XL.—*The Eurhodines, a New Class of Colouring Matters.*

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ONE of the methods which lead to the synthesis of dyestuffs consists in the jointoxidation or rather dehydrogenisation of mixtures of various amines, or of amines with phenols; several classes of new colouring matters may thus be obtained according to the amines employed. Thus, the oxidation of a paradiamine with one molecule of a monamine leads to the formation of a member of the indamine-group, whilst one molecule of paradiamine with two molecules of a mon-

amine yield a safranine, if subjected to the action of powerful oxidisers. Again, a mixture of a paradiamine and a metadiamine in molecular proportions yields on oxidation a compound belonging to the toluylene-blue-group, and if still more hydrogen be removed, a condensation into a derivative of the toluylene-red group is the result. Mixtures of paradiamines and phenols, if oxidised in alkaline or neutral solution, give rise to dyestuffs of the indophenol class, whilst more powerful oxidation in acid solutions results in the formation of substances similar to those discovered and described by R. Meldola. All the classes of dyestuffs enumerated have been studied more or less completely in some of their most important representatives, and we even know the exact chemical constitution of some of them.

Now, in all these reactions, one of the ingredients is always a paradiamine. No attempt has been made to replace this by other substances capable of similar reactions. The reason for this is probably the fact that most of these reactions have not been discovered in the form here given to them. As a rule, certain colour-reactions were obtained with amido-azo- or nitroso-compounds, and it was only recognised on subsequent examination, that the diamine formed by the reduction of these azo- or nitroso-derivatives must be considered as the first cause of the colour-reaction itself. Now as all amido-azo-compounds and nitrosamines known up to a few years ago belonged to the para-series of benzene-derivatives, the constant recurrence of paradiamines in these reactions was very natural.

In 1882, however, the first orthamido-azo-compound was discovered by Nölting and Witt (*Ber.*, 17, 77), who obtained it by heating pure diazoparamidotoluene with paratoluidine hydrochloride in paratoluidine solution on the water-bath. This substance crystallises in needles (from acetone) or leaflets (from benzene) of a brilliant orange colour, and melts at 118.5°; on reduction, it splits up into paratoluidine and orthotoluylenediamine of the m. p. 88.5°, the constitution of which is known to be—

The new amido-azo-compound is therefore, of necessity,

If this substance is treated with hydrochloric acid in alcoholic solution, it yields a hydrochloride which, unlike the salts of paramido-azo-

derivatives dissolves with a green coloration. In the solid state, it forms needles of pale straw colour. If this salt is acted on by primary monamines, such for instance as aniline, it produces, like the salt of a paramido-azo-compound, a dye of the induline-group; now it has been shown by Thomas and Witt (Trans., 1883, 112), that in the induline reaction the amido-azo-compound employed plays no other part than that of dehydrogenising the primary monamine acted upon, and if new proof were needed for the correctness of that view, it would be found in the very fact that an orthamido-azo-compound, acting on aniline, produces the same final result as that obtained with paramido-azo-compounds. But on the other hand, this experiment shows that no reply can be obtained in so simple a manner to the question whether the orthodiamine (formed by the reduction of the orthamido-azo-compound) is capable of forming dyes like its para-isomeride. An unexpected answer to that question was, however, afforded when α -naphthylamine was substituted for aniline in the above experiment; a new dyestuff was obtained, which was so perfectly unlike any colouring matter hitherto observed, that it could at once be recognised as belonging to a new class of compounds, the parent-substance of which could only be the orthotoluylenediamine. This hypothesis was confirmed when other orthamido-azo-compounds were treated with α -naphthylamine hydrochloride. In all cases colouring matters were formed closely resembling the one first obtained. It then became interesting to know how chrysoidine would behave under similar circumstances. This well-known dyestuff is, as may be seen from its constitutional formula—

both a para- and an ortho-amido-azo-compound. If its hydrochloride is heated with α -naphthylamine at 130° , a dyestuff belonging to the new class, and showing all its peculiarities, is obtained; it can, therefore, no longer be doubted that the ortho-position of the amido- and the azo-group is the sole cause of the new reaction, which was carefully investigated. The results obtained I have now the pleasure of laying before the Society.

Action of α -Naphthylamine on Orthamido-azotoluene.

If 22.5 grams (1 mol.) of orthamido-azotoluene (m. p. 118.5°) is mixed with 17.9 grams (1 mol.) of α -naphthylamine hydrochloride, and 50 grams of phenol added, a thick solution of dark emerald-green colour is obtained. The phenol acts merely as a convenient

solvent, and may be replaced by α -naphthylamine, which is, however, not so easily got rid of afterwards. The green coloration is the result of the formation of the hydrochloride of the azo-compound, the salt of the α -naphthylamine yielding up part of its acid to the azo-compound. If this mixture be placed on the water-bath, the green coloration will gradually disappear and be replaced by an intense and brilliant scarlet colour. The reaction is then finished and the new dyestuff may be isolated from the mixture. Two different methods may serve equally well this purpose. The first consists in adding to the warm mixture a sufficient quantity of toluene to precipitate all that is insoluble in that solvent. A bright scarlet precipitate, consisting of the hydrochloride of the new dyestuff, is the result. This is collected on a filter, washed with ether, and then introduced into boiling water, acidulated with hydrochloric acid, and dissolved by prolonged boiling. The filtered liquid on cooling deposits long interlaced needles of the pure hydrochloride, which may be collected, washed with very dilute hydrochloric acid, and dried.

Another method of working up the crude melt consists in adding sufficient caustic soda solution to dissolve all the phenol and collecting the yellow precipitate which separates. By treating it with dilute hydrochloric acid, it is transformed into hydrochloride, which may then be treated as before.

If the pure hydrochloride obtained by either of these methods is decomposed by boiling weak ammonia solution, the free base separates as an amorphous precipitate of brilliant yellow colour, which becomes distinctly crystalline on prolonged boiling. It is collected, dried, and recrystallised either from aniline or from phenol, with addition of alcohol. By this means, it is obtained in dark orange glistening needles, which on analysis were found to have the composition $C_{17}H_{13}N_2$.

	Calculated for $C_{17}H_{13}N_3$.	Found.		
		I.	II.	III.
C.....	78.8	78.53	78.7	—
H.....	5.0	—	6.4	—
N.....	16.2	—	—	15.8

To this substance I have given the name of eurhodine, from $\epsilon\upsilon$ and $\rho\acute{\omega}\delta\acute{o}s$, to recall the red colour of its salts and the eminent crystallising power of the free base.

In order to establish with greater certainty the molecular weight of eurhodine, its hydrochloride was subjected to analysis. This salt was prepared in a state of absolute purity, and in the shape of long, soft, brilliant garnet-coloured needles, by adding dilute hydrochloric acid to a solution of the pure base in acetic acid, filtering, washing with

dilute hydrochloric acid, and drying in a vacuum over quicklime and sulphuric acid. It contains 1 mol. H_2O , which cannot be driven out by heating without partial decomposition of the salt. The elementary constituents of this salt were determined as well as the quantity of free eurhodine base it contains.*

Calculated for $\text{C}_{17}\text{H}_{13}\text{N}_3\cdot\text{HCl} + \text{H}_2\text{O}$.		Found.			
		I.	II.	III.	IV.
C	65·07	65·71	—	—	—
H	5·10	5·15	—	—	—
N	13·40	—	14·02	—	—
Cl	11·33	—	—	11·20	—
$\text{C}_{17}\text{H}_{13}\text{N}_3$	82·60	—	—	—	82·77

The sulphate, oxalate, and tartrate of eurhodine closely resemble the hydrochloride. The nitrate is absolutely insoluble even in boiling water. The acetate could not be obtained in a dry state, but its existence is proved by the fact that eurhodine dissolves with the scarlet colour of its salts in acetic acid.

Eurhodine and its salts show several most striking reactions. In concentrated sulphuric acid they dissolve with intense red colour. This solution on being carefully diluted with water becomes of an intense green. Further addition of water produces a change to scarlet, and the crystalline normal sulphate separates from the solution. Crystallised eurhodine is almost insoluble both in alcohol and in ether; but if it is precipitated in its amorphous condition by adding ammonia to one of its salts in the cold, and then shaken with ether, it is freely taken up by this solvent. The solution is of a bright yellow colour, and shows an intense green fluorescence, quite as strong as that of fluorescein but of a more yellow shade. This solution shows a spectrum similar to that of sodium fluorescein. Free eurhodine, as well as all its derivatives, show a remarkable indifference to high temperatures. Unlike all other dyestuffs—which are decomposed by dry distillation—eurhodine is volatilised without decomposition. Its vapour on cooling condenses to a voluminous cloud of microscopic crystals. This sublimate strongly resembles the one obtained from certain anthraquinone-derivatives. A few milligrams of eurhodine may be made to fill a large space in this sublimed condition.

All the salts of eurhodine are partly decomposed by pure water. In the presence of an excess of acid, however, they are quite stable.

Eurhodine is a true dye. On silk it dyes a scarlet shade in an acid

* In my preliminary notice (*Ber.*, 19, 443) the calculated data were erroneously given as found, and *vice versa*. This error was subsequently corrected (*Ber.*, 19, 592).

bath. Its tartrate mixed with tannin and acetic acid, suitably thickened, and printed on cotton mordanted with Turkey-red oil, steamed and washed, produces a red similar to Turkey-red. But the shades produced both on silk and cotton are changed to yellow on prolonged washing in ordinary calcareous water. The original red may be restored by acids.

The formation of eurhodine may be easily accounted for by assuming that equal molecules of orthotolylenediamine and α -naphthylamine are condensed by the elimination of 6 atoms of hydrogen, the latter being taken up—as is always the case in such reactions—by the reduction of the azo-group—

If this hypothesis be correct, the other half of the amidoazo-compound, paratoluidine, must be found free in the crude melt. This is actually the case; paratoluidine was shown to be present in abundance in the mother-liquors from the preparation of the new dye.

Eurhodine is a substance of such marked properties, and its formation is so simple and sure, that it may be utilised as a test, indicating the relative position of any new amidoazo-compound. It is only necessary to heat a trace of the latter with a few crystals of α -naphthylamine hydrochloride and a drop of liquefied phenol, to add an excess of caustic soda and to shake up with ether. If a yellow solution with bright-green fluorescence be obtained, one may be certain that the amidoazo-compound employed belongs to the ortho-series.

Having established the mode of formation as well as the properties of eurhodine, I made some experiments with a view to determining the constitution of the new dye.

Action of Acetic Anhydride.

If acetic anhydride be poured on to eurhodine crystals contained in a dry flask, solution takes place. But very soon crystals begin to separate, and the whole mixture solidifies to a crystalline cake. The acetyl-derivative thus formed may be collected on a filter and washed with alcohol. It forms fine felted needles of straw-yellow colour, which are split up into acetic acid and the free base by the action of strong mineral acids.

The formation of an acetyl-derivative makes it probable that eurhodine contains a primary amido-group, and this probability became a certainty by the examination of the

Action of Acids on Eurhodine.

If eurhodine or one of its salts is heated with dilute hydrochloric or sulphuric acid in a sealed tube, it undergoes a complete and very remarkable decomposition; 3—4 hours at 180° suffice to make every trace of eurhodine disappear. In its stead, yellow crystals separate from the colourless supernatant liquid. On evaporating the latter to dryness, no organic substance could be detected. The entire residue consisted of ammonium chloride or sulphate. The ammonia could only have been formed by an amido-group being eliminated from eurhodine by the action of the acid.

The crystals formed in the tube consisted of a new substance, which possesses both basic and acid properties. It is consequently the phenol corresponding with the primary amine eurhodine. If this be the case, its composition must be $C_{17}H_{12}N_2O$. Analysis proved this supposition to be correct.

	Calculated for $C_{17}H_{12}N_2O$.	Found.		
		I.	II.	III.
C	78.5	78.6	78.2	—
H	4.6	5.1	4.9	—
N	10.7	—	—	10.5
O	6.2	—	—	—

To this phenol of the eurhodine-group, I have given the name of *eurhodol*.

Eurhodol is very insoluble in all solvents with the exception of aniline and phenol. In the amorphous state it dissolves pretty freely in ether; this solution is of a yellow colour, but it is not fluorescent. If slowly crystallised from aniline or phenol, the crystals are of an indistinct orange colour. If, however, the phenolic solution be cooled rapidly, the crystals will be of a bright yellow shade, whilst the aniline solution, by rapid cooling, yields crystals of a vermilion colour. This phenomenon is due to dichroism of the crystals. They possess both red and yellow planes, which are differently developed according to the solvent used.

Eurhodol may be volatilised almost without decomposition. It forms a yellow sublimate similar to that of eurhodine.

In concentrated sulphuric acid, eurhodol dissolves with a dark red colour; water precipitates the sulphate from this solution in yellow flakes.

Concentrated caustic soda solution dissolves eurhodol with an orange colour, and on cooling, a crystallised sodium salt separates. From the dilute soda solution, free eurhodol may be precipitated by the addition of acetic acid.

It thus became evident that eurhodine is the amine, eurhodol the phenol, of a substance $C_{17}H_{12}N_2$, which I tried to discover by studying the

Action of Nitrites on Eurhodine.

If sodic nitrite be added to an acid solution of eurhodine, reaction takes place, and a diazo-compound is formed, as may be seen from the action of the liquid on sodium β -naphthol. It is impossible, however, owing to the great insolubility of all eurhodine-derivatives, either to finish the reaction or to isolate a diazo-compound from the mixture.

Better results were obtained by the action of alkylic nitrites on alcoholic solutions of eurhodine salts. If the acetate is dissolved in alcohol, ethyl nitrite added, and the mixture boiled for two hours on the water-bath, red crystals separate. This substance, which in all probability is the amidoazo-compound of the hypothetical $C_{17}H_{12}N_2$, has not yet been fully examined. It is feebly basic, and dissolves with dark colour in sulphuric acid; on dilution with water, the colour changes to red, and a sulphate separates in crimson flakes.

In presence of a mineral acid, the reaction takes place somewhat differently. Small quantities of the red substance are formed, but the greater part of the eurhodine is acted on with elimination of nitrogen; the liquid soon becoming yellow. The alcohol is then distilled off, and the residue treated with dilute (15 per cent.) hydrochloric acid, which takes up a new base. On adding an alkali, the base is precipitated, and may be collected and recrystallised from a mixture of glacial acetic acid and alcohol. It is thus obtained in long, glistening needles of bright lemon-yellow colour. On analysis these needles proved, however, not to be the expected base $C_{17}H_{12}N_2$. The data obtained showed that it contained oxygen, and that its composition was $C_{19}H_{16}N_2O$.

		Found.	
		I.	II.
Calculated for $C_{19}H_{16}N_2O$.			
C	79.16	78.96	—
H	5.56	5.92	—
N	9.72	—	10.23
O	5.56	—	—

This new substance melts at 175° . It is volatilised almost without decomposition at a high temperature. It is easily soluble, with yellow

colour and a faint green fluorescence, in benzene, ether, and acetic acid, less so in alcohol.

Alcoholic potash, even at 150° , is without any action on the new compound. It is easily soluble in concentrated sulphuric acid, with red colour. It is dissolved by concentrated hydrochloric acid with an orange coloration, and after a while, brown, bronzy crystals of the hydrochloride separate from the solution. If this solution is heated at 180° in sealed tubes, the compound is transformed into an acid substance resembling eurhodol.

It became evident by these reactions, as well as from the analytical results, that the action of ethyl nitrite had not resulted in the substitution of hydrogen for NH_2 , but that, as is sometimes the case, the ethylic ether of the corresponding phenol had been formed, and that the rational formula of the new substance must be written

Although thus far my experiments with a view to isolate $\text{C}_{17}\text{H}_{12}\text{N}_2$, the parent-substance of the whole eurhodine-group, had been failures, there was still something to be learned from them respecting the nature of the compound $\text{C}_{17}\text{H}_{12}\text{N}_2$. It will be remembered that phenolic ethers invariably show a strong resemblance to the corresponding hydrocarbons. Thus anisoil is a compound strongly resembling benzene. In all probability, therefore, the properties of $\text{C}_{17}\text{H}_{12}\text{N}_2$ would be very similar to those of the substance $\text{C}_{17}\text{H}_{11}\text{N}_2\text{O}\cdot\text{C}_2\text{H}_5$.

Now, in going over what is known about such substances, we find that a compound, $\text{C}_{17}\text{H}_{12}\text{N}_2$, has already been prepared by Hinsberg (*Ber.*, **18**, 1228), who obtained it by acting on orthotolylenediamine with β -naphthaquinone, and to which he ascribes the constitutional formula—

which I prefer to write, for reasons set forth hereafter—

This compound, naphthylene-toluquinoxaline, belongs to the class known as quinoxalines, the first and typical representative of which is phenylenequinoxaline—

also prepared by Hinsberg (*Ber.*, **17**, 320) by the action of glyoxal on orthophenylenediamine.

I have prepared Hinsberg's naphthylene-toluquinoxaline, and compared its properties with those of my ether, obtained by the action of ethylic nitrite on eurhodine. The two substances are remarkably similar, and it became thus highly probable that eurhodine is amido-naphthylene-toluquinoxaline.

I was anxious, however, to prove by some other method that the introduction of the amido-group into the molecule of a quinoxaline was sufficient to form a dyestuff of the eurhodine character. I have, therefore, tried to obtain by synthetical means other amidoquinoxalines. My endeavours in that direction were successful.

Phenanthro-eurhodine.

Glyoxal, as may be seen by a glance at its constitutional formula—

is the prototype of a long series of compounds which may be described as orthodiketones, and which may be derived from glyoxal by its hydrogen atoms being displaced by other radicals. Thus, by substituting phenyl for hydrogen, we obtain benzil—

whilst the introduction of the diphenylene-group gives rise to the formation of diphenylene diketone, or phenanthraquinone—

Now all these substances, when exposed to the action of ortho-diamines, act on the latter like glyoxal, producing substituted quinoxalines. For my purpose, I had, therefore, to react with any or

either of these substances on an amidorthodiamine, or, in other words, on a triamine, two amido-groups of which are in the ortho-position relatively to each other. Such a substance is 1 : 2 : 4-triamido-benzene—

a substance which is formed by the reduction of dinitraniline or chrysoidine. I soon found that it was not necessary for my purposes to isolate this highly unstable substance. It is sufficient to act with any orthodiketone on the crude reduction product of chrysoidine in order to obtain the corresponding eurhodine.

If 2 grams of chrysoidine crystals are dissolved in 50 grams of glacial acetic acid, and an excess of zinc-dust added to this solution, reduction takes place instantaneously, and a colourless liquid is obtained. This is poured off from the zinc-dust (not filtered to avoid the contact of the air), and mixed with the solution of 1 gram of phenanthraquinone in 50 grams of glacial acetic acid. The mixture assumes instantaneously an intense red colour, and the new eurhodine is formed. By adding a large quantity of water, the new compound is precipitated in yellowish-brown flakes, which become bright yellow on prolonged boiling. The precipitate is then collected, and recrystallised from phenol and alcohol. In this way 1.5 grams of small brown crystals are obtained, which on being subjected to analysis proved to have the expected composition $C_{20}H_{13}N_3$.

	Calculated for $C_{20}H_{13}N_3$.	Found.	
		I.	II.
C	81.4	81.4	—
H	4.4	4.7	—
N	14.2	—	14.5

This substance, the constitution of which is undoubtedly—

is shown by all its reactions to belong to the eurhodine class of colouring matters.

Its solution in concentrated sulphuric acid is red, and on being

diluted with water becomes yellowish-green, and then again red. Its salts are highly insoluble, and of a carmine-red colour. On adding an alkali to their solution, the free base is precipitated in its amorphous state, and is taken up by ether with yellow colour and the characteristic green fluorescence of the eurhodines. The free base is very insoluble in all solvents, except aniline and phenol. It is volatilised at a high temperature almost without decomposition, and a woolly sublimate is formed in the cooler portions of the tube.

Similar eurhodines were obtained by acting on 1 : 2 : 4-triamidobenzene with any of the orthodiketones capable of forming quinoxalines. The experiment was tried with glyoxal, dioxytartaric (carboxytartronic) acid, benzil, β -naphthaquinone, and isatin. A red dye of the eurhodine character was invariably the result.

The reaction holds good even for polyketones. Thus leuconic acid, which was proved by R. Nietzki to be pentaketopentamethylene—

if treated with triamidobenzene, produces a violet colouring matter, which becomes brown on addition of alkalis.

With the results thus obtained, it could no longer be doubted that eurhodine is amidonaphthylenetoluquinoxaline, but there was still one point to elucidate.

Only one naphthylenetoluquinoxaline has hitherto been mentioned, and only one has been prepared by Hinsberg. But, according to our present theoretical views on the constitution of naphthalene, a second isomeride may be predicted. This becomes evident from the following consideration.

Two orthonaphthaquinones are capable of existence, one of which only has hitherto been prepared by Stenhouse and Groves (*Chem. Soc. J.*, 1877, ii, 47 ; 1878, 415).

β -Naphthaquinone of
Stenhouse and Groves.

Missing
isomeride.

Now the second of these, if accessible, would be equally capable of producing a naphthylenetoluquinoxaline if exposed to the action of

orthotolulylenediamine; thus two such bases of the respective formulæ—

may be anticipated, and there is no reason why eurhohine should not be the amido-derivative of the second of these instead of that of the first.

The following experiments which were undertaken with a hope to answer this question have not definitely settled it, but they have resulted in the discovery of the second isomeric quinoxaline and are therefore worthy of being communicated.

Simultaneous Oxidation of α - and β -Naphthol and Orthotolulylenediamine.

If molecular quantities of α -naphthol and orthotolulylenediamine are exposed in an alkaline aqueous solution to the action of potassic ferricyanide, a blue precipitate is obtained, which dissolves in alcohol with a magnificent blue coloration. This dyestuff is very unstable, undergoing spontaneous decomposition in a very short time. As it is, according to all its reactions, a member of the indophenol-group, a description of it is not within the objects of this communication.

Very different results are obtained, however, if β -naphthol be substituted for the α -derivative in this reaction. In this case a dark somewhat tarry precipitate is formed which is collected on a filter and carefully washed with water. It is then treated with dilute (15 per cent.) hydrochloric acid and boiled with it for some time; this treatment is repeated as long as the acid acquires a yellow tint. The dark insoluble substance remaining after this treatment is put aside, whilst the acid extracts are precipitated with caustic soda solution. The grey precipitate thus obtained is collected, washed, dried, and recrystallised from a mixture of glacial acetic acid and alcohol. By this means interlaced needles of a pale straw colour are obtained, which for analysis may be recrystallised from boiling toluene. The substance is thus obtained in the shape of long, well-defined, glistening needles of remarkably definite melting point,

namely, 179.8° , and on analysis gave results agreeing with the formula of a naphthylenetoluquinoxaline, $C_{17}H_{12}N_2$.

	Calculated for $C_{17}H_{12}N_2$.	Found.	
		I.	II.
C	83.61	83.50	—
H	4.91	5.34	—
N	11.48	—	11.15

This substance is distinctly different from Hinsberg's naphthylene-toluquinoxaline, which melts at $139-142^\circ$, and is far more soluble in all the ordinary solvents. Both substances dissolve with an intense red coloration in concentrated sulphuric acid, but the solution of the new substance is of a much more bluish shade. Heated in a dry test tube, the new quinoxaline is volatilised without the slightest decomposition. It dissolves in hydrochloric acid with a bright yellow coloration, and on adding water to this solution, it deposits the hydrochloride in yellow crystals. When treated with fuming sulphuric acid, it is transformed into a sulphonic derivative, whilst concentrated nitric acid gives rise to the formation of a well-defined nitro-derivative.

In the production of this base, other oxidising agents may be substituted for potassic ferricyanide. The substance is formed equally well with hydric peroxide, chloride of lime, or freshly prepared plumbic or manganic peroxide. Its formation may be explained by the equation—

As only two naphthylenetoluquinoxalines are possible, my new compound must have the constitution—

it is a derivative of the missing $\beta\beta$ -naphthaquinone, and as may casually be remarked, the first $\beta\beta$ -derivative of naphthalene ever prepared.

Before concluding I have to explain my reasons for adopting formulæ for the quinoxalines different from those given to them by Hinsberg.

Throughout the experiments connected with this research, I could not help being constantly reminded of two well-known substances, viz., anthraquinone and acridine. Between these two there exists a

definite relationship expressed by the rational formulæ now universally adopted for them.

This relationship becomes still more evident if the anthracene formula be added as a connecting link.

Now if my formula for the quinoxalines be adopted, the similarity of these to anthraquinone and acridine becomes a matter of course, whilst it remains a mystery if Hinsberg's formulæ be adhered to.

ββ-Naphthylenetoluinoxaline.

My formula.

Hinsberg's formula.

Moreover, with Hinsberg's formulæ great difficulties arise if an attempt be made to fill in the double connections of the benzene nuclei. And, notwithstanding all that has been said against them, we have the less reason to treat them lightly, since Fittig's elegant synthesis of *a*-naphthol from phenylparaconic acid has actually demonstrated their presence. Finally, I may plead in favour of my formulæ that all the other reactions of the quinoxalines, as well as their mode of formation from fatty diketones, may quite as well be accounted for by using my formulæ instead of those of Hinsberg.

I am engaged in the continuation of my researches on the eurhodine class of dyes, and I hope to be able to lay before the Society, in a subsequent communication, the results of experiments now in progress.

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