (8.2 grams) was filtered off. 6.6 grams of this substance, 12 grams aniline/

aniline, 3.0 cc. sodium bisulphite solution, 1.0 cc. nitrobenzene, and 150 cc. water were boiled together for 16 to 18 hours. The excess nitrobenzene and aniline were steam distilled off, the liquors concentrated and cooled, when 4.0 grams of beautiful bronze crystals of the above naphthophenosafraninone were obtained.

When 2.0 grams of this substance were treated with 6 cc. 88 ammonia, 20 cc. water for 8 hours at 140°C aniline was given off, and the above naphthophenosafraninone was isolated on acidification.

Preparation of 2-di-methyl naphthophenosafraninone
8-sulphonic acid. (XXXVII).

As 2-di-methyl naphthophenosafraninone 8-sulphonic acid was insoluble in water or in ammonia, this substance was first sulphonated by monohydrate at ordinary temperature. 22 grams of the sulphonated product were treated with 66 cc. 88 ammonia, 250 cc. water at 140°C for 6 hours. On the completion of the reaction 13.15 grams of a crystalline product were found in suspension. With sulphuric acid this gave a bluish green colour, changing to violet with precipitation on dilution with water. It was slightly soluble in absolute alcohol to a brilliant pink colour with yellow fluorescence, but was practically insoluble in water/

water or alkalies. From the liquors 3.81 grams of sulphanic acid were isolated, and identified as such by transforming into tri bromaniline of m.p. 118° - 119° C.

Fischer and Hepp state that on sulphonation of the anilido group in substances of the naphthophenosafranin type, the SO_3H group enters the side chain in the meta position, as metanilic acid was isolated from among the scission products.

Preparation of naphthophenosafraninone 1-8 di-sulphonic acid, and its acyl derivative. (XXXII).

3.0 grams of 9-phenyl naphthophenosafranin 1-8 di-sulphonic acid 9 cc. 88 ammonia, and 30 cc. water were maintained at 140° C for 5 hours. A red solution was obtained, which on acidification deposited 2.62 grams of a substance which was recrystallised from 80% spirit to yield 1.65 grams of fine crystals showing a greenish bronze lustre, soluble in water and ethyl alcohol, the latter showing a yellow fluorescence. When this substance was however boiled up for a few minutes with acetic anhydride, the acyl compound was formed, which, though still soluble in alcohol, showed practically no fluorescence.

With sulphuric acid the colour given is green, changing to red on dilution with water.

Found/

Found N = 10.95%. S = 12.72%.

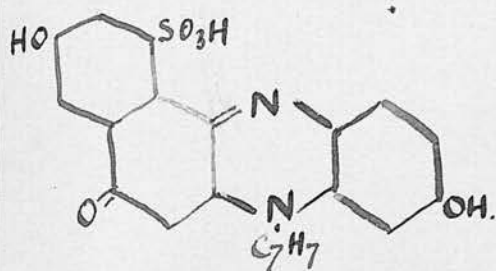
Required for $C_{22}H_{18}N_4S_2O_7$ (i.e. mono ammonium salt)

N = 10.89%. S = 12.55%.

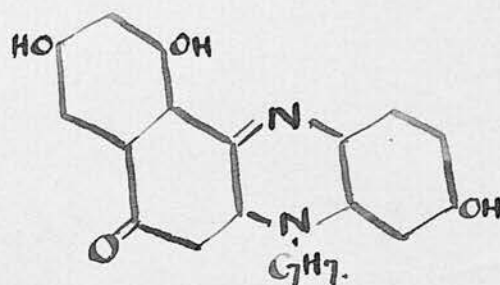
PART III.

ON HYDROXY NAPHTHOPHENOSAFRANOLS.

On treating 2- di-methyl N-tolyl naphthopheno-
 5-7 di-sulphonic acid
 safraninone with 10% caustic soda solution at 200°C
 for 12 hours in an autoclave, di-methylamine was split
 off, the sulphonic acid groups were, for the most part,
 replaced by hydroxyl groups, and two substances were
 isolated, viz.-



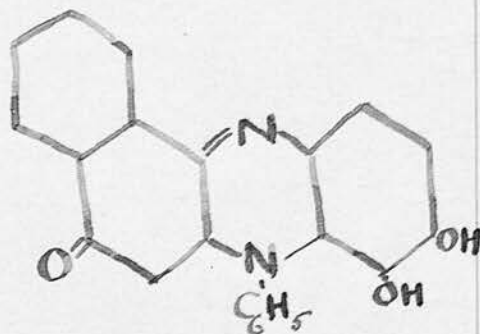
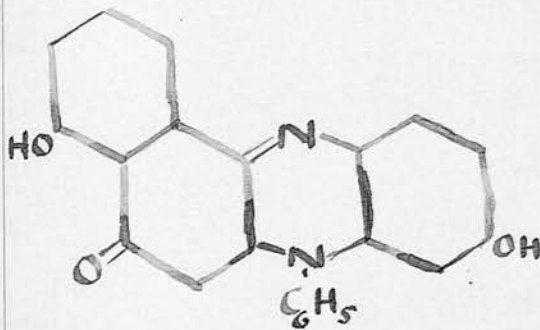
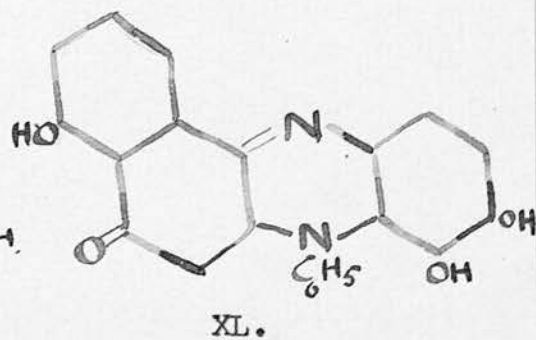
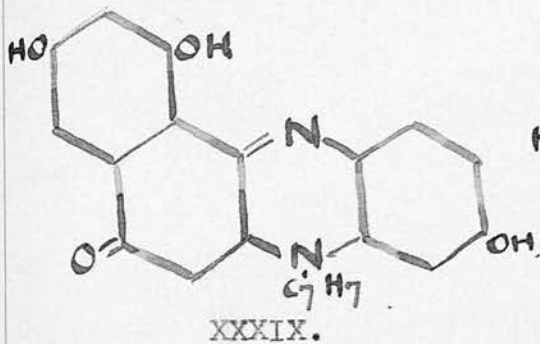
XXXIXa.



XXXIX.

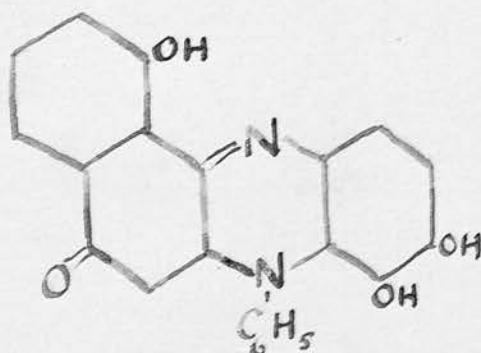
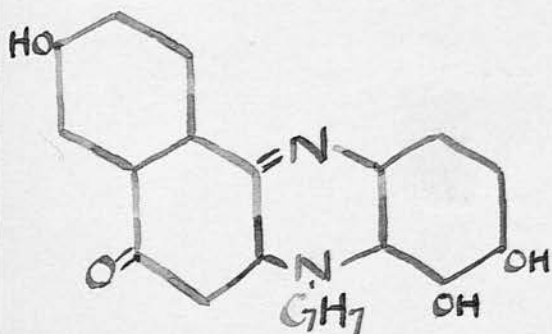
the former was deposited from the liquors as the di-
 sodium salt, and was purified by recrystallisation from
 ethyl alcohol, the latter was isolated from the
 filtered liquors by acidification, and obtained in the
 form of the free acid, which was recrystallised from
 a mixture of pyridine and water. Both these substances
 are extremely hygroscopic and, if left open to the air,
 take up rapidly two molecules of water of crystallisa-
 tion. It is probable that the sulphonic acid group
 in XXXIXa is in the 5- position rather than in the 7-
 position, as one would expect a β sulphonic acid
 group to be more easily hydrolysed than an α group.

This reaction with caustic soda solution has been carried out with practically every safraninone mentioned in this paper. The following hydroxy safranols in particular have been prepared.



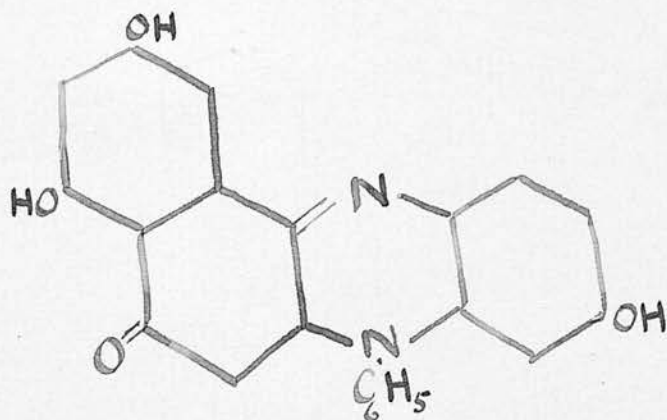
XLI.

XLII.



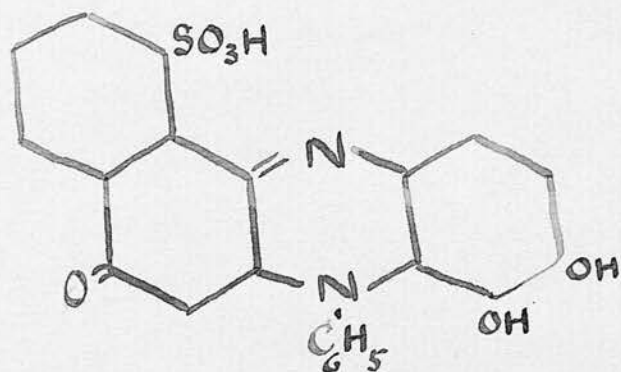
XLIII.

XLIV.



XLV.

In the case of XLIV the product isolated in the pure state proved to be a monosulphonic acid, probably XLVII.



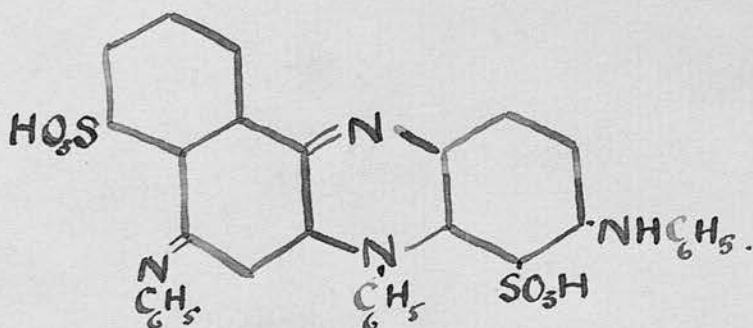
XLVII.

whilst the corresponding hydroxy safranols, having the same spectrum as above, was obtained in a somewhat impure state. In all the other cases the substances isolated were free from sulphur.

All of these substances are extremely hygroscopic, but give off their water of crystallisation at 120° - 130°C .

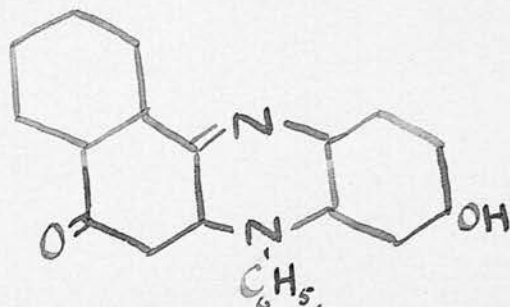
XXXIX, XL, XLIII, were studied in particular, and

a spectroscopic study made of all the products. The bands of the spectrum shown by XXXIX, XLII, XLIII and XLIV are all identical, whilst the bands of XL, XLI, and XLV are also identical with each other but entirely different to the other spectrum. With sulphuric acid the colour given by the former series is red, changing to yellow with slight precipitate on dilution with water. With the other series sulphuric acid gives a blue colour, changing to red on dilution. Owing to their extreme hygroscopic tendencies, it was difficult to obtain satisfactory analysis figures for these substances. At first it was surmised that, in the case of all sulphonic acid groups not in the 8- position, the action of the caustic soda was to reduce the $-SO_3H$ group to hydrogen, but that the sulphonic acid group in the 8- position behaved differently and gave rise to a hydroxyl group by simple hydrolysis. When however



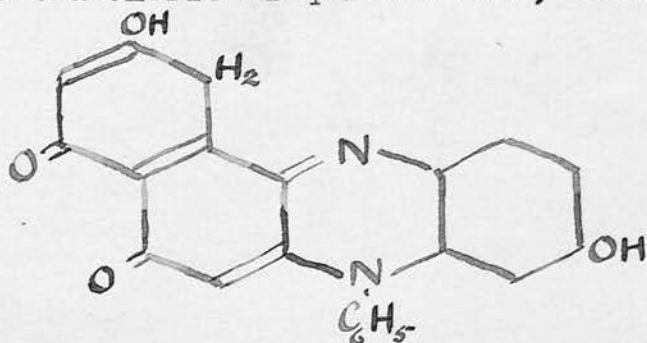
was treated with a mixture of hydrochloric acid and acetic acid at $200^{\circ}C$ in a bomb tube, the product isolated from the reaction mixture proved to have the same/

same spectrum as XXXIX above, and not as XL. The colour reactions with sulphuric acid were also similar to XXXIX, i.e. red to yellow, but giving no precipitate. It would appear that in this case the sulphonic acid groups have been replaced by hydrogen, and the resulting product is thus:-

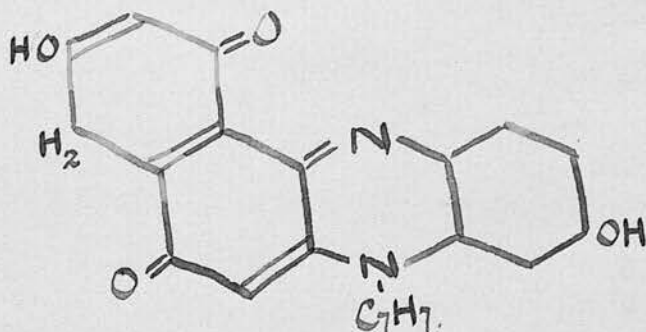


XLVI.

Now it would appear also that this product shows the bands in the spectrum as others of similar constitution having hydroxyl groups in any other position except in the 8- position, but that if a hydroxyl group appears in the 8- position, no matter whether hydroxyl groups appear in other positions in addition, the spectrum is entirely different. The only explanation that seems to fall into line with the observed facts is that substance XLV, for example, must assume its tautomeric di-quinoid form, thus:-



whereas any other similar substance, e.g. XLIII cannot assume this form. Those which can assume a di-quinoid form, e.g. XXXIX thus:-

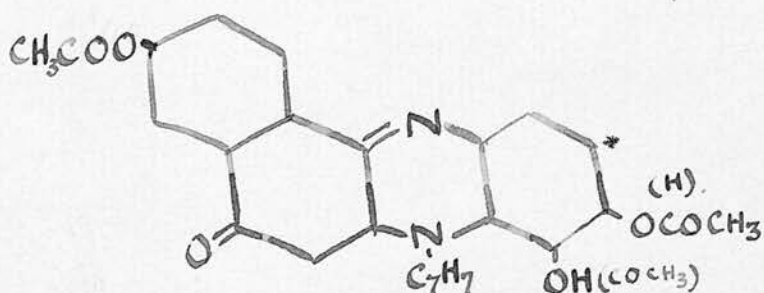


still do not show the same spectrum bands associated with the first di-quinoid form, where the quinone formation is in the 8-position, giving two quinone groups in the peri position to each other.

Again when naphthalene 2-5-7 tri-sulphonic acid was treated with 10% caustic soda solution under exactly similar conditions as the safraninones were treated, SO₂ was observed in quantity in the reaction mixture on acidification, and there was evidence of considerable quantities of hydroxyl bodies present, as was proved by the formation of azo dyes by condensation with diazo salts. It is therefore probable that the sulphonic acid groups in the safraninones have been replaced by hydroxyl groups, and that the explanation of the difference in behaviour with regard to the bands in the spectrum is as indicated above, i.e. is due to the possibility of a di-quinoid formation with the two quinone oxygens in the peri position to each other.

Again/

Again when the substance XLIII was acetylated, and the product hydrolysed, it was found that in the acyl derivative there were two acyl groups only, and that the constitution agreed with the formula.-



The substance 2-9-di-phenyl naphthophenosafranine 1-8 di-sulphonic acid was subjected to treatment with different reagents under varying conditions and the scission products were studied in each case. The reagents used were a mixture of hydrochloric and acetic acids at different temperatures, sulphuric acid, and caustic soda at different temperatures.

When 10% caustic soda acted on the above safranine at 220°C for 12 hours aniline was isolated from among the scission products. The same also applied to the action of hydrochloric and acetic acids, but when the safranine was boiled up with 76% sulphuric acid for 16 hours no aniline was found, but sulphanilic acid was isolated; when 65% sulphuric acid was substituted for/

for the stronger acid a trace of aniline was detected among the scission products.

Caustic soda, as has been stated, caused also the hydrolysis of the sulphonic acid groups, giving rise to hydroxyl groups.

Hydrochloric and acetic acids, on the other hand, reduced the sulphonic acid groups to hydrogen. There was evidence that sulphuric acid gave rise to a safranolic sulphonic acid, as the percentage of sulphur in this case was much higher, though the spectrum of the substance was substantially the same as that from the caustic soda scission. Pure substances, however, could not be obtained in this case. Reduction of the temperature from 220°C to $195^{\circ} - 200^{\circ}\text{C}$ in the caustic soda scission gave a product which differed from the previous caustic soda scission product in that it contained sulphur in large amount.

Found S - 9.62%. N - 6.56%.

N/S - 3/2.

The substance seemed to be somewhat impure and could not be recrystallised from any solvent. The high percentage of sulphur and low percentage of nitrogen tends to show that the first action of the caustic soda is to attack the side chains prior to attacking the sulphonic acid groups. This view is supported by the products isolated when the scission was carried out at 200°C , as above enumerated, one of/

of the products still retaining one sulphonic acid group.

Turning to the scission with the mixture of hydrochloric and acetic acids, it was found that the reverse seemed to be the case. As has been stated, when the temperature of the reaction was 200°C for 12 hours, naphthophenosafranone XLVI was isolated. When however the temperature was reduced to 150°C a substance giving with sulphuric acid the green colour of a safranin (changing to blue on dilution) was obtained. On extracting this substance with water, which removed a red impurity, a substance insoluble in alkalies remained which gave the following analysis -

N - 9.41% and 9.50%. S - 5.90%.

N/S - 3.6/1.

The substance was impure and could not be recrystallised further.

However it would appear from the high percentage of nitrogen and low percentage of Sulphur that the action of the acid is first to eliminate the sulphonic acid groups prior to attacking the side chains.

At 175°C a product was isolated which gave

N - 10.42%. S - 4.25%

which tends to further this theory and would show that somewhere in the region of 180°C we might find a critical temperature at which the sulphonic acid groups would be completely eliminated. Time however did not permit/

permit of a more complete investigation, and owing to the seeming impossibility of purifying these substances, the question was not further investigated.

EXPERIMENTAL.

Preparation of 5-7 di-hydroxy N-tolyl naphthopheno-
safranols and 7- mono-hydroxy N-tolyl naphthopheno-
safranols 5 sulphonic acid. (XXXIX and XXXIXa).

When 20 grams of 2- di-methyl N- tolyl naphtho-phenosafraninone 5-7 di-sulphonic acid were heated at 220°C with 200 grams of caustic soda solution (10%) in an autoclave for 12 hours, di-methylamine was given off, trapped in oxalic ester and identified; SO_2 was also given off, and the liquors deposited 4.9 grams of beautiful lustrous green plates. This substance proved to be the di-sodium salt of XXXIXa, and contained two molecules of water of crystallisation, being extremely hygroscopic.

Found Na - 9.25%.

Required for $\text{C}_{23}\text{H}_{14}\text{N}_2\text{O}_6\text{S Na}_2, 2\text{H}_2\text{O}$, Na - 8.71%.

When the sodium salt is taken up in water and hydrochloric acid added the free acid is obtained as a bright red powder, insoluble in water or acids. It contains two molecules of water of crystallisation which/

which are only driven off at 140°C .

Found for the hydrated substance

C - 56.79%. H - 4.08%. N - 5.92%.

Required for $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_6\text{S}, 2\text{H}_2\text{O}$, is

C - 57.03%. H - 4.13%. N - 5.78%.

On adding hydrochloric acid to the original mother liquors of the reaction SO_2 was given off and 8.75 grams of a bright red powder were obtained, which was re-crystallised from a mixture of pyridine and water. This substance was soluble in alkalies and in methylated spirits but insoluble in water or acids. It did not contain sulphur, and was very hygroscopic, retaining two molecules of water of crystallisation.

Found C - 65.92%. H - 3.87%. N - 6.39%.

Required for $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_4, 2\text{H}_2\text{O}$,

C - 65.71%. H - 3.81%. N - 6.66%.

The bands shown in the spectrum by these two substances were practically identical. Each was soluble in spirit to a red solution showing a yellow fluorescence. With sulphuric acid the colour was red violet, changing to yellow on dilution, with slight precipitation.

Preparation of 1-8 di-hydroxy Naphthophenosafranols.(XL).

When 10 grams of 2-phenyl naphthophenosafraninone 1-8 di-sulphonic acid were subjected to treatment with 100 grams of 10% NaOH solution at 200°C for 12 hours, aniline was given off, and after filtering off the red solution, 3.45 grams of a copper coloured precipitate were obtained on acidification. With sulphuric acid this substance gave a blue colour, changing to red on dilution. It was possible to recrystallise this substance from aniline, but the yield was poor.

Found N - 7.71% and 7.80%.

Required for $C_{22}H_{14}N_2O_4$ is N - 7.57%.

Preparation of 8-hydroxy Naphthophenosafranols. (XLI)

When 10 grams of 2-di-methyl naphthophenosafraninone 8-sulphonic acid (obtained by splitting off sulphanilic acid from the corresponding sulphonated naphthophenosafraninone by means of ammonia) were treated with 100 grams of 10% caustic soda at 200°C for 15 hours, the red liquors resulting from the reaction gave off di-methylamine, and, on acidification, SO_2 , whilst a fine crystalline product was obtained from the slightly acid solution.

The/

The spectrum of this product agreed with that of 1-8 di-hydroxy naphthophenosafrol, and with sulphuric acid the colour given was blue to red on dilution. From the liquors, however, was obtained a small quantity of a substance which showed bands in the spectrum similar to those of bodies having no hydroxyl group in the 8- position. This shows that the first and much the main reaction of caustic soda is to hydrolyse the sulphonic acid groups to hydroxyl groups, but that a further reaction occurs to a small degree and the hydroxyl groups are reduced to hydrogen.

Preparation of 1-7 di-hydroxy N-tolyl naphthophenosafrol. (XLIII).

10 grams of the corresponding naphthophenosafrol were heated in an autoclave with 100 grams of 10% caustic soda at 200° for 12 hours. Aniline was isolated from among the scission products, and 6.7 grams of a brown powder obtained from the liquors on acidification. This substance was soluble in spirit to a yellow colour and showed no fluorescence; on adding a drop of caustic potash solution the colour changed to pink and the solution now exhibited a yellow fluorescence, with excess hydrochloric acid the solution turned yellow and the fluorescence disappeared. This behaviour is general with hydroxy naphthophenosafrols of/

of this type. Those having a hydroxyl group in the 8- position show no fluorescence at all and dissolve in spirit to a red solution, which turns violet in alkalies. This substance (the 1-7 di-hydroxy compound) crystallised from a mixture of pyridine and water in fine crystals.

Found N - 7.53%.

Required for $C_{23}H_{16}N_2O_4$ is N - 7.3%.

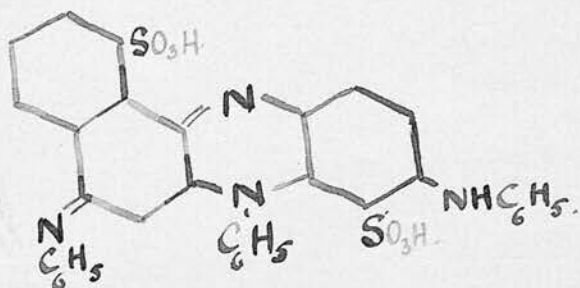
This substance was also acetylated with acetic anhydride, and the acyl groups were then split off and the acetic acid estimated. Two acyl groups were accounted for, and it would appear that this substance formed only a di-acyl derivative.

Preparation of 1- hydroxy naphthophenosafranol
5-sulphonic acid (XLIV).

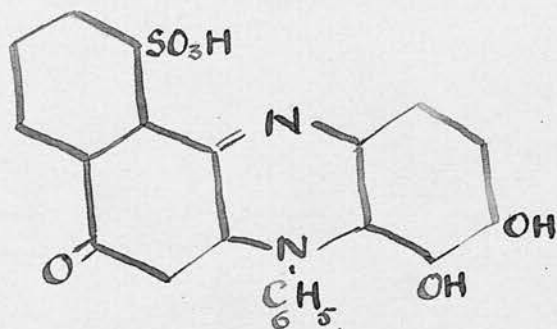
6.0 grams of phenyl β naphthylamine 8- sulphonic acid, 5.8 grams of p-amino di-phenylamine o-sulphonic acid, 80 cc. water, 33 cc. glacial acetic acid were mixed and maintained at $80^{\circ} - 90^{\circ}C$. A solution of 6 grams of sodium bichromate in 12 cc. water was run in, and the mixture boiled for $2\frac{1}{2}$ hours. The product was filtered off on cooling, and taken up in 150 cc. water, 20 cc. aniline, 3 cc. $NaHSO_3$ solution, 2 cc. nitrobenzene, and the mixture again boiled for $2\frac{1}{2}$ hours. After steam distilling the liquors were salted/

salted out and yielded 13 grams of XXIII.

This substance was then heated in an autoclave with ten times its weight of 10% caustic soda solution for 12 hours at 200°C. Aniline was split off, and from the liquors on acidification 7.5 grams of XLVII were obtained.



XXIII.



XLVII.

This substance (XLVII) contained two molecules of water of crystallisation, and was recrystallised with great difficulty from a mixture of pyridine and water.

Found N - 6.04%. S - 6.75%.

Required for $C_{22}H_{14}N_2O_6S, 2H_2O$. is N - 5.96%.

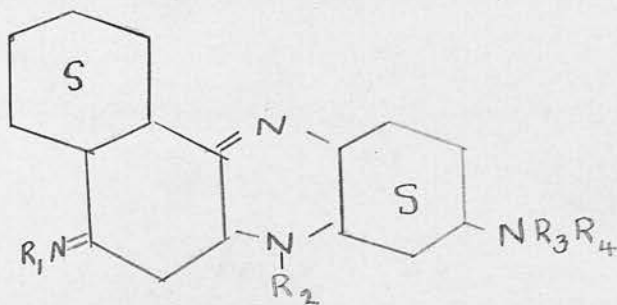
S - 6.81%.

With sulphuric acid this substance gave a red violet colour, changing to yellow, with precipitation, on dilution. The spectrum of this body in ethyl alcohol was practically identical with those of the group having no hydroxyl group in the 8- position.

From the liquors there was obtained a small amount of a substance containing no sulphur, and having similar bands in the spectrum to the group just mentioned.

(XLIV).

From the foregoing we have thus a method of determining the constitution of any sulphonated naphtho-phenosafranine of the type



Firstly, by subjecting the substance to treatment with NH_3 at 140°C , we determine R_1 by the product NH_2R_1 formed. Secondly the product formed is subjected to treatment with dilute caustic soda solution at 200°C , when R_3 and R_4 are determined by the product $\text{NHR}_3\text{R}_4/$

NHR_3R_4 formed. The evolution of SO_2 indicates the presence of SO_3H groups in the nucleus, and a study of the spectrum determines the position of the SO_3H groups in the nucleus. If no SO_2 is evolved on treatment with caustic soda solution and subsequent acidification, the SO_3H groups are in the side chains and should be detected in the radicles R_1 , R_3 or R_4 .

CONCLUSIONS.

1. Naphthophenosafranine sulphonic acids can be synthesised by the action of sodium bisulphite and a primary or secondary amine, which may also contain a Sulphonic acid group, on isorosinduline sulphonic acids, using nitrobenzene as an oxidising agent. This reaction seems to admit of only one exception, viz. when a Sulphonic acid group occupies the peri position to the active hydrogen of the isorosinduline. The reaction is explained by the formation of an intermediate sulphonic acid compound by the replacement of the active Hydrogen by SO_3H , through oxidation, which group then/

then reacts with the alkyl or aryl amine to give the required Naphthophenosafranine.

2. This same reaction, using ammonia as the amine, gives rise to Naphthophenosafranines at temperature of 140°C . At higher temperatures the reaction proceeds further, the imino group is replaced by oxygen, and the resulting product is a Naphthophenosafraninone sulphonic acid. The same exception to this reaction is again noted. When Naphthophenosafranine sulphonic acids are treated with ammonia at high temperatures Naphthophenosafraninones are produced, the alkyl or aryl amino group being replaced by the imino group, which then is replaced by oxygen.
3. The Naphthophenosafranines show no fluorescence when dissolved in ethyl alcohol, whereas the Naphthophenosafraninones do show fluorescence when the substituent alkyl or aryl amino group is sufficiently basic, but when this basicity is decreased, e.g. by introducing the group $-\text{NH C}_6\text{H}_5$, or NH COOCH_3 in that position, then the fluorescence vanishes.
4. The action of ammonia on Naphthophenosafranine sulphonic acids gives rise to Naphthophenosafraninone sulphonic acids, all the sulphonic acid groups/

groups remaining intact, and only one alkyl or aryl amino group being replaced by oxygen. This was so in the case of a completely symmetrical substance, and this fact tends to prove the para quinonoid structure of the Naphthophenosafranines. The action of a 10% Caustic soda solution on the Naphthophenosafranine sulphonic acids at 200°C on the other hand eliminated both alkyl or aryl amino groups giving rise to Naphthophenosafranols; the sulphonic acid groups are for the most part replaced by hydroxyl groups, though in two cases one sulphonic acid group remained unattacked.

A series of experiments tends to show that caustic soda at lower temperatures first attacks the side chains, at higher temperatures subsequently attacking the sulphonic acid groups; whereas a further series of experiments tends to show that the reverse is the case when scission is brought about by a mixture of hydrochloric acid and acetic acid, - at lower temperatures the $-SO_3H$ groups are first eliminated, at higher temperatures the side chains are also attacked.

5. A curious phenomenon relating to the bands shown in the spectrum by these hydroxy Naphthophenosafranols is noted. There are two series of compounds, the same bands being shown by each of its/

its own series. This is explained by the supposition that these compounds capable of assuming the tautomeric diquinoid form all show the same bands, irrespective of the position of the other hydroxy groups, while those incapable of this transformation all show another series of bands, and that the difference in spectrum is in some way related to this diquinoid tautomeric formation.

At the same time Naphthophenosafraninone Sulphonic acids show different spectrums, the difference being due not only to the different alkyl or aryl amino side chains but also to the difference in position of the sulphonic acid groups.

6. Dyestuffs of the Naphthophenosafraninone sulphonic acid type were examined as microscopic stains and were found to be of use as protoplasmic stains for tissues.

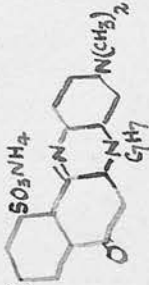
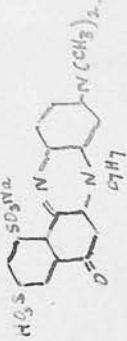
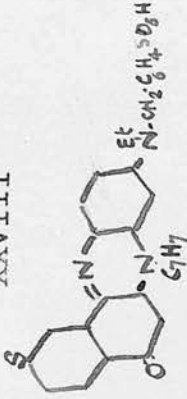
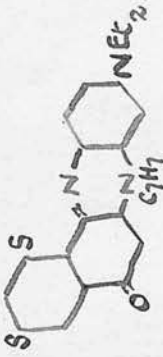
NOTE. Since this work has been completed a preliminary specification for a German Patent has appeared in the Autumn of 1924. A. 38930 and 39033, claiming the use of sodium sulphite and air oxidation with amino bodies in the formation of naphthophenosafranines. The work described in/

in Part I of this paper was completed by July 1922,
and the work described in Part II and Part III was
commenced in December 1923, and completed about
August 1924.

Fawley.
Haults.

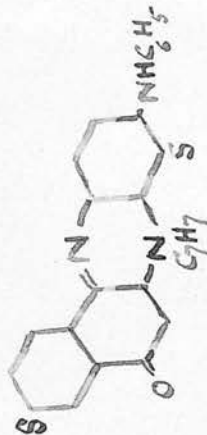
April 18th 1925 -----

TABLE SHOWING SPECTRUM ANALYSIS OF THE SUBSTANCES DESCRIBED ABOVE.

Number	XXV.	Na salt of XXV.	XXVIII	XXIX.
Formula				
in EtOH	542 507	542 507	554-555	549
colour	pink, yellow fluorescence.	pink, y.f.	pink, orange fluor.	pink, orange fluor.
KOH	544 509	544 509	554 516	543 508.5
colour	pink, yellow fluorescence.	pink, y.f.	pink, orange fluor.	pink, yellow fluor.
HCl	545 diffuse.	545 diffuse.	558 diffuse.	546 diffuse.
colour.	pink, no fluorescence.	pink, no f.	pink, no fluor.	pink, no fluor.



XXXVIII.



558, diffuse

red, no
fluor.

554

518

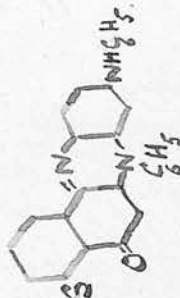
red, no fluor.

558, diffuse.

red violet

no fluor.

XXXVI.



562

522

violet pink

no fluor.

560

522

violet pink

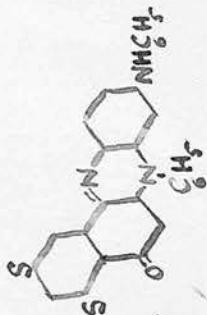
no fluor.

567-9

violet, no

fluor.

XXXIV.



566-570

528

pink, no

fluor.

566-570

528

pink, no

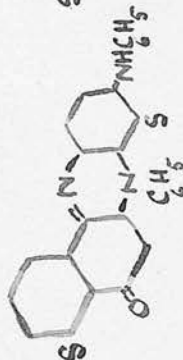
fluor.

573

violet, no

fluor.

XXXI.



550

513

pink, no

fluor.

552

514

redder, no

fluor.

556, diffuse

deep violet

Number

Formula

in EtOH

colour

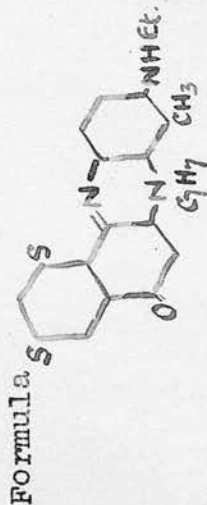
KOH

colour

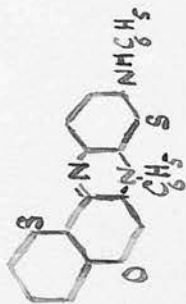
HCl

colour

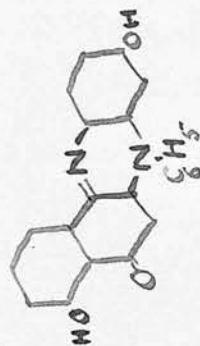
Number XXXVIII.



XXXV.



XLI.

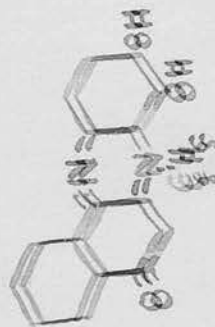


in EtOH	537 502	539 505	546 507	555 515	566-7
colour	pink, yellow fluor.	pink, no fluor.	red, slight fluor.	red, no fluor.	violet, no fluor.
KOH	ditto	537 505	558 516	555 515	555 515
colour	ditto	pink, no fluor.	red, orange fluor.	red, faint yellow, no fluor.	red, faint yellow, no fluor.
HCl	ditto	540 diffuse	546 (faint)		
colour	ditto practically no fluor.	violet.	dull reddish yellow, no fluor.		

Number

Formula:

XLVII:



in EtOH ≤ 495 (v: faint)

colour

yellow

KOH

$\frac{544}{505}$

colour

pink, yellow
fluor.

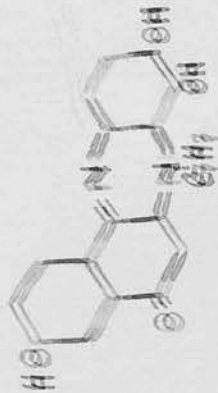
HCl

≤ 490

colour:

yellow, no
fluor.

XLVIII:



≤ 490

yellow, no
fluor.

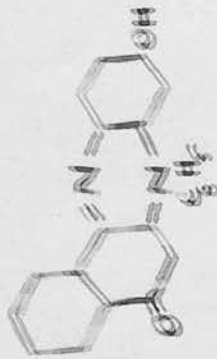
$\frac{547}{509}$

pink, yellow
fluor.

≤ 490

yellow, no
fluor.

XLVI:



≤ 490

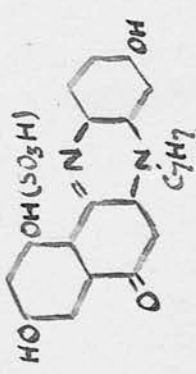
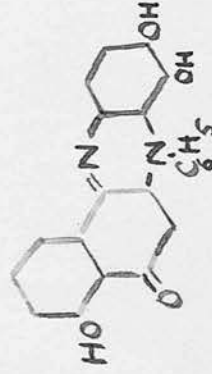
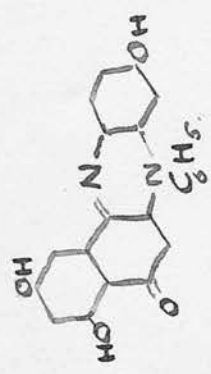
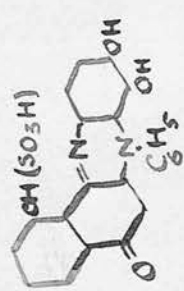
yellow,

$\frac{544=7}{504=8}$ (faint)

pink, yellow
fluor.

≤ 490

yellow, no
fluor.

Number	XXXIXa & XXXIX.	XL.	XLV.	XLVII & XLIV.	similar in all respects to XL and XLI.
Formula					
in EtOH	< 490	555 515	< 490	< 490	
colour	yellow	red, no fluor.	yellow, no fluor.	yellow, no fluor.	
KOH	$\frac{544}{505}$	566-7	$\frac{547}{509}$		
colour.	pink, yellow fluor.	violet, no fluor.	pink, yellow fluor.		
HCl	< 490	555 515	< 490		
colour.	yellow, no fluor.	red, faint yellow, no fluor.	yellow, no fluor.		
