CLXXI.—*The Cyanine Dyes. Part III. The Constitution of Pinacyanol.*

By WILLIAM HOBSON MILLS and FRANCES MARY HAMER.

ONE of the most valuable of the photographic sensitisers in common use is a substance patented in 1905 by the Farbwerke vorm. Meister, Lucius & Brüning (Brit. Pat. 16227 of 1905; D.R.-P. 172118), and sold under the name of pinacyanol.

The action of alkali on a hot alcoholic solution of a mixture of a quinoline and a quinaldine alkyl haloid brings about, as is well known, the development of an intense reddish-purple colour, on account of the formation of an *iso*cyanine. If, however, formaldehyde, as well as alkali, is added to the solution, the colour produced is a beautiful deep blue, and the substance to which this is due is a dye of the type of pinacyanol. Corresponding with the difference in colour, these blue dyes sensitise much further into the red than the *iso*cyanines. A large number of compounds of this class have been prepared and examined in this laboratory, and the name carbocyanine has been proposed for them to provide a basis for their systematic nomenclature (Pope and Mills, *Phot. J.*, 1920, **60**, 253).

In view of the practical importance of these dyes, and of the interest attaching to the relationship between photo-sensitising

activity and structure, a definite knowledge of their constitution
is much to be desired.   Two structural formulæ have previously
been put forward, but neither of them can be regarded as free
from objection.

O. Fischer (*J. pr. Chem.*, 1918, [ii], **98**, 204) has proposed
formula I, and Wise, Adam, Stewart, and Lund (*J. Ind. Eng.
Chem.*, 1919, **11**, 460) suggest the constitution II.

(I.)   (II.)
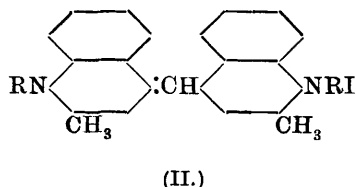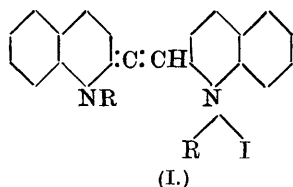
Fischer's formula appears not to represent the composition of
the dyes correctly.   It contains one atom of carbon less than is
indicated by our analytical results.   It is also improbable that
compounds of this structure would possess the intense colour of the
carbocyanines.

The formula suggested by the American investigators represents
the carbocyanines as dimethyl derivatives of the true cyanines.
This does not accord with their photo-sensitising action, nor does
it agree with their behaviour on oxidation.   The formula which
our experiments have led us to regard as the most probable repre-
sentation of the structure of the carbocyanines is III.   It is based



(III.)
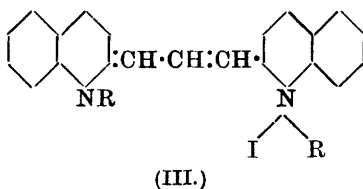
on the following facts and considerations.

(1) The carbocyanines are quaternary ammonium salts evidently
containing two atoms of nitrogen and one equivalent of acid radicle
in the molecule.   A series of careful halogen determinations made
on the dye obtained by treating quinaldine ethiodide with form-
aldehyde and sodium hydroxide (1:1'-diethylcarbocyanine iodide),
and on the corresponding bromide, showed that the molecular
weight of the iodide was 479 ± 1.

Two molecules of quinaldine ethiodide are clearly concerned in
the production of one molecule of the dye, but, since it contains
carbon, hydrogen, nitrogen, and iodine only, the maximum mole-
cular weight it could possess if derived from two molecules of

quinaldine ethiodide, with the loss of hydrogen iodide, would be 470. The observed molecular weight therefore shows that, contrary to the view of O. Fischer (*loc. cit.*), it must contain the residue of one molecule of formaldehyde.

Simple condensation with one molecule of formaldehyde would result in the addition of 12 units to the molecular weight. The observed increase of about 10 units indicates that, in addition to the elimination of hydrogen iodide and water, hydrogen (probably 2 atoms) has been removed by some process of oxidation.

The probable reaction for the formation of the dye is therefore

$$2C_{10}H_9N,C_2H_5X + CH_2O = C_{25}H_{25}N_2X + H_2O + HI + 2H,$$
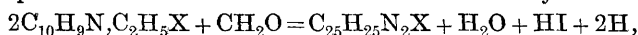
and the formula $C_{25}H_{25}N_2X$ thus indicated is in excellent agreement with the analytical results.

(2) Whilst the *iso*cyanines are formed by condensation of one molecule of a quinoline alkyl iodide with one of a quinaldine alkyl iodide, two molecules of a quinaldine alkyl iodide are necessary for the formation of a carbocyanine; a quinoline alkyl iodide, if present, takes no direct part in the condensation.

This fact was discovered by O. Fischer (*loc. cit.*), and also strongly suspected by the American investigators. It was similarly discovered in this laboratory through observing that the compound produced by the action of alkali and formaldehyde on a mixture of the ethiodides of quinoline and quinaldine was identical with that obtained from quinaldine ethiodide alone.

The yield is, however, very much better in the former case, and this suggested that possibly the additional amount of carbocyanine might be formed from one molecule of quinoline alkyl iodide, two molecules of formaldehyde, and one of quinaldine alkyl iodide. The action of alkali and formaldehyde on a mixture of p-toluquinaldine ethiodide and quinoline ethiodide was therefore investigated.

The amount of sensitiser produced was about the same as from the corresponding mixture of quinaldine ethiodide and quinoline ethiodide, and it was found to be a homogeneous substance, since, by extraction with successive quantities of methyl alcohol, it was divided into six fractions identical in properties, and analysis showed that these consisted of the $1:1'$-diethyl-6:6'-dimethylcarbocyanine iodide described by Pope and Mills (*loc. cit.*). The whole of the carbocyanine formed thus contained two p-toluquinaldine residues, and the quinoline ethiodide did not contribute to the carbon skeleton of any portion of the dye produced. The behaviour of many other substituted quinaldine alkyl iodides in the carbocyanine condensation has been examined in this laboratory with similar results (Pope and Mills, *loc. cit.*); thus, for

example, from bromoquinaldine ethiodide and quinoline ethiodide,
a dibromocarbocyanine iodide is formed.

It therefore appears that the alkyl iodides of the quinoline bases
can only take part in the carbocyanine condensation provided they
contain a 2-methyl group, and in this condensation two molecules
of such an alkyl iodide and one of formaldehyde are concerned.

(3) When a solution of diethylcarbocyanine bromide in dilute
nitric acid is heated, the dye is rapidly oxidised, and the liquid,
after becoming almost immediately bright orange-red, is gradually
decolorised, the colour practically disappearing after about an
hour's boiling. From the residue left after the nitric acid has
been evaporated, which consists of a mixture of highly soluble
substances, a crystalline quaternary nitrate can be isolated. The
composition of this nitrate, together with its properties, and the
fact that it gives 1-ethyl-2-quinolone on oxidation with potassium
ferricyanide, shows it to be quinaldinic acid ethyl nitrate (A).
It is clearly derived from one of the quinaldine residues present
in the pinacyanol molecule, and the yield of analytically pure
material isolated varied, in four experiments, from 89 to 93 per
cent. of the theoretical. The production of this compound shows
that pinacyanol contains the grouping IV.


$$(A.) \qquad (IV.) \qquad (V.)$$
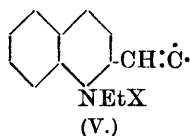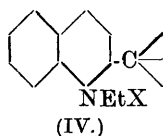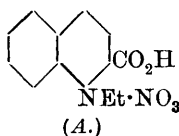
Moreover, that it is formed so smoothly and easily further
indicates that this residue is united to the rest of the molecule by
an ethylenic linking, and thus that pinacyanol contains the
grouping V.

The other main oxidation product, or products, are exceedingly
soluble, and have not yet been identified. The residue left after
the removal of the quinaldinic acid ethyl nitrate was therefore
further oxidised with alkaline ferricyanide, and was found to give
rise to 1-ethyl-2-quinolone.* The weight of distilled, colourless,
crystalline product was 60 per cent. of the weight of ethylquinolone
theoretically obtainable from one quinaldine residue in the pina-
cyanol originally taken. It was not quite pure (m. p. 50—54°
with incipient softening at 40°; pure 1-ethyl-2-quinolone melts at
53—55·5°), but analytically pure ethylquinolone was easily isolated
from it, and it was evident that far more quinolone had been pro-
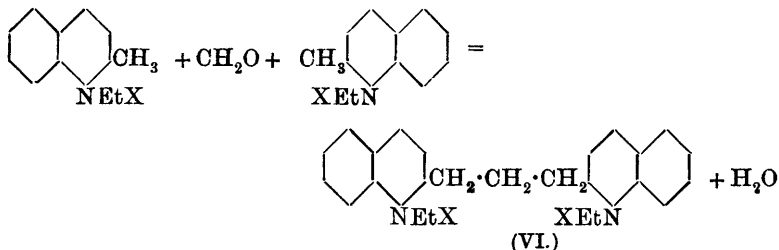duced than could possibly have been derived from the 11 per cent.

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* The production of ethylquinolone by the oxidation of pinacyanol
by potassium ferricyanide was observed by O. Fischer (*loc. cit.*).

of the first quinaldine residue unaccounted for as quinaldinic acid
ethyl nitrate. It must therefore have been formed mainly from
the second quinaldine residue present in pinacyanol. That this
second quinaldine residue should be split off on oxidation as 1-ethyl-
2-quinolone shows that the quinoline nucleus contained in it must
be attached to the rest of the molecule through the 2-position.
More precise conclusions can scarcely be drawn from this fact, for
oxidation with alkaline ferricyanide is not fitted to decide more
delicate points of constitution; for example, Decker and Remfry
(*Ber.*, 1905, **38**, 2773) have shown that quinaldine alkyl iodides
are converted by this reagent into the corresponding quinolones.
The action of potassium permanganate on pinacyanol acetate in
aqueous acetone solution at 0° was therefore studied (compare
Mills and Wishart, this vol., p. 579). The permanganate was
added gradually, and the end of the reaction was sharply marked
by the persistence of the permanganate colour after a quantity
corresponding with 4·8 atoms of oxygen to one molecule of pina-
cyanol had been added. Oxidation under these conditions brought
about the fission of the pinacyanol molecule, with the production
of 1-ethyl-2-quinolone. The quantity of pure substance isolated
amounted to 79 per cent. of that theoretically obtainable from one
quinaldine residue. The other product was exceedingly soluble
and showed the behaviour of a quaternary salt. When boiled with
dilute nitric acid, it gave quinaldinic acid ethyl nitrate, but the
oxidation did not proceed smoothly, and the quantity of the nitrate
isolated was only 25 per cent. of the theoretical yield from half
the pinacyanol molecule. These observations, especially when con-
sidered in relationship to the action of potassium permanganate
on dimethyl*iso*cyanine acetate (Mills and Wishart, *loc. cit.*),
indicate that whilst oxidation with dilute nitric acid splits off from
the pinacyanol molecule the quinaldine residue which contains the
quinquevalent nitrogen atom (forming quinaldinic acid ethyl
nitrate), potassium permanganate splits off, as ethylquinolone, that
containing the tervalent nitrogen atom. It thus appears that the
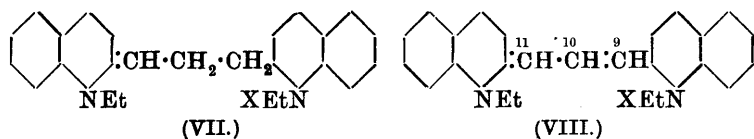second quinaldine residue is present in pinacyanol in the form
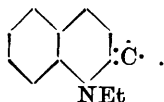
(4) It has thus been shown that (i) the carbocyanine condensa-
tion takes place between two molecules of quinaldine alkyl iodide
and one of formaldehyde, and that (ii) the two quinaldine residues
are both attached to the rest of the molecule through the carbon

atoms of their 2-methyl groups.   The main reaction concerned in the condensation must therefore be

$$\text{(naphthoquinoline)}CH_3 + CH_2O + CH_3\text{(naphthoquinoline)} =$$
$$\text{(naphthoquinoline)}CH_2\cdot CH_2\cdot CH_2\text{(naphthoquinoline)} + H_2O$$

(VI.)

This is analogous to several well-known reactions in which one molecule of formaldehyde condenses with two molecules of a compound containing a group of similar reactivity to the 2-methyl group in quinaldine ethiodide (compare Knoevenagel, *Ber.*, 1894, **27**, 2345).

In the alkaline reaction mixture, the hypothetical intermediate product, VI, would lose hydrogen iodide, forming the substance

$$\text{(naphthoquinoline)}:CH\cdot CH_2\cdot CH_2\text{(naphthoquinoline)} \qquad \text{(naphthoquinoline)}:\overset{11}{C}H\cdot\overset{10}{C}H:\overset{9}{C}H\text{(naphthoquinoline)}$$

NEt   XEtN   NEt   XEtN

(VII.)   (VIII.)

VII, for the existence of reactions of this type is well established (compare Decker, *Ber.*, 1905, **38**, 2493).
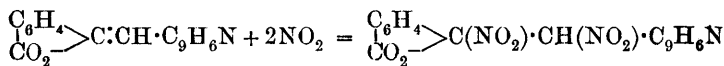
VII is, however, not a possible formula for a substance as intensely coloured as pinacyanol. From analogy to other basic dyes, the saturated and the unsaturated nitrogen atoms in this compound must be connected by a chain of conjugated unsaturated linkings. There are reasons which make the presence of an ethylenic linking between the carbon atoms 9 and 10 exceedingly probable, and therefore we assign to pinacyanol the formula VIII. These reasons are, first, that in the closely related *iso*cyanine condensation a similar oxidation, involving the removal of two hydrogen atoms, occurs,* and, secondly, as has already been pointed out, that the great readiness with which pinacyanol can be oxidised

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* The two hydrogen atoms by which formula VII differs from VIII would be unusually reactive on account of their respective positions relative to unsaturated linkings, and would therefore be readily removable. That the carbocyanine condensation involves a process of oxidation would also explain why a larger yield of sensitiser can be obtained from a given quantity of quinaldine ethiodide when the condensation is carried out in presence of quinoline ethiodide ; the latter probably gives rise to substances which serve to take up this hydrogen.

to quinaldinic acid ethyl nitrate is scarcely to be accounted for unless an ethylenic linking is present in this position.

There is a somewhat remarkable reaction of pinacyanol, which is probably dependent on the presence of this unsaturated three-carbon chain uniting the two quinoline residues. If a solution of the nitrate of the dye in dilute nitric acid is carefully warmed to 60°, the orange-red colour, to which reference has already been made, suddenly appears, and, on cooling the solution, a bright red compound crystallises. This is a quaternary nitrate, and analysis indicates that it is formed by the entrance, either by substitution or addition, of two nitro-groups into the pinacyanol molecule.

Since on oxidation it gives, like pinacyanol itself, quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone, both nitro-groups must be attached to the 3-carbon chain connecting the two quinoline residues, unless, as is less probable, one of them is in the 2′-position. This reaction, which does not take place in the presence of carb-amide, accordingly recalls the action of nitrogen peroxide on quinoline-yellow (Eibner and Lange, *Annalen*, 1901, **315**, 342),

$$\underset{\mathrm{CO_2}}{\overset{\mathrm{C_6H_4}}{>}}\mathrm{C{:}CH{\cdot}C_9H_6N} + 2\mathrm{NO_2} = \underset{\mathrm{CO_2}}{\overset{\mathrm{C_6H_4}}{>}}\mathrm{C(NO_2){\cdot}CH(NO_2){\cdot}C_9H_6N}$$

and the stability of this pinacyanol derivative, in comparison with Eibner and Lange's additive compound, would indicate that it is a substitution derivative.
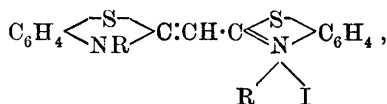
(5) According to this view of the constitution of the carbo-cyanines, they stand in an interesting relationship to the cyanines.

The cyanines can be regarded as consisting of a 1-alkylquinolenyl radicle united through the methenyl group :CH· to a univalent residue of an alkylquinolinium salt. Since the union can take place from a 2- to a 2′-position, a 4- to a 4′-position, or from a 2- to a 4′-position, there are three types of cyanines:

(I.)   (II.)

(III.)
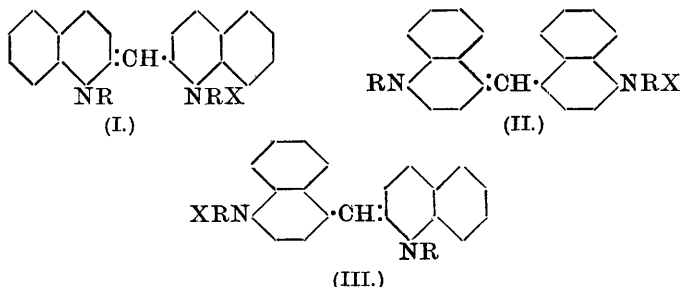
The dyes of type II are the true cyanines, those of type III are the *iso*cyanines. Dyes of type I are at present unknown in the

quinoline series, but the compounds obtained by Hofmann (*Ber.*, 1887, **20**, 2262) by the action of ammonia on a mixture of the alkyl iodides of benzothiazole and 1-methylbenzothiazole are so closely analogous to the *iso*cyanines in the method by which they are formed and in their properties that they undoubtedly possess the constitution

$$C_6H_4\diagdown{}^{-S-}_{NR}\diagup C{:}CH{\cdot}C\diagup{}^{S-}_{N}\diagdown C_6H_4 ,$$

$$R \qquad I$$

and thus are representatives of this class.

According to the constitution now assigned to the carbocyanines, they are cyanines of class I, in which the carbon chain connecting the two quinoline nuclei has been lengthened by the introduction of the group ·CH:CH·. The great resemblance between the carbocyanine and the cyanine dyes thus finds a simple explanation, and the deeper colour of the carbocyanines, compared with the reddish-purple of the cyanines of the benzothiazole series, is associated with the lengthening of the chain of conjugated unsaturated linkings which connects the two nitrogen atoms.

Corresponding with the three types of cyanines, the following three classes of carbocyanines should be capable of existence :

(I'.)   (II'.)

(III'.)
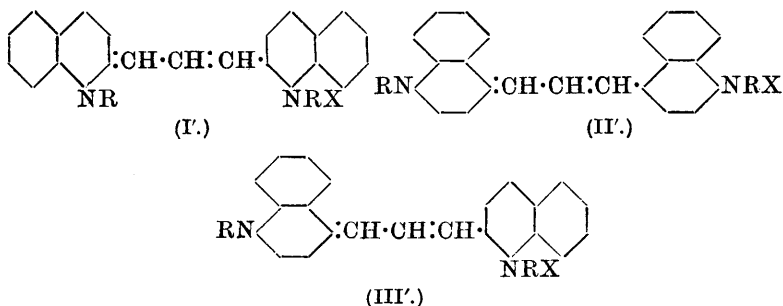
Thus, in addition to the dyes of the type of pinacyanol (I'), it should be possible to prepare compounds of the formulæ II' and III', which would probably prove to be dyes possessing powerful photo-sensitising properties similar to those shown by the rest of this group of compounds.

EXPERIMENTAL.

Composition of 1:1'-*Diethylcarbocyanine Salts.*

1:1'-Diethylcarbocyanine iodide, prepared, as described by Pope and Mills (*loc. cit.*), by the action of formaldehyde and alkali on

a mixture of quinaldine ethiodide and quinoline ethiodide, after having been crystallised five times from methyl alcohol and dried to constant weight at $145°/20$—30 mm., was found, on analysis by the Carius method, to contain $I = 26·60$ per cent. The iodide prepared from quinaldine ethiodide alone was found in two analyses to contain $I = 26·61$ and $26·68$ per cent. The iodide prepared from quinaldine ethiodide and quinoline methiodide gave $I = 26·53$ and $26·54$ per cent. The mean of these values, which are probably slightly too high, on account of occlusion of silver nitrate by the silver iodide, is $26·59$ * ($C_{25}H_{25}N_2I$ requires $I = 26·43$; Fischer's formula, $C_{24}H_{23}N_2I$ requires $I = 27·23$ per cent.).

$1 : 1'$-Diethylcarbocyanine bromide, after drying to constant weight at $140°/20$—30 mm., was found to contain $Br = 18·49$ and $18·53$ per cent. in two experiments carried out by Mr. J. E. G. Harris. These analyses, to which, on account of the accuracy of the Carius method for the estimation of bromine, we attach especial importance, give a molecular weight of 432 for the bromide (corresponding with a molecular weight of 479 for the iodide) ($C_{25}H_{25}N_2Br$ requires $Br = 18·45$; Fischer's formula, $C_{24}H_{23}N_2Br$ requires $Br = 19·06$ per cent.).

Combustion of the dried bromide gave results in excellent agreement with the formula $C_{25}H_{25}N_2Br$ (Found: $C = 69·18$; $H = 5·83$; $N = 6·55$. Calc.: $C = 69·26$; $H = 5·82$; $N = 6·47$ per cent.).

Oxidation of $1 : 1'$-Diethylcarbocyanine Bromide with Nitric Acid.

$1 : 1'$-Diethylcarbocyanine bromide (2 grams) was boiled under reflux with a mixture of nitric acid (D $1·42$; 40 c.c.) and water (40 c.c.). Nitrous fumes were evolved, and the liquid rapidly became orange-red, but the colour gradually disappeared, and, after about one hour's boiling, the liquid became colourless.† The liquid was then evaporated, first on the water-bath and finally over sulphuric acid under 2 mm. pressure. The residue was treated with water, and a small quantity (about $0·1$ gram) of undissolved material was removed by extraction with chloroform. The aqueous layer was again evaporated on the water-bath, and finally in a highly exhausted desiccator over sulphuric acid. The residue gradually solidified, and, by trituration with a little acetone, an almost colourless, crystalline solid was readily isolated. After

* These analyses were carried out by one of us and Mr. F. H. Jeffery.

† During this operation a small quantity of a heavy volatile oil with a pungent odour resembling that of chloropicrin appeared in the condenser. The amounts obtained were insufficient to enable the substance to be identified, but it contained nitrogen and bromine and was possibly bromonitromethane.

recrystallisation from absolute alcohol, it melted and decomposed at 109°.

The following observations show that this compound is quinaldinic acid ethyl nitrate:

(i) It is a nitrate. An estimation of the NO_3 radicle by "nitron" gave $NO_3 = 23\cdot6$. $C_{12}H_{12}O_2N\cdot NO_3$ requires $NO_3 = 23\cdot5$ per cent. (Found: $N = 10\cdot8$. $C_{12}H_{12}O_5N_2$ requires $N = 10\cdot6$ per cent.).

(ii) Although a quaternary ethyl nitrate (as shown by its conversion into ethylquinolone on oxidation and its behaviour with excess of alkali), it was strongly acid, and could be sharply titrated with alkali and phenolphthalein, and therefore contained a carboxyl group (Found: $CO_2H = 17\cdot05$. $C_{11}H_{11}O_3N_2\cdot CO_2H$ requires $CO_2H = 17\cdot04$ per cent.).

(iii) Its conversion by alkaline ferricyanide into ethyl-2-quinolone shows that the carboxyl group was in the 2-position. An aqueous solution of the nitrate ($0\cdot5$ gram) was slowly dropped into a solution of potassium ferricyanide (6 grams) in 5 per cent. sodium hydroxide (60 c.c.) maintained at 0—5°. The resulting liquid was extracted with ether, and the residue left on evaporation of the ether, after drying with potassium hydroxide, was pure 1-ethyl-2-quinolone. Its melting point, 53—55·5°, was identical with that of a specimen of ethylquinolone, prepared for comparison by oxidising quinoline ethiodide, and a mixture of the two specimens melted at the same temperature. The weight of quinolone obtained was $0\cdot27$ gram, or 82 per cent. of the theoretical amount.

The material from which the quinaldinic acid ethyl nitrate had been separated by means of acetone was then examined. It was left, after evaporation of the acetone, as a clean, brown oil, which was excessively soluble in water, alcohol, or acetone. It was investigated in various ways, such as by crystallisation of the platinichloride, without much further information being gained. It was therefore oxidised with alkaline potassium ferricyanide. The material obtained from 2 grams of diethylcarbocyanine bromide by oxidation with dilute nitric acid, and subsequent removal of the quinaldinic acid ethyl nitrate, was dissolved in water, a small quantity of insoluble matter being removed by filtration, and the liquid was dropped into a solution of potassium ferricyanide (8 grams) in 5 per cent. sodium hydroxide solution at 0—5°. The quinolone produced was extracted with ether and dried with potassium hydroxide.

The material from three such experiments was united and distilled under 2 mm. pressure from an oil-bath at 155—168°. The distillate was a colourless oil, which solidified to crystals melting

at 50—54°, with previous softening at 40°. It was therefore not quite pure, and was recrystallised from light petroleum. It then melted at 50—54·5°, and was shown by its general characters and analysis to be 1-ethyl-2-quinolone (Found: $N = 8·3$. Calc.: $N = 8·1$ per cent.).

The quantities obtained in these experiments were as follows. By the oxidation of 6 grams of $1 : 1'$-diethylcarbocyanine bromide, $C_{25}H_{25}N_2Br,CH_3OH$, 3·03 grams of quinaldinic acid ethyl nitrate were obtained. This melted at 107—108°, and was pure (Found: $CO_2H = 17·2$; $NO_3 = 23·6$. Calc.: $CO_2H = 17·04$; $NO_3 = 23·5$ per cent.). This weight is 89 per cent. of that theoretically obtainable.

The weight of crude 1-ethyl-2-quinolone obtained was 1·64 grams. The weight of redistilled material was 1·35 grams, which is 60 per cent. of the weight of quinolone theoretically obtainable from one quinaldine nucleus in the pinacyanol taken. The weight of recrystallised material from which the sample for analysis was taken was 0·76 gram.

Oxidation of $1 : 1'$-Diethylcarbocyanine Acetate with Potassium Permanganate.

To prepare the acetate, a solution of $1 : 1'$-diethylcarbocyanine bromide (4 grams) in boiling rectified spirit (450 c.c.) was treated with a hot saturated aqueous solution of silver acetate (1·44 grams). The residue obtained after evaporating the filtrate from the precipitated silver bromide was dissolved in a mixture of acetone (450 c.c.) and water (450 c.c.). Into this solution, which was mechanically stirred and kept at 0—5°, 140 c.c. of a solution of potassium permanganate containing 3·16 grams per litre were slowly dropped, an end-point having been reached when 137 c.c. had been added. The red filtrate, which was neutral to litmus, was extracted with ether after evaporating the acetone under diminished pressure. The brown, ethereal extract was shaken with very dilute hydrochloric acid, which extracted some tarry matter (0·18 gram), leaving an almost colourless solution. This was dried with potassium hydroxide and then evaporated; the residue (1·26 grams), which soon crystallised, melted at 45—50°. When distilled under diminished pressure, this gave a colourless distillate of pure 1-ethyl-2-quinolone (melting point, 52—55°; melting point of a mixture with pure 1-ethyl-2-quinolone, 52—55°) (Found: $C = 76·1$; $H = 6·7$. Calc.: $C = 76·3$; $H = 6·4$ per cent.). The weight of the distillate was 1·18 grams, which is 79 per cent. of the theoretical yield.

The aqueous solution left after extraction of the ethylquinolone

was acidified with hydrochloric acid, evaporated, and the residue then treated with absolute alcohol to separate the organic matter from potassium chloride.

The brown material left after evaporation of the alcohol was boiled for thirty hours with 140 c.c. of dilute nitric acid (D 1·2), and the solution was then examined in the same way as that obtained by oxidising diethylcarbocyanine bromide with nitric acid.

The weight of quinaldinic acid ethyl nitrate obtained was 0·61 gram, or 27 per cent. of the theoretical amount, and further oxidation of the residual material with alkaline ferricyanide gave 0·46 gram of ethylquinolone, equivalent to 31 per cent. of the theoretical yield from the original diethylcarbocyanine acetate.

The Red Salts obtained by the Action of Nitric Acid on 1 : 1'-Diethylcarbocyanine Salts.

1 : 1'-Diethylcarbocyanine bromide (1 gram) was dissolved in dilute nitric acid by warming to 40° with a mixture of 4 c.c. of nitric acid (D 1·42), previously boiled to expel oxides of nitrogen, and water (16 c.c.). The bromine was then exactly precipitated with silver nitrate, and the blue or green filtrate, containing the nitrate of the dye, was warmed to 60—65°, when the liquid suddenly turned orange, and red crystals began to separate. The liquid was cooled to 0°, and the crystals were collected. By boiling the filtrate a short time and cooling to 0°, a further yield was obtained, and the process of boiling the filtrate and cooling was repeated as long as fresh quantities of crystals separated ; 13 grams of 1 : 1'-diethylcarbocyanine bromide thus treated gave 7·36 grams of the red crystals. The yield is less if larger quantities of carbocyanine than 1 gram are taken.

The reaction is dependent on the production of oxides of nitrogen. If commercial nitric acid, not previously boiled, is employed, the colour change takes place considerably below 60°. On the other hand, if carbamide is added, the mixture can be boiled without the formation of the red salt. This red salt is a quaternary nitrate. To obtain a compound which could be more accurately analysed, it was converted into the corresponding bromide by dissolving in boiling water and adding the solution to an equal volume of a hot concentrated solution of potassium bromide. The red bromide began to crystallise from the hot solution, and separated practically completely on cooling. This treatment with potassium bromide was then repeated three times, and the product was finally recrystallised from hot water.

For analysis, it was dried at 50°/20—30 mm. The dried material melted and decomposed at 201—202° (Found: $C = 56.76$, 56.65; $H = 4.80$, 4.58; $N = 10.52$, 10.73; $Br = 15.37$, 15.37, 15.16. $C_{25}H_{23}O_4N_4Br$ requires $C = 57.4$; $H = 4.42$; $N = 10.7$; $Br = 15.27$ per cent. Loss on drying: 6.92, 7.75. $C_{25}H_{23}O_4N_4Br,2H_2O$ requires $H_2O = 6.9$ per cent.).

Oxidation of the Red Nitrate.—One gram was boiled with a mixture of 10 c.c. of nitric acid (D 1.42) and water (10 c.c.). Oxides of nitrogen were evolved, the colour slowly faded, and, after boiling under reflux for six hours, a pale yellow liquid was obtained. This liquid was treated in the same way as the similar solution obtained by oxidising diethylcarbocyanine bromide with dilute nitric acid (p. 1558), and the same products, namely, quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone, were similarly isolated. From 4 grams of the red nitrate, corresponding with 3.95 grams of anhydrous substance, were obtained 1.51 grams of quinaldinic acid ethyl nitrate (73 per cent. of the theoretical quantity) and 0.84 gram of ethylquinolone melting at 52—53° (62 per cent. of the theoretical quantity).

Corresponding experiments were carried out with the bromide. This salt was much more rapidly attacked by the dilute nitric acid, the bromine present evidently assisting the oxidation, and the volatile, heavy oil, to which reference has already been made (p. 1558), appeared in the condenser, otherwise the products of oxidation were the same. Quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone were obtained in quantities corresponding with 93 per cent. and 60 per cent., respectively, of the theoretical amounts.

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